Trona Use In Dry Sodium Injection For Acid Gas Removal

Abstract

In recent years, federal and state regulatory agencies have tightened air emission standards. Two of the acid gases, 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 sodium injection (DSI) is an alternative technology that has been shown to be effective in HCl and SO₂ removal, without the drawbacks of traditional systems.

This paper covers the mechanics of dry injection scrubbing using the most effective sorbents, sodium bicarbonate and mechanically refined trona (natural sodium sesquicarbonate).

It presents DSI performance data for Chambers Medical, originally located in Hampton, SC. This facility incinerated local medical and municipal solid waste, and had begun using mechanically refined trona for HCl and SO₂ removal in late 1991. The data presented for mechanically-refined trona covers two products marketed by Solvay Chemicals: T-50® trona, which is coarse grade (~250-300 μm) and T-200® trona which is fine grade (~23 μm).

Dry Sodium Injection

Dry sodium injection is a low cost alternative to a spray dry or wet scrubbing system for the removal of HCl and SO₂. As Figure 1-A illustrates, the process requires no slurry equipment or reactor vessel because the sorbent is stored and injected dry into the flue duct where it reacts with the acid gas. The spent sorbent is collected dry, either through a baghouse or electrostatic precipitator. It also can be collected wet through an existing wet scrubber vessel should DSI be used for trim scrubbing of acid mist.

Sodium bicarbonate and sodium sesquicarbonate are the most effective products for use in this application. Both products undergo rapid calcination of contained sodium bicarbonate to sodium carbonate when heated at or above 275°F. The “popcorn-like” decomposition creates a large and reactive surface by bringing unreacted sodium carbonate to the particle surface for HCl and SO₂ neutralization (see Figure 1-B). The byproducts of the reactions are sodium chloride and sodium sulfate, respectively, and are collected with fly ash. Table 1 summarizes the chemical compositions and reactions of both sorbents in acid gas removal.
Table 1. Acid Gas Removal Using Sodium Sorbents

Sodium Sorbent Decomposition

Sodium Bicarbonate: \[ 2\text{NaHCO}_3 \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \]

Sodium Sesquicarbonate: \[ 2 [\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}] \xrightarrow{\Delta} 3\text{Na}_2\text{CO}_3 + 5\text{H}_2\text{O} + \text{CO}_2 \]

Acid Gas Neutralization

HCl Removal: \[ \text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \]

SO₂ Removal: \[ \text{Na}_2\text{CO}_3 + \text{SO}_2 \rightarrow \text{Na}_2\text{SO}_3 + \text{CO}_2 \]
and
\[ \text{Na}_2\text{SO}_3 + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 \]

Sodium Sorbents Reactivity

The amount of sorbent injected into the flue gas is presented on a normalized basis and is referred to as the normalized stoichiometric ratio (NSR). The NSR expresses the stoichiometric amount of sorbent required to react with all of the acid gas. HCl neutralization requires one mole of sodium per one mole of HCl present whereas SO₂ neutralization requires two moles of sodium per one mole of SO₂ present. On a molar basis, this relation is:

\[
\text{NSR} = \left( \frac{\text{moles of sodium injected}}{\text{moles of acid gas entering system}} \right)
\]

Or on a mass basis:

\[
\text{NSR} = \left( \frac{\text{mass of sodium theoretically needed to react with a mole of acid gas}}{\text{mass of sodium theoretically needed to react with a unit mass of acid gas}} \right)
\]

The sorbent utilization rate (U) is the fraction of the injected sorbent that reacts with the acid gas. It is expressed as:

\[
U(\%) = 100 \times \frac{\text{Fraction of Acid Gas Removal}}{\text{NSR}}
\]

The Central Study and Research Center (CER) of Solvay S.A. located in Dombasle, France has a pilot micro-injection unit for DSI testing of sorbents. In 1993, they conducted pilot-scale tests using sodium bicarbonate and T-200 trona (natural sodium sesquicarbonate) to compare HCl and SO₂ removal rates on an NSR basis. The results are highlighted in Figure 2 for HCl removal and Figure 3 for SO₂ removal.
Stoichiometrically, Solvay Chemicals T-200 trona should yield greater neutralization of both acid gases than sodium bicarbonate due to the higher percent of contained sodium carbonate. However, actual lab tests and field applications reveal contrary performance data. Both sorbents essentially are equal in HCl removal. In contrast, sodium bicarbonate has a removal efficiency of up to 33% over the performance of T-200 trona when SO$_2$ removal is less than or equal to 90%. Enhanced DSI performance results with sodium bicarbonate, especially in the case of SO$_2$, are attributed to greater carbon dioxide (CO$_2$) liberation during calcination. The phenomenon is thought to further augment surface area, thus exposing more sodium carbonate for reaction.

According to the pilot work performed by Solvay S.A.'s CER group in July 1993, sodium bicarbonate and T-200 trona achieved 90% HCl removal at a 2.0 NSR. T-200 was further tested in three separate municipal solid waste facilities for HCl removal. The test results showed the product achieved greater than 95% HCl removal at a 1.0 NSR. Although sodium bicarbonate wasn't tested, previous testing and field experience indicate similar results would have been achieved.

It is evident by examining Figure 3 that the utilization rate of both sorbents declines dramatically when SO$_2$ removal surpasses 90%. This occurrence is well documented in field applications. It stresses the point that DSI is not an efficient technology in medium-to-high sulfur abatement applications.

Nitrous oxide (NO$_x$) removal ranging between 10-20% also occurs during SO$_2$ abatement in DSI. The actual amount of NO$_x$ removed is directly related to the amount of SO$_2$ removed. Figure 3 highlights the percent of NO$_x$ removed in tandem with SO$_2$ in the CER tests.

A plant's operating conditions will ultimately affect the performance of the sodium bicarbonate and sodium sesquicarbonate in acid gas removal. The most important variables for high removal efficiency are injection temperature (325-501°F), H$_2$O concentration (=5%), fine particle size (=20 μm), and retention time where acid gas is in contact with the sorbent.

Solvay Chemicals T-50 trona and T-200 trona are the most cost-effective sorbents in DSI applications, even taking into consideration the enhanced removal efficiency of sodium bicarbonate in SO$_2$ removal. These products cost significantly less than sodium bicarbonate, especially if finer grades are purchased as a means to eliminate on-site milling.

The following case study illustrates the ease of retrofitting DSI into an operation. It also shows the effect operating parameters have upon the ultimate effectiveness of the sorbent.
### Table 2. Chambers Medical Air Emission Test Results (May 1992)

#### Test A - Medical & MSW

<table>
<thead>
<tr>
<th>Inlet</th>
<th>Test No.</th>
<th>PPMdv A</th>
<th>PPMdv B</th>
<th>PPMdv Avg.</th>
<th>PPMdv Outlet</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCI Removal</td>
<td>M26-R2A</td>
<td>150</td>
<td>151</td>
<td>150</td>
<td>7.1</td>
<td>95.3</td>
</tr>
<tr>
<td></td>
<td>-R3A</td>
<td>207</td>
<td>283</td>
<td>245</td>
<td>11.5</td>
<td>95.3</td>
</tr>
<tr>
<td></td>
<td>-R4A</td>
<td>226</td>
<td>215</td>
<td>220</td>
<td>9.3</td>
<td>95.5</td>
</tr>
<tr>
<td>Average</td>
<td>194</td>
<td>216</td>
<td>205</td>
<td>9.5</td>
<td>95.4</td>
<td></td>
</tr>
</tbody>
</table>

#### Test B - Tires & Medical Waste

<table>
<thead>
<tr>
<th>Inlet</th>
<th>Test No.</th>
<th>PPMdv A</th>
<th>PPMdv B</th>
<th>PPMdv Avg.</th>
<th>PPMdv Outlet</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCI Removal</td>
<td>M26-R1B</td>
<td>109</td>
<td>33</td>
<td>71</td>
<td>20.9</td>
<td>70.6</td>
</tr>
<tr>
<td></td>
<td>-R2B</td>
<td>97</td>
<td>38</td>
<td>67</td>
<td>23.3</td>
<td>65.3</td>
</tr>
<tr>
<td></td>
<td>-R4B</td>
<td>149</td>
<td>43</td>
<td>96</td>
<td>28.9</td>
<td>69.9</td>
</tr>
<tr>
<td>Average</td>
<td>119</td>
<td>38</td>
<td>78</td>
<td>24.4</td>
<td>68.7</td>
<td></td>
</tr>
</tbody>
</table>

#### S02 Removal

<table>
<thead>
<tr>
<th>Inlet</th>
<th>Test No.</th>
<th>PPMdv A</th>
<th>PPMdv B</th>
<th>PPMdv Avg.</th>
<th>PPMdv Outlet</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>M7C-R1B</td>
<td>281</td>
<td>269</td>
<td>275</td>
<td>20.8</td>
<td>92.4</td>
<td></td>
</tr>
<tr>
<td>-R2B</td>
<td>223</td>
<td>198</td>
<td>191</td>
<td>10.5</td>
<td>94.5</td>
<td></td>
</tr>
<tr>
<td>-R4B</td>
<td>283</td>
<td>249</td>
<td>266</td>
<td>11.0</td>
<td>95.9</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>262</td>
<td>225</td>
<td>244</td>
<td>14.0</td>
<td>94.3</td>
<td></td>
</tr>
</tbody>
</table>

**Case Study - Chambers Medical**

In 1989, Chambers Medical, originally of Hampton, SC, operated three incinerators that were fired with medical and municipal solid waste. Two 20,000-pound-per-hour boilers were followed by economizers.

This facility had a waste burn capacity of 200 tons per day. Typical waste composition averages were 35% medical waste and 65% municipal solid waste.

In early 1989, Chambers retrofitted the facility to add dry sodium injection for HCl removal. The project included the addition of a reaction chamber (serpentine duct configuration) to allow a retention time of 3 seconds for sorbent-to-gas contact. A hopper-to-mill unit was added to the discharge to pulverize sorbent before injection. The facility had a two-field electrostatic precipitator on site for particulate collection. Figure 4 (see page 6) is a DSI process flow diagram for Chambers.

Chambers started the DSI unit using sodium bicarbonate. It achieved an average HCl removal rate of 98% or 100 PPMdv exit the stack. This rate far surpassed the state's emission standard of 63% removal or 100 PPMdv exit the stack. In subsequent years, Chambers' state emission regulation for HCl tightened to 90% removal or 30 PPMdv at the stack, whichever provided the highest removal rate. S02 emissions had never been regulated by the state. However, Chambers had periodically included S02 in its HCl compliance test to verify the level.

In late 1991, Chambers tried Solvay Chemicals' T-200 trona as a means to save on sorbent cost. They found the particle sizing of the product was too fine to handle through the existing hopper-to-mill unit. This situation led Chambers to temporarily use the coarser grade of mechanically-refined trona product that Solvay Chemicals offers under the name of T-50 trona. This product has a mean particle size range of 250-300 μm before pulverization.

Chambers performed an air emission test in May 1992. It used Solvay Chemicals' T-50 trona as the sorbent, which had a mean particle average size of 35 μm after milling. The sorbent injection rate was 272 kilograms per hour and the duct injection temperature was 302-316°C. Chambers documented both HCl and S02 removal rates. The emission tests were performed for two different waste streams: Test A) medical & municipal solid waste; and Test B) tires and medical waste.
Table 3. Chambers Medical Air Emission Test Results (September 1994)

| Test No. | PPM
dv A | PPM
dv B | PPM
dv Avg. | Outlet | % Removal |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>M26-RIA</td>
<td>285</td>
<td>258</td>
<td>271</td>
<td>3</td>
<td>98.9</td>
</tr>
<tr>
<td>R2</td>
<td>337</td>
<td>235</td>
<td>286</td>
<td>1</td>
<td>99.6</td>
</tr>
<tr>
<td>RH3</td>
<td>258</td>
<td>226</td>
<td>242</td>
<td>1</td>
<td>99.6</td>
</tr>
<tr>
<td>Average</td>
<td>293</td>
<td>240</td>
<td>266</td>
<td>2</td>
<td>99.3</td>
</tr>
</tbody>
</table>

| Test No. | PPM
dv A | PPM
dv B | PPM
dv Avg. | Outlet | % Removal |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NOT PERFORMED</td>
</tr>
</tbody>
</table>

Summary

DSI is a simple technology that is easily added into an operation. Many lab, pilot and plant applications have shown sodium bicarbonate and natural sodium sesquicarbonate are the most effective sorbents for acid gas removal, whether the gases are neutralized together or independently. Solvay Chemicals markets mechanically-refined trona under the trade names of T-50 trona (coarse grade) and T-200 trona (fine grade). As Chambers demonstrated, both grades will perform adequately in DSI for acid gas removal. Solvay Chemicals' T-200 trona is the choice product because of its fine particle size. Chambers achieved greater than 99% HCl removal using T-200 trona.

Regardless of the product grade and the greater efficiency of sodium bicarbonate in SO₂ removal, the cost effectiveness of Solvay Chemicals' T-50 trona and T-200 trona products positions them as the lowest cost sorbent to companies utilizing DSI.
Book

Reports


Hooper, R.G., "Full Scale Demonstration of Flue Gas Desulfurization by the Injection of Dry Sodium Bicarbonate Upstream of an Electrostatic Precipitator," CRSS, Inc., Denver, CO.


Figure 4. Chambers Medical - Dry Sodium Injection Process Flow