2002

Utilization of Sulfur Oxides for the Production of Sodium Sulfate

J.A.B. Satrio
Iowa State University

S.B. Jagtap
Iowa State University

Thomas D. Wheelock
Iowa State University, wheel@iastate.edu

Follow this and additional works at: http://lib.dr.iastate.edu/cbe_pubs

Part of the Complex Fluids Commons, Other Chemical Engineering Commons, and the Process Control and Systems Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/cbe_pubs/285. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.
Utilization of Sulfur Oxides for the Production of Sodium Sulfate

Abstract
The use of coal and other fossil fuels generates large quantities of sulfurous byproducts which could find an outlet in the manufacture of Na₂SO₄. In this work, the feasibility of converting SO₂ and SO₃ into Na₂SO₄ by employing modern technology, i.e., a fluidized-bed reactor, was investigated. Bench-scale and larger fluidized-bed reactors were used to study the reaction of SO₂ or SO₃ with NaCl, steam, and air at temperatures ranging from 400 to 600 °C. Because the rate of reaction of SO₂ with salt as in the Hargreaves process proved too low to be practical, only the results of reacting SO₃ are reported. Reasonable rates of reaction and trouble-free operation were generally achieved by employing SO₃ concentrations in the range of 1−3 vol % and temperatures in the range of 500–600 °C. With higher SO₃ concentrations and lower temperatures, particle agglomeration and bed caking took place as a result of the formation of lower melting point byproducts believed to be NaHSO₄ and Na₂S₂O₇. This problem was overcome in some cases by increasing the fluidizing gas velocity and/or bed turbulence. Therefore, better results were achieved with gas distributors which created more turbulence. Through selection of appropriate reaction conditions and careful design of the gas distributor, the technical feasibility of the process seems assured. Furthermore, because similar results were achieved with reactors which differed greatly in size, the scale-up to larger reactors should be straightforward.

Disciplines
Complex Fluids | Other Chemical Engineering | Process Control and Systems

Comments
Utilization of Sulfur Oxides for the Production of Sodium Sulfate

J. A. B. Satrio, S. B. Jagtap, and T. D. Wheelock*

Department of Chemical Engineering, Iowa State University, Ames, Iowa 50011-2230

The use of coal and other fossil fuels generates large quantities of sulfurous byproducts which could find an outlet in the manufacture of Na₂SO₄. In this work, the feasibility of converting SO₂ and SO₃ into Na₂SO₄ by employing modern technology, i.e., a fluidized-bed reactor, was investigated. Bench-scale and larger fluidized-bed reactors were used to study the reaction of SO₂ or SO₃ with NaCl, steam, and air at temperatures ranging from 400 to 600 °C. Because the rate of reaction of SO₂ with salt as in the Hargreaves process proved too low to be practical, only the results of reacting SO₃ are reported. Reasonable rates of reaction and trouble-free operation were generally achieved by employing SO₃ concentrations in the range of 1–3 vol % and temperatures in the range of 500–600 °C. With higher SO₃ concentrations and lower temperatures, particle agglomeration and bed caking took place as a result of the formation of lower melting point byproducts believed to be NaHSO₄ and Na₂S₂O₇. This problem was overcome in some cases by increasing the fluidizing gas velocity and/or bed turbulence. Therefore, better results were achieved with gas distributors which created more turbulence. Through selection of appropriate reaction conditions and careful design of the gas distributor, the technical feasibility of the process seems assured. Furthermore, because similar results were achieved with reactors which differed greatly in size, the scale-up to larger reactors should be straightforward.

Introduction

In the search for ways to utilize the rising output of waste sulfur oxides resulting from the increasing use of fossil fuels, consideration should be given to the production of sodium sulfate because large quantities of this material are consumed in the manufacture of paper, soaps, detergents, and glass.¹ At present most of the sodium sulfate consumed in the United States either is derived from natural brines or salt deposits or is recovered as a byproduct of various manufacturing operations. Some of the demand for sodium sulfate could be met by utilizing a plentiful waste material.

In the past substantial amounts of sodium sulfate were produced either by the Hargreaves process or by the Mannheim process, which are still used in other countries.² In the classical Hargreaves process, fixed beds of NaCl briquettes were reacted with SO₂, air, and steam to produce crude sodium sulfate or salt cake.³ The rate of reaction was extremely slow, and materials handling was a problem. A potentially significant improvement in the process was patented by Cannon,³ who proposed reacting fine-size salt particles with vaporized H₂SO₄ at about 840 °C. Again a potentially significant improvement was patented by Cannon,⁶ who proposed reacting fine-size salt particles with vaporized H₂SO₄ in a fluidized-bed reactor. This concept appears to have been commercialized in the Climax process conducted at about 500 °C.⁷

The present investigation was undertaken to see what problems underlie this technology, particularly when used in conjunction with fluidized-bed reactors, and whether the technology can be improved. Initial consideration was given to modifying the Hargreaves process because it utilizes SO₂ directly. However, when an attempt was made to conduct the process in a small bench-scale fluidized-bed reactor using conditions suggested by Cannon, the rate of reaction was almost nil. Adding powdered hematite to the fluidized bed of salt to serve as a catalyst did improve the rate of reaction, but the rate was still too low to be practical.

Consideration was given then to the reaction of NaCl particles in a fluidized state with SO₃ and steam as indicated below.

\[ 2\text{NaCl}(s) + \text{SO}_3(g) + \text{H}_2\text{O}(g) = \text{Na}_2\text{SO}_4(s) + 2\text{HCl}(g) \]

(1)

Fielder et al. ⁸ had observed that this reaction predominated when single crystals of NaCl were exposed to a gaseous mixture of SO₂, SO₃, O₂, and H₂O at 450–625 °C. Also, it is probably similar to the reaction which takes place in the modified version of the Mannheim process.⁶,⁷ While a process based on reaction (1) would first require converting SO₂ to SO₃, it would still be simpler than converting SO₂ to H₂SO₄ as is required for the classical Mannheim process.

For the present study, a fluidized-bed reactor was supplied with a dilute mixture of SO₃ and water vapor instead of with vaporized H₂SO₄. This made it possible to vary the concentrations of SO₃ and H₂O independently. It was soon discovered that particle agglomeration and loss of fluidization could be a major problem. Therefore, the main focus of the investigation became determining process conditions which provided a reasonably fast rate of reaction while avoiding serious particle agglomeration and bed slumping. While most
flow rates were measured with calibrated rotameters obtained as pure gases in high-pressure cylinders. Gas experimental section (PDU).

reactor which was part of a process development unit further demonstrated with a much larger fluidized-bed reactor, the practical feasibility of the process was of the work was conducted with a small bench-scale reactor, the practical feasibility of the process was further demonstrated with a much larger fluidized-bed reactor which was part of a process development unit (PDU).

Experimental Section Materials. Food-grade NaCl was used as a starting material for investigating the production of Na₂SO₄ in fluidized-bed reactors. Morton brand table salt having an indicated purity of 99.8 wt % was used in the smallest reactor, and Superior TX 10 salt supplied by Akso Salt Inc. was used in the largest reactor. Information supplied by Akso indicated a minimum NaCl content of 99.70 wt %, with CaSO₄ and Na₂SO₄ being the major impurities. A screen analysis of the two materials provided the results shown in Table 1.

<table>
<thead>
<tr>
<th>size range, mm</th>
<th>wt %</th>
<th>size range, mm</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Morton</td>
<td>Akso</td>
<td>Morton</td>
</tr>
<tr>
<td>+0.59</td>
<td>19.0</td>
<td>0.18–0.25</td>
<td>2.7</td>
</tr>
<tr>
<td>0.42–0.59</td>
<td>32.6</td>
<td>26.5</td>
<td>-0.18</td>
</tr>
<tr>
<td>0.25–0.42</td>
<td>64.7</td>
<td>48.6</td>
<td>total</td>
</tr>
</tbody>
</table>

of the work was conducted with a small bench-scale reactor, the practical feasibility of the process was further demonstrated with a much larger fluidized-bed reactor which was part of a process development unit (PDU).

Bench-Scale System. This system included the equipment shown in Figure 1 plus instruments for measuring and controlling the temperature and gas flow rates. The system was supplied with SO₂, O₂, and N₂ obtained as pure gases in high-pressure cylinders. Gas flow rates were measured with calibrated rotameters and controlled manually. SO₂, O₂, and part of the N₂ were first passed through a heated bed of vanadium pentoxide catalyst pellets to convert from 65 to 80% of the SO₂ to SO₃ before entering the fluidized-bed reactor. The remainder of the N₂ was saturated with water vapor and then preheated before joining the reactor feed stream. The tubular reactor included a gas preheating section, a fritted quartz gas distributor, space for the fluidized bed, and a very high freeboard. The gas preheating section was packed with silicon carbide particles to a depth of 7.6 cm. The reactor was made of quartz tubing having an inside diameter of 3.6 cm. The top of the reactor was removable to permit loading and unloading of salt. A quartz thermowell was suspended from the top and extended down to within 2.54 cm of the gas distributor to accommodate a thermocouple for measuring the temperature. The lower and middle sections of the reactor were surrounded by a tubular electric furnace for temperature control.

The reactor off-gas was passed through a packed-bed absorption column to remove HCl and SO₃ before venting. The PDU also included equipment for supplying the large reactor with a mixture of gases similar to that furnished to the bench-scale reactor except that only SO₂ was provided in cylinders. SO₂ was combined with preheated compressed air and conducted through a catalytic converter where much of the SO₂ was converted to SO₃. The resulting mixture was combined with steam and heated further before entering the fluidized-bed reactor. The catalytic converter was based on a conventional design and utilized a packed bed of vanadium pentoxide catalyst pellets (Monsanto, type 11). The bed depth and diameter were 66.0 and 25.4 cm, respectively. Electric strip heaters were mounted on the outer surface of the converter for preheating, and the converter was also insulated thoroughly. Steam was generated by pumping water at a controlled rate through an electric tubular heater. For some runs, only part of the air was combined with SO₂ ahead of the catalytic converter; the rest of the air was preheated separately and combined with the other gases just ahead of the fluidized-bed reactor.

The off-gas from the fluidized-bed reactor was cooled and passed through a series of three packed columns designed to remove HCl, SO₃, and dust before being...
discharged through a compressed-air-driven ejector which maintained a slightly negative pressure on the system. Each of the packed columns was made of glass pipe having a diameter of 15 cm and height of 1.5 m, and each was packed with either Berl saddles or Rashig rings. The first two columns were supplied with a dilute caustic solution at a controlled rate, whereas the third column was supplied with tap water.

Bench-Scale System Operating Procedure. Before a run was conducted, the small fluidized-bed reactor was heated to about 150 °C while N₂ was introduced at a low flow rate. At this point 76 g of NaCl was introduced, which provided a fixed bed depth of 5.1 cm, and the flow of gas was increased to maintain the particles in an agitated state as heating was continued to bring the entire system up to operating temperature. At this point the operation was started by feeding a mixture of SO₂, O₂, and half of the N₂ through the catalytic converter and by feeding the remaining N₂ through the water saturator and then through the gas preheater. Both gas streams were combined and fed to the fluidized-bed reactor. As the run was continued, the feed gas flow rate and composition were kept constant, and the temperature of the catalytic converter was maintained between 450 and 500 °C. The temperature of the fluidized-bed reactor was maintained nearly constant by controlling the power input to the furnace surrounding the reactor. While the run was in progress, over 98% of the HCl produced was recovered by contacting the off-gas with a 2 M NaOH solution at 50–55 °C. Samples of the recirculating caustic solution were collected at 5 or 10 min intervals and analyzed for their chloride content by the Volhard titration method. In this way it was possible to monitor the rate of production of SO₃ and it was weighed and analyzed for its sulfate content. However, after some runs the product was partly caked or agglomerated. In that case the product was separated, and the amount and sulfate content of each part were determined. In a few cases X-ray diffraction analysis was employed to determine the composition of the caked material.

Results and Discussion

A large number of runs were made first with the bench-scale reactor and later with the PDU. Many of these runs were completed successfully without incident. However, in more than a few runs particle agglomeration and bed caking were encountered, which interfered with particle fluidization.

Bench-Scale Reactor Runs. A partial list of the runs conducted with the bench-scale fluidized-bed reactor is presented in Table 2. These runs were conducted primarily to observe the effects of the bed temperature, gas composition, and flow rate on the apparent rate of reaction and on the tendency of the particles to stick together and agglomerate. Among different runs, the fluidized-bed temperature ranged from 400 to 560 °C, the SO₃ concentration from 0.63 to 2.05 vol %, and the gas flow rate from 200 to 300 mL/s measured at room temperature and pressure. The corresponding range of superficial gas velocity in the reactor was 0.53–0.79 m/s. Over this range of velocity, the salt particles were well fluidized unless they became sticky, which was not an unusual occurrence.

Following each run, the reactor was inspected for evidence of bed caking. In 45% of the runs listed in Table 2, some caking was observed. Caking was considered severe if 25% or more of the material was stuck together. After several runs, the bed appeared to be completely caked. However, in these runs the particles were loosely stuck together so that the caked material was easily removed from the reactor. It is quite possible that in some cases bed caking did not occur until the run ended and the gas flow stopped because it was not possible to discern bed slumping during a run. Caking appeared to be related primarily to the bed temperature, although in runs 156 and 157, it seemed to be caused by higher levels of H₂O concentration. Generally, whenever the bed temperature was kept within a range of 500–550 °C during a run, the particles remained free flowing. If the bed temperature fell below 490 °C, caking was observed. Some of the most severe caking was observed in runs 149 and 150, which were conducted at 400–430 °C. Following several runs, samples of both the caked and free-flowing products from the same run were subjected to X-ray diffraction analysis, which showed that the principal difference in the two materials was the presence of a small amount of Na₂SO₃ in the caked material. Because the melting point of Na₂SO₃ is relatively low (i.e., 187 °C), a small amount could easily make the bed particles sticky. The presence of troublesome amounts of NaHSO₄ in the product was somewhat unexpected because NaHSO₄ should have been converted to Na₂S₂O₇ by the following reaction at the temperatures that were employed.

\[
2\text{NaHSO}_4(l) \rightarrow \text{Na}_2\text{S}_2\text{O}_7(l) + \text{H}_2\text{O}(g) \quad (2)
\]

However, after some runs the product was partly caked or agglomerated. In that case the product was separated, and the amount and sulfate content of each part were determined. In a few cases X-ray diffraction analysis was employed to determine the composition of the caked material.
He had also warned about conducting the process above 590 °C “to avoid fusion of the salts and their eutectic mixtures”.

For the runs reported in Table 2, conversion is based on the conversion of NaCl to HCl because this provided a measure of the overall or total conversion regardless of whether the final product was Na₂SO₄ or NaHSO₄. When the product was entirely free flowing as in runs 124 and 125, the extent of reaction based on the formation of HCl was essentially the same as the extent of reaction based on the formation of sulfate, which confirmed that Na₂SO₄ was the only solid product. When the product was partly caked as in run 123, the extent of reaction based on sulfate was not the same as that based on HCl, indicating the presence of more than one form of sulfate.

The general effect of temperature on the reaction rate can be inferred from Figure 2 which presents the results of runs conducted at five different temperature levels. It is apparent that the rate increased substantially over the temperature range indicated. Bed caking was observed at the three lowest temperature levels but not at the two highest levels. Although the bed of particles was partly caked after run 151 conducted at 480–485 °C, the curve corresponding to this run in Figure 2 was more like the curves for noncaked beds than for caked beds, which suggests that caking may have taken place near the end of the run.

In addition to temperature, gas composition has a major effect on the reaction rate. The effect of the SO₃ concentration can be inferred from Figure 3, which shows the results of four different runs conducted at about the same temperature. A free-flowing product was produced in each of these runs. The apparent reaction rate seemed to be approximately a second-order function of the SO₃ concentration.

The effect of the H₂O concentration on the apparent reaction rate can be inferred from Figure 4, which presents the results of four runs conducted at nearly the same temperature and SO₃ concentration. The results suggest that, for an SO₃ concentration of 1.9 vol %, the optimum H₂O concentration was 2.5 vol % because this concentration provided the highest rate of reaction. The increase in the rate of reaction as the H₂O concentration was raised from 1.7% to 2.5% agreed with the results of Fielder et al., who found that the rate was a first-order function of the H₂O concentration. The decline in rate which occurred when the H₂O concentration was increased from 2.5 to 5 vol % seemed to be due to particle agglomeration because the resulting product changed from a completely free-flowing material to a completely caked material.
To shed light on the reaction mechanism, several particles recovered from run 133 were cross-sectioned and examined with a scanning electron microscope (Figure 5). These particles had been reacted sufficiently at 520–525 °C to provide a conversion of 70%. Because the particles remained free flowing, Na₂SO₄ was the most likely product. A view of the particle cross sections shows that each particle consisted of an unreacted core surrounded by a shell of reacted material. Furthermore, the shell appeared to be relatively porous because a large number of small voids can be seen. Therefore, the reaction mechanism is in accord with the well-known model of a particle which undergoes a shrinking unreacted core process that produces an increasingly thick shell of product while the overall particle size remains the same.11

According to this model, the overall rate of reaction should remain constant over time if the rate is controlled by gas film diffusion, whereas the rate should decline markedly over time if it is controlled either by product layer diffusion or by chemical reaction. Consequently, the results of runs 124 and 125 in Figure 6 indicate that, for these runs conducted at 515 ± 15 °C, the rate of conversion was controlled by gas film diffusion, at least for conversions up to 90%. The results were markedly different at a lower temperature where the rate of chemical reaction was slower and could have become the rate-controlling step. This possibility was suggested by the decline in the reaction rate over time. However, another possibility was suggested by bed caking which occurred during lower temperature runs. The caking was probably due to the presence of small amounts of fused NaHSO₄. The resulting particle agglomeration could easily have interfered with gas diffusion and probably accounted for the decrease in the reaction rate part of the way through the runs indicated in Figure 7.

The film diffusion model also did not apply well to the results of runs conducted at higher temperatures or with larger SO₃ concentrations where the rate of reaction appeared to increase as the runs proceeded (see Figures 2 and 3). This unusual behavior cannot be readily explained, although it suggests the formation of a reaction product which catalyzed the reaction. Another possibility is that the mass-transfer film coefficient increased with an increase in the particle density.
as NaCl was converted to Na₂SO₄. Complete conversion would have produced a 21.5% increase in density, which would have increased the free-fall velocity of a particle and caused a corresponding increase in the film coefficient.¹¹

**PDU Operation.** A large number of runs conducted with the PDU generally supported and confirmed the results achieved with the bench-scale system. These runs showed that with proper selection of operating conditions it was possible to achieve a relatively high rate of conversion of NaCl to Na₂SO₄ while avoiding particle agglomeration and bed caking. The runs also identified conditions which tended to promote agglomeration and conditions which tended to inhibit agglomeration.

Most of the runs were made with the drilled-plate gas distributor because the runs made with this distributor generally produced a completely free-flowing product, whereas the runs made with the sintered-metal-plate distributor produced a partially caked product. The difference in the results is believed to be due to the difference in bed turbulence produced by the different gas distributors. Earlier observations indicated that a drilled-plate gas distributor generally produced a higher level of bed turbulence than a sintered metal plate. The greater turbulence produced by the drilled plate would have tended to break up agglomerates of sticky particles which prevented bed caking.

The most relevant runs made with the drilled-plate gas distributor are listed in Table 3. In each run a 2–6 kg batch of salt was treated with a gas mixture having the indicated composition and flow rate. The SO₃ feed concentration was estimated by assuming that the well-designed catalytic converter produced a conversion of SO₂ to SO₃ approaching 90% of the equilibrium value. This assumption was verified by analyzing the converter product on several occasions. For the first set of runs listed, most of the gas was introduced through the distributor plate and only steam was introduced through a sparger. For the second set of runs, all of the gas was introduced through the plate, and for the third set of runs, the entire output of the catalytic converter was introduced through the sparger while supplemental air was passed through the plate.

At the beginning of each run it took 15 min or more to saturate the catalytic converter with SO₂ before SO₃ was produced. Therefore, the net reaction time reported in Table 3 is the total time SO₂ was fed less 15 min. Also reported in Table 3 is the amount of loose, free-flowing material left in the reactor at the end of each run expressed as a percent of the total amount of solid product. It is apparent that for most of the runs the solid product was entirely free flowing. The occurrence of agglomerates in runs 13, 34, and 49 seems to have been due largely to the higher concentrations of SO₃ employed in these runs. Interestingly, agglomeration was not observed in run 32 made under conditions which were very similar to those used for run 34. The formation of agglomerates in the 5–15 mm diameter range in run 34 seemed to result from either a slight increase in the SO₃ concentration or a small decrease in the superficial gas velocity or both because agglomeration appeared to depend on both the SO₃ concentration and fluidized-bed turbulence. The effect of gas velocity or turbulence is shown also by the results of runs 13, 31, and 49 all made with relatively high concentrations of SO₃. For these runs the extent of particle agglomeration was inversely proportional to the superficial gas velocity. In runs 31 and 32 bed turbulence may have been enhanced further by sparging a large fraction of the gas.

Also reported in Table 3 is the percent conversion of NaCl to Na₂SO₄ in the loose or free-flowing product based on the measured sulfate content of the product. It was assumed that only Na₂SO₄ and NaCl were present in this material because it was unagglomerated. In addition, values of the percent recovery of sodium as either Na₂SO₄ or NaCl are reported for the loose product. For three-fourths of the runs, the recovery of sodium in the loose product was 95% or more of that supplied. Some material was lost through particle entrainment in the fluidizing gas, through agglomeration and caking, and through material handling.

The average apparent reaction rate was taken to be the ratio of the total conversion to the net reaction time for any given run. The results presented in Table 3 show that the highest rates of reaction were achieved without sparging when all of the gas was introduced through

---

**Table 3. Results of Runs Made with the PDU Using the Drilled-Plate Gas Distributor**

<table>
<thead>
<tr>
<th>run no.</th>
<th>NaCl, kg</th>
<th>plate</th>
<th>sparger</th>
<th>SO₃</th>
<th>SO₂</th>
<th>O₂</th>
<th>H₂O</th>
<th>temp, °C</th>
<th>u, m/s</th>
<th>time, min</th>
<th>loose product, %</th>
<th>amt</th>
<th>Na rec</th>
<th>convn rate, %/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>2.00</td>
<td>307</td>
<td>7.2</td>
<td>2.0</td>
<td>0.3</td>
<td>19.9</td>
<td>2.3</td>
<td>530</td>
<td>0.79</td>
<td>45</td>
<td>Sparged with Steam</td>
<td>100</td>
<td>97</td>
<td>37</td>
</tr>
<tr>
<td>10</td>
<td>2.00</td>
<td>304</td>
<td>7.8</td>
<td>1.9</td>
<td>0.3</td>
<td>19.2</td>
<td>2.5</td>
<td>555</td>
<td>0.81</td>
<td>45</td>
<td></td>
<td>100</td>
<td>98</td>
<td>55</td>
</tr>
<tr>
<td>13</td>
<td>2.00</td>
<td>300</td>
<td>11.0</td>
<td>2.9</td>
<td>0.5</td>
<td>18.4</td>
<td>3.5</td>
<td>545</td>
<td>0.79</td>
<td>85</td>
<td></td>
<td>40</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>2.00</td>
<td>300</td>
<td>4.3</td>
<td>2.3</td>
<td>0.3</td>
<td>19.2</td>
<td>1.6</td>
<td>575</td>
<td>0.81</td>
<td>90</td>
<td></td>
<td>100</td>
<td>96</td>
<td>97</td>
</tr>
<tr>
<td>16</td>
<td>2.00</td>
<td>311</td>
<td>0</td>
<td>2.0</td>
<td>0.3</td>
<td>19.2</td>
<td>2.3</td>
<td>575</td>
<td>0.82</td>
<td>45</td>
<td></td>
<td>100</td>
<td>98</td>
<td>87</td>
</tr>
<tr>
<td>17</td>
<td>2.00</td>
<td>309</td>
<td>0</td>
<td>2.0</td>
<td>0.3</td>
<td>19.2</td>
<td>2.5</td>
<td>580</td>
<td>0.82</td>
<td>15</td>
<td></td>
<td>100</td>
<td>99</td>
<td>30</td>
</tr>
<tr>
<td>18</td>
<td>2.00</td>
<td>306</td>
<td>0</td>
<td>2.1</td>
<td>0.3</td>
<td>19.2</td>
<td>2.6</td>
<td>580</td>
<td>0.81</td>
<td>30</td>
<td></td>
<td>100</td>
<td>96</td>
<td>54</td>
</tr>
<tr>
<td>19</td>
<td>2.00</td>
<td>312</td>
<td>0</td>
<td>2.0</td>
<td>0.3</td>
<td>19.2</td>
<td>2.6</td>
<td>600</td>
<td>0.85</td>
<td>15</td>
<td></td>
<td>100</td>
<td>99</td>
<td>28</td>
</tr>
<tr>
<td>20</td>
<td>2.00</td>
<td>318</td>
<td>0</td>
<td>2.0</td>
<td>0.3</td>
<td>19.2</td>
<td>2.5</td>
<td>650</td>
<td>0.83</td>
<td>45</td>
<td></td>
<td>100</td>
<td>99</td>
<td>63</td>
</tr>
<tr>
<td>21</td>
<td>2.00</td>
<td>317</td>
<td>0</td>
<td>2.0</td>
<td>0.3</td>
<td>19.3</td>
<td>2.1</td>
<td>550</td>
<td>0.81</td>
<td>15</td>
<td></td>
<td>100</td>
<td>99</td>
<td>22</td>
</tr>
<tr>
<td>22</td>
<td>2.00</td>
<td>311</td>
<td>0</td>
<td>2.0</td>
<td>0.3</td>
<td>19.2</td>
<td>2.3</td>
<td>555</td>
<td>0.80</td>
<td>75</td>
<td></td>
<td>100</td>
<td>98</td>
<td>97</td>
</tr>
<tr>
<td>49</td>
<td>4.00</td>
<td>392</td>
<td>0</td>
<td>3.2</td>
<td>0.8</td>
<td>17.4</td>
<td>7.0</td>
<td>535</td>
<td>0.99</td>
<td>20</td>
<td></td>
<td>97</td>
<td>95</td>
<td>50</td>
</tr>
<tr>
<td>30</td>
<td>6.00</td>
<td>282</td>
<td>109</td>
<td>2.2</td>
<td>0.4</td>
<td>19.0</td>
<td>2.7</td>
<td>570</td>
<td>1.03</td>
<td>165</td>
<td>Sparged with Converter Output</td>
<td>100</td>
<td>97</td>
<td>82</td>
</tr>
<tr>
<td>31</td>
<td>6.00</td>
<td>282</td>
<td>118</td>
<td>2.7</td>
<td>0.5</td>
<td>18.2</td>
<td>3.0</td>
<td>570</td>
<td>1.05</td>
<td>165</td>
<td></td>
<td>100</td>
<td>89</td>
<td>96</td>
</tr>
<tr>
<td>32</td>
<td>6.00</td>
<td>282</td>
<td>117</td>
<td>3.4</td>
<td>0.6</td>
<td>18.0</td>
<td>3.8</td>
<td>570</td>
<td>1.05</td>
<td>95</td>
<td></td>
<td>100</td>
<td>94</td>
<td>90</td>
</tr>
<tr>
<td>34</td>
<td>6.00</td>
<td>263</td>
<td>118</td>
<td>3.5</td>
<td>0.7</td>
<td>17.8</td>
<td>4.4</td>
<td>545</td>
<td>0.97</td>
<td>95</td>
<td></td>
<td>75</td>
<td>67</td>
<td>95</td>
</tr>
</tbody>
</table>

- **Sparged with Steam**
- **Not Sparged**
- **Sparged with Converter Output**

**Notes:**
- **a** Gas flow rate at 20 °C and 1.00 atm.
- **b** Average fluidized-bed temperature.
- **c** Superficial gas velocity at reactor operating conditions.
- **d** Estimated net reaction time.
- **e** Average apparent reaction rate.
the distributor plate. When one or more of the reactants was introduced through a sparger, the gas to particle contact appeared to suffer, decreasing the reaction rate. This effect was most pronounced in runs 30–34, where all of the reactants were sparged into the fluidized bed, and the reaction rates were the lowest observed for comparable SO3 concentrations.

The effect of the SO3 concentration on the rate of reaction at 570 °C is apparent from the results of runs 30–32, where the rate increased steadily with increasing SO3 concentration. The effect can also be seen by comparing the results of run 49 with those of runs 21 and 22 conducted at slightly higher temperatures. The trend associated with the SO3 concentration is similar to that observed with the bench-scale reaction system.

The effect of temperature on reaction rate can be inferred from Figure 8 showing the results of runs 16–22, which were conducted at basically two different temperatures but otherwise similar conditions. At 555 ± 5 °C, the apparent average reaction rate was 1.4%/min, and at 585 ± 10 °C, it was 1.9%/min. These values are not greatly different from those observed with the bench-scale reaction system.

After several runs which resulted in significant particle agglomeration, samples of caked material were analyzed and found to contain small concentrations of either NaHSO4 or Na2S2O7 or both.

**Control of Particle Agglomeration.** The preceding results indicate that particle agglomeration and bed caking were significant problems under some reaction conditions. The problems were exacerbated by a low bed temperature (e.g., 400–480 °C) or a large SO3 concentration (e.g., >3 vol %) or possibly a large concentration of steam. The problems were mitigated by increasing the superficial gas velocity and fluidized-bed turbulence. The problems appeared to be caused by the formation of lower melting point byproducts which were likely to have been NaHSO4 and Na2S2O7 because small amounts of these compounds were found among the caked solids. The presence of these compounds on the surface of particles being fluidized at temperatures above the melting points of the compounds would have made the particles sticky and caused them to agglomerate. Cannon3 mentioned NaHSO4 specifically as causing such a problem. Furthermore, both byproducts have been implicated in the formation of corrosive, sticky deposits on boiler tubes in kraft pulp mills.10,12 It has also been generally observed that, as the temperature of a fluidized bed approaches the melting point of the solids, the particles become sticky and tend to agglomerate.13

Sodium bisulfate may occur in a system producing Na2SO4 because it is a reactive intermediate. This possibility is suggested by a reaction mechanism proposed previously to explain the sulfation of NaCl in kraft mill recovery furnaces which included the following steps:4,14

\[
\text{SO}_3(\text{ads}) + \text{H}_2\text{O}(\text{ads}) \rightarrow \text{H}_2\text{SO}_4(\text{ads}) \quad (3)
\]

\[
\text{H}_2\text{SO}_4(\text{ads}) + \text{NaCl}(s) \rightarrow \text{HCl}(g) + \text{NaHSO}_4(\text{ads}) \quad (4)
\]

\[
\text{NaHSO}_4(\text{ads}) + \text{NaCl}(s) \rightarrow \text{Na}_2\text{SO}_4(s) + \text{HCl}(g) \quad (5)
\]

Although NaHSO4 may be formed by reaction (4), it is unstable at higher temperatures because it is converted to Na2S2O7 by reaction (2).9,10 Na2S2O7, in turn, can undergo the following decomposition reaction:

\[
\text{Na}_2\text{S}_2\text{O}_7(l) \rightarrow \text{Na}_2\text{SO}_4(s) + \text{SO}_3(g) \quad (6)
\]

The thermal stability of these materials in air was examined previously by employing a combination of differential thermal analysis and thermogravimetric analysis (DTA/TGA).10 This work showed that NaHSO4 decomposes slowly at its melting point (180 °C) and much more rapidly at 300 °C. The Na2S2O7 formed is relatively stable up to its melting point (380 °C). (The values of 180 and 380 °C are slightly lower than those reported by other workers.9,15) Further heating of the molten Na2S2O7 converts part of the material to solid Na2SO4, which reacts with the remaining Na2S2O7 to form 3Na2S2O7⋅2Na2SO4 with a melting point of 570 °C. This previously unidentified compound forms a eutectic melt with Na2S2O7 at about 540 °C. These results suggest that 3Na2S2O7⋅2Na2SO4 could also contribute to particle stickiness in the process under consideration. The system is complicated further by the eutectic formed with a mixture of NaCl and Na2SO4, which melts at 628 °C.16

Avoiding particle agglomeration during the production of Na2SO4 will require either minimizing the formation of low melting point byproducts or eliminating them once formed. The decomposition of NaHSO4 and Na2S2O7 by reactions (2) and (6) is favored by higher temperatures and lower partial pressures of the gaseous products which is in line with the conditions found here to give the best results. Because it may not be possible to completely eliminate the offending materials, small amounts may be tolerated by appropriate design of the fluidized-bed reactor gas distributor and by employment of a large gas velocity.13

**Conclusions**

The results of this study confirm the general technical feasibility of producing Na2SO4 by reacting NaCl with SO3 and steam in a fluidized-bed reactor. By careful selection of appropriate operating conditions, reasonable rates of reaction and trouble-free operation can be achieved. Favorable operating conditions include temperatures in the range of 500–600 °C, SO3 concentrations in the range of 1–3 vol %, and steam concentrations equal to or slightly higher than the SO3 concentration. Within this range of operating conditions, excessive particle agglomeration and fluidized-bed slumping can be avoided by providing adequate superficial gas velocities and bed turbulence. Lower temperatures and higher SO3 concentrations tend to promote particle agglomeration and bed caking, because of the formation and/or presence of lower melting point byproducts such as...
NaHSO₄ and Na₂S₂O₇. Although these compounds are unstable above 400 °C, they may exist in a transitory state or may form other more stable but troublesome compounds such as 3Na₂S₂O₇·2Na₂SO₄, which has a melting point of 570 °C. Because the results achieved with a much larger reactor were as good or better than the results achieved with a small reactor, size scale-up should be straightforward. However, the design of the gas distributor will be critical because it affects bed turbulence.

The results also showed that individual salt particles undergo a shrinking unreacted core process which produces a growing layer of product as the particle reacts. For the fluidization conditions employed, the overall rate of reaction was controlled by gas film diffusion. The average apparent rate of reaction was proportional to the temperature and SO₃ concentration and a complex function of the steam concentration.

Acknowledgment

Financial support for this work was provided by Prima Resources, N.A., of Australia and by Iowa State University. The technical assistance of Royce Abbott is gratefully acknowledged.

Literature Cited

(14) Henrikszson, M.; Warnqvist, B. Kinetics of Formation of HCl(g) by the Reaction between NaCl(s) and SO₂, O₂, and H₂O-(g). Ind. Eng. Chem. Process Des. Dev. 1979, 18, 249–254.

Received for review November 6, 2001
Revised manuscript received May 29, 2002
Accepted May 29, 2002