**Trona-Sodium Sesquicarbonate**

**Abstract**
Trona, a natural form of sodium sesquicarbonate, has great success in removing acid gas for a variety of applications in other industries. The physical characteristic of trona is an important factor to the capture of SO₂. At the Newmont refractory ore treatment roaster facility, trona was added in the roaster feed to control SO₂ in the roaster off gas. Laboratory roasting tests confirmed that the effectiveness of trona in roaster feed for SO₂ fixation is greater than that with addition of lime or soda ash. In this publication, the characteristics of trona and the benefit of trona addition in the roasting process will be discussed.

**Introduction**
In recent years, federal and state regulatory agencies have tightened air emission standards. Acid gases such as hydrochloric acid (HCl) and sulfur dioxide (SO₂) are under heavy scrutiny for reduction. Most traditional scrubbing systems, i.e., wet scrubbers and spray dryers, meet the standards but they typically are high in capital cost, have significant space requirements for equipment, and are difficult to maintain. Dry sorbent injection (DSI) is an alternative technology that has been shown to be effective in HCl and SO₂ removal, while being inverse to the problems listed with traditional systems. Today, DSI technology is used in the Medical, Municipal and Waste to Energy Incinerators; in Secondary Aluminum Smelters; in Clay, Refractory and Structural Brick Kilns; and in the Cement Industry to meet the new emission standards.

**Background of Trona Ore**
Trona is a rare mineral. Its formation at Green River, Wyoming is the result of rapidly repeated evaporation cycles of Lake Gosiute approximately 500-600 million years ago. The original lake was fresh water and supported abundant flora and fauna. When the climate changed from humid to arid, Lake Gosiute evaporated and trapped the remnants of the once abundant life. The lake bottom became a mixture of mud and organic sediments that formed oil shale. Runoff water from the nearby mountains continued to supply sodium, alkaline earth and bicarbonate to the lake. Since the rate of evaporation was high, the clear waters changed to brine that finally precipitated a sodium carbonate-bicarbonate compound known as the mineral “trona” (chemical formula: Na₂CO₃ · NaHCO₃ · 2H₂O). Alternating climates prevailed for about two million years. Periods of rains washed mud into the lake to cover previously formed carbonate type precipitates while interim periods of arid climate produced new precipitates. This caused numerous beds of trona to be formed. In total, they contain billions of tons of trona and related minerals.

The tropical rains eventually returned to expand Lake Gosiute. This washed sand and mud from the surrounding mountains into its waters. Sediments of clay and shale built new formations as the geological evolution of the Green River Basin progressed. Buried under these sediments remain the trona beds that have become the basis of the present soda ash and sodium-based industry located around Green River, Wyoming.
Solvay Chemicals, Inc. currently mines trona ore from bed number 17, located at an approximate depth of 1500 feet. This ore body under Solvay Chemicals’ lease holdings is approximately 12 feet thick and of very high quality. Bed 17 will provide ore for many years; however, should the need arise, additional trona ore may be extracted from other beds as well.

Solvay Chemicals employs both the “room and pillar” and “longwall” methods of mining. Using room and pillar, long drifts (tunnels) are mined with cross cuts at specified distances; the remaining pillars support the overburden of the mine. Roof bolting machines insert steel rods into the roof of the mined areas. This supports the immediate rock roof and prevents rock falls.

Presently, the long wall is 500 feet wide and removes a continuous block of ore one (1) mile long. Rather than have supporting pillars and roof bolting, the roof collapses as the long wall advances.

Once cut, the ore is transported via shuttle car or continuous haulage units to a series of belt conveyors which discharge into underground storage bins. From these storage bins, the ore is hoisted to the surface in 20-ton capacity skips.

Solvay Chemicals offers mechanically refined sodium sesquicarbonate (natural trona) to the merchant market. Coarse product for the animal feed market is sold exclusively by an outside company. Alternative products, T-50® trona (250-300µms) and T-200® trona (23µms), are marketed directly by Solvay Chemicals for acid gas and acid neutralization applications.

Trona product operations are located in the ore-crushing portion of the soda ash plant. Trona ore is crushed and screened before being sent through a drying system. The dryer serves to remove free moisture from the product and to separate the coarse (T-50 trona) from fine (T-200 trona) product. Trona products are stored in bulk quantity awaiting truckload out. A bagging operation exists for the packaging of trona products into 50-pound bags and 2000-pound super sacks.

**De-acidification of Acid Gases with Trona**

Trona is rapidly calcined to sodium carbonate when heated at or above 408°K (275°F). The “popcorn-like” decomposition creates a large and reactive surface by bringing un-reacted sodium carbonate to the particle surface for acid neutralization. The byproducts of the reactions are sodium salts. For example the SO₂ chemistry is:

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2(Na_{2}CO_{3} + NaHCO_{3} + 2H_{2}O) + 3SO_{2} \rightarrow 3Na_{2}SO_{3} + 4CO_{2} + 5H_{2}O
\]

\[
3Na_{2}SO_{3} + 1.5O_{2} \rightarrow 3Na_{2}SO_{4}
\]

Sodium carbonate is brought in contact with SO₂ in the flue gas stream by a simple direct injection of a sodium-bearing compound such as trona that will thermally decompose to form sodium carbonate. After the initial sorbent surface of the sodium carbonate has reacted with SO₂ to form sodium sulfite, or sulfate, the reaction slows due to pore blockage-resisting gas phase diffusion of SO₂. In order for the reaction to continue, the sorbent particle must decompose further. This decomposition evolves H₂O and CO₂ gases into the surrounding atmosphere creating a network of void spaces throughout the particle. This process exposes fresh reactive sorbent and allows SO₂ once again to diffuse into the particle interior. This increase in surface area (popcorn effect) is on the order of 5 to 20 times the original surface area.
The rates of decomposition and subsequent sulfation of a sodium compound particle are a complicated function of gas temperature, rate of heat transfer to the particle, flue gas, H₂O and CO₂ partial pressure and the effects of other flue gas components present. In an actual sodium DSI system additional parameters and physical constraints will also affect overall sorbent utilization. These include:

- Sorbent injection rate
- NSR (normalized stoichiometric ratio) between the sorbent and the system inlet SO₂ concentration considering that two moles of Na are required to react with one mole of SO₂
- Sorbent particle size
- Sorbent residence time in the flue gas stream
- Sorbent penetration and mixing within the flue gas
- Particulate control device used

The optimum temperature range of sodium sorbent/gas reactions is much more forgiving than the calcium systems. The sodium sorbent has demonstrated high removal efficiencies in the temperature range of 398 - 752°K (257-894°F) on both laboratory and commercial scale systems. Most calcium sorbents are only effective at low temperatures and the byproduct salts have substantial vapor pressures at the higher temperatures of their own.

The particle size of the sorbent can have a dramatic effect on the removal efficiency of SO₂ as can be seen in Figure 1.

When assessing the bottom line, assuming all other factors are equal, such as the same extent of mixing, retention time, temperature, etc., the cost will be the deciding factor. The relative costs for DSI for various sorbents are shown in Figure 2.

**Newmont Carlin Refractory Gold Ore Roaster Plant**

Newmont Refractory Ore Treatment Plant (ROTP) at Carlin, Nevada controls SO₂ concentration in the roaster off-gas with the addition of trona in the roaster feed.

The Carlin ROTP Circulating Fluid Bed Roaster circuit operates about 8200 tonnes refractory ore per day. The roaster feed is a varying mixture of open pit and underground ores from Carlin and gold/pyrite flotation concentrate from the Newmont Lone Tree N2TEC Flotation Plant. The sulfur content and ore mineralogy characteristics of the roaster feed vary widely. The plant contains a crushing system, dry grinding circuit, ore pre-heater system, two CFB roasters, a gas cleaning circuit and sulfuric acid plant. The roasters run at approximately 538°C or 1000°F and a retention time of about five to six minutes, with a maximum retention time of 10 minutes. During operation, it is important to maintain an SO₂ concentration of 8-10% in the gas stream to the sulfuric acid plant. The designed gas feed SO₂ concentration was 9.5% for the sulfuric acid plant.
Before 1998, the Carlin ROTP blended hydrated lime in the roaster feed to control the SO$_2$ in the gas phase for acid plant feed. The lime addition averaged about 14 kg/t. Since August 1998, the operation changed to add trona in place of hydrated lime. Raw trona, commercially available as T-50® trona from Solvay Chemicals, Green River, Wyoming, was added to the ore in the grinding mill circuit at an average rate of 7 kg/t depending on the sulfide mineralization of the roaster feed. The actual rate of trona addition varied in response to the SO$_2$ concentration in the roaster off gas. The trona was mixed with the ore and ground to about 80% <200 mesh and 68% <400 mesh. One advantage of using T-50 trona in the grinding circuit is that it can be ground to the same size as the refractory ore, which is believed to maintain a well distributed mix with the ore in the CFB roaster. Also, because of the sturdy crystal structure, fewer fines are carried over to the bag house, as compared with refined soda ash, which is more friable. Since addition of trona in the operation, the SO$_2$ concentration in the roaster off-gas (or the feed gas of acid plant) was controlled at about 9.5%. The SO$_2$ concentration was well controlled by regular adjustments to the trona addition rate as needed.

**Newmont Minahasa Refractory Gold Ore Fluid-Bed Roasting Study**

PT Newmont Minahasa Raya operates a whole ore roasting plant (2600 TPD) in Indonesia. The plant does not have a sulfuric acid plant and was originally designed without an SO$_2$ recovery circuit. The sulfide in the Minahasa refractory ore deposit is low, averaging 0.8% sulfide sulfur. The dominant carbonate minerals in the ore include calcite (CaCO$_3$) and dolomite (CaCO$_3$. MgCO$_2$), and the ores contain greater than 20% combined carbonates. These carbonates decompose during roasting and capture SO$_2$. The roasting temperature is an important factor for gold recovery. The operation temperature chosen was 580°C, which was the best compromise between gold recovery and sulfur dioxide capture. Gold recovery was better at lower temperatures; however, offset against this was improved sulfur dioxide captured as the temperature increased. Generally, at 580°C sufficient magnesium oxide was formed to capture the majority of the SO$_2$ with the concentration in the off-gas sufficiently low to enable discharge. In 1999, a study of roaster additives on the effect of off-gas SO$_2$ capture and gold recovery was conducted using a 4-inch diameter continuous stationary fluid-bed roaster. The objective of this study was to optimize SO$_2$ fixation and gold recovery with additives in the roaster feed. The additives tested were trona, soda ash and hydrated lime. The roaster feed sample tested contains 17.87 grams Au/t and 1.2% S-sulfide. Carbonate minerals content is lower than that generally operated in Minahasa, about 2.3% C-carbonate. Roaster exhaust gas concentrations, including O$_2$, SO$_2$, CO, CO$_2$ and NO$_x$, were monitored continuously by a Rosemount Gas Analyzer during the roasting test. Oxygen concentration was controlled and maintained at the desired level. Roast temperatures showed a pronounced effect on SO$_2$ capture. Emission of SO$_2$ in the roaster exhaust gas was reduced as the temperature increased.

Natural sodium sesquicarbonate (trona), soda ash and hydrated lime were compared as an additive in the roaster feed to assist SO$_2$ capture. Test results indicated that the effectiveness of the additives on SO$_2$ capture is in the following order: trona>hydrated lime>soda ash, as shown in Figure 3. Trona is more effective for SO$_2$ fixation. From test results, a minimum amount of 2kg/t trona was required. The effectiveness of lime for SO$_2$ capture was lower than that of trona. The amount of lime required was also higher.

Figure 3 shows the SO$_2$ concentration measured in the exhaust gas under test conditions. It should be noted the SO$_2$ concentration in the stationary fluid bed roaster off-gas is relatively much higher than that of the circulating fluid bed roaster operated in Minahasa due to the difference of gas flow rate. However, results indicate the relative comparison effect of the additives on SO$_2$ fixation. Test results confirmed the benefit of using trona.
Summary
Trona is a mineral with the natural form of sodium sesquicarbonate. It has many applications in neutralizing acidic gases in many different industries. Trona is rapidly calcined to sodium carbonate when heated at or above 135°C (or 275°F). The popcorn-like crystal structure change in trona creates a large and reactive surface for adsorption and neutralization with acidic gases. Since 1998, Newmont Carlin Refractory Ore Roasting Plant added trona in their roaster feed to control the SO₂ concentration in the roaster off-gas that enters into the sulfuric acid plant. A pilot plant fluid-bed roasting study on Newmont Minahasa refractory ore confirmed the effectiveness using trona to capture SO₂ in the roaster off-gas. Trona compared to soda ash and lime was the most effective additive for providing sulfur fixation in the roaster feed.

References
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