

Flue Gas Desulfurization Using Recycled Sodium Bicarbonate

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Abstract

This paper presents a breakthrough cost effective FGD technology using regenerated sodium bicarbonate/carbonate to remove SO_x and NO_x , while producing valuable fertilizer co-products. Described herein is the advanced regeneration technology developed by AIRborne Technologies Inc. (ATI), combined with the commercial sodium scrubbing experience deployed by Babcock & Wilcox (B&W), and the fertilizer marketing/distribution capability supplied by Potash Corporation.

The development status of the technology, including historical results from AIRborne and the current program of the demonstration plant, is described in this paper. This timely examination will conclude with a study of a commercial installation identifying capital and operating costs of the Babcock & Wilcox/AIRborne sodium carbonates system, as compared to a typical LSFO/SCR installation.

Introduction

Flue gas desulfurization (FGD) using sodium carbonate (soda ash) or sodium bicarbonate was identified long ago as a highly efficient process. However, the sodium reagent costs were prohibitively high. In addition, the sodium sulfite produced from the process had limited economic value and posed a disposal problem.

AIRborne Technologies recognized that, while using sodium carbonate (soda ash) or sodium bicarbonate sorbent for FGD had potential, there was a significant technical and commercial obstacle to overcome before the process would be adopted in the industry. If the reacted reagent, sodium sulfate, could be eco-

nominally regenerated into sodium bicarbonate for reuse as the reagent, then these barriers could be overcome. Early work by the Russians and others, on the conversion of sodium sulfate to sodium bicarbonate, indicated that this process was very difficult, since mixed salts of approximately similar proportions were produced. This meant low yields of recovered sodium bicarbonate and ammonium sulfate that were heavily contaminated with sodium sulfate. This rendered the material unsaleable. The sodium sulfate to sodium bicarbonate conversion system has been almost completely ignored since then.

AIRborne Advancement of Sodium Scrubbing

AIRborne reviewed the phase work on this process and found the low temperature region of the phase diagram poorly defined. It was discovered that conditions existed whereby good yields of high purity sodium bicarbonate and ammonium sulfate could be obtained. A process was designed to take advantage of these observations and a 20-ton per day pilot plant was constructed to test the process to produce high purity ammonium sulfate. The demonstration proved successful. AIRborne made it possible to recycle sodium, as sodium bicarbonate, and produce agricultural grade ammonium sulfate fertilizer. This advance now makes sodium FGD environmentally and economically attractive. The ammonium sulfate can be sold directly or can be used as a feedstock to produce high value potassium sulfate fertilizer. The overall FGD economics to the utility company for pollution abatement are now significantly improved.



Figure 1 Jim Bridger Power Station with sodium carbonate scrubbers installed by B&W.

Existing Sodium Carbonate Scrubbing Facilities

Sodium scrubbing has been successfully employed at the Jim Bridger power plant in Wyoming. B&W installed 3 x 550 MW sodium-based wet scrubbers at Jim Bridger from 1986-1990. PacifiCorp had secured a unique arrangement for cost effective sodium carbonate sorbent. See Figure 1.

Low cost sodium carbonate (soda ash) waste streams were available from nearby mines for FGD scrubbing and waste sodium sulfate streams could be easily disposed of. This combination leads to favorable economics.

The Electric Power Research Institute (EPRI) carried out the initial work on sodium scrubbing in 1978 and the Jim Bridger plant opened up in the early 80s. The Bridger plant is rated at 2,200 MW (4 units). This installation clearly demonstrated the efficiency of sodium-based FGD, however, the costs of the sodium absorbent for the system and waste stream management have prevented widespread use of sodium-based scrubbing.

The crucial step in developing the process was the discovery of operating conditions wherein the sodium sulfate waste stream from the absorption step during FGD is transformed back into sodium bicarbonate sorbent and ammonium sulfate fertilizer. This is the subject of the experimental section of this paper.

Pilot Plant Design and Operation

AIRborne completed its sodium sulfate to sodium bicarbonate process development at their commercial sodium sulfate mine in Ormiston, Saskatchewan. The original concept at Ormiston was to upgrade the sodium sulfate into commercially marketable sodium bicarbonate (baking soda) for sale as a commodity product. The demonstration plant production rate was 15 tons per day with a capacity of 20 tons per day and operated for 18 months. The results of the demonstration are presented in Figures 2, 3 and 4.

The pilot plant produced grades of sodium bicarbonate 98%+ in purity, a product suitable for FGD markets. Later in the program the ammonium sulfate was eventually produced at 99%+ purity levels. This was critical to selling ammonium sulfate into fertilizer markets. Both the sodium bicarbonate and the ammonium sulfate were sold as commodity products from the pilot plant. With the conversion efficiency and the product purity achieved, the pilot was deemed to be a major success.

The demonstration plant results serve as the basis for a process design whereby absorbent is regenerated and marketable

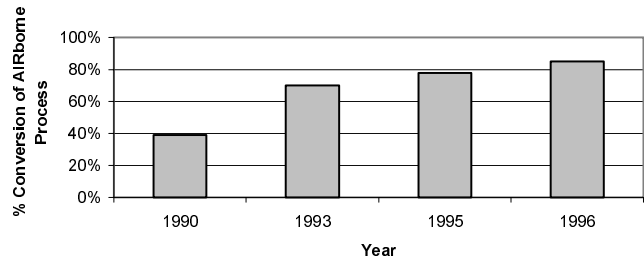


Figure 2 Stoichiometric conversion of sodium sulfate to sodium bicarbonate (unit operation).

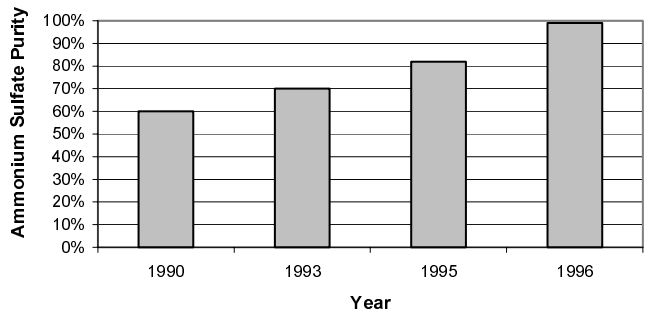


Figure 3 Ammonium sulfate purity over process development.

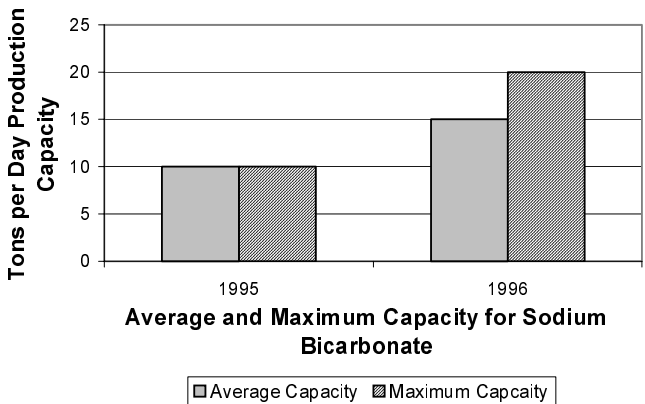


Figure 4 Daily production capacity of sodium bicarbonate at Ormiston Mines.

fertilizer is co-produced. This enables efficient pollution abatement. In turn, abatement becomes a revenue stream rather than a cost and is, therefore, a major step forward in improving the operations of coal-fired electric power plants.

The B&W/AIRborne Acid Gas Abatement Process

Using the information from the Ormiston pilot, a process has been engineered for FGD. The process is based on use of sodium bicarbonate as wet, wet and dry combined, or dry sorbent in the flue gas stream. Under the conditions of the hot flue gas, the bicarbonate is converted to a highly porous and reactive sodium carbonate (soda ash) that leads to high absorbent efficiency. Ammonium sulfate fertilizer is recovered from the regeneration process for sale.

The process is divided into sequential unit operations of FGD SO_x reaction with sodium bicarbonate, sodium sulfate feedstock preparation, ammonium bicarbonate production, sodium bicar-

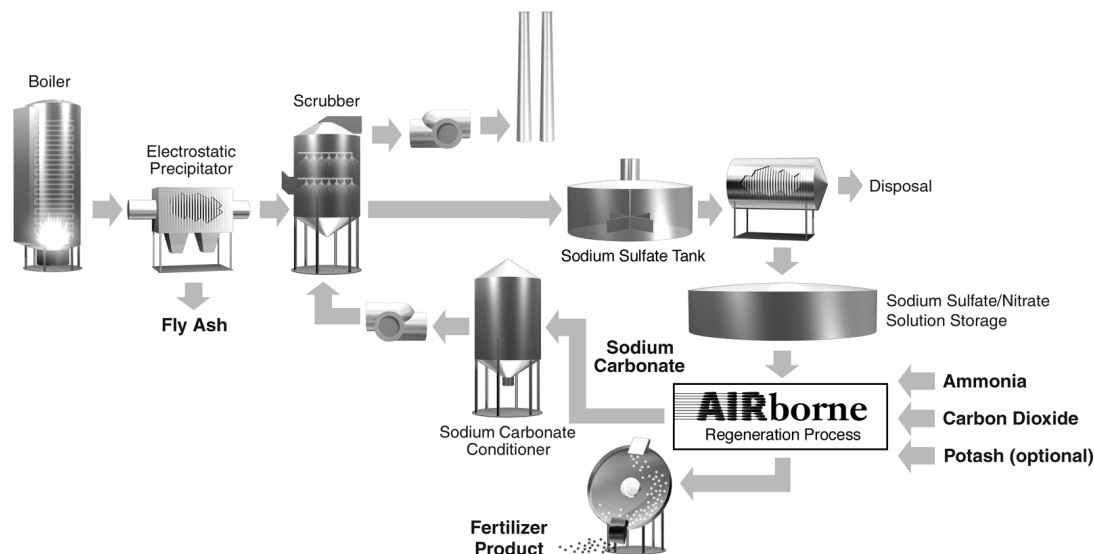
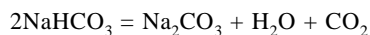


Figure 5 B&W/AIRborne process.

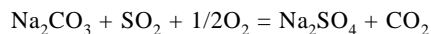
bonate production, ammonium sulfate production, and potassium sulfate production. The NO_x /nitrate reaction is ignored for the purpose of illustration. See Figure 5.

The process is defined by the following basic chemical reactions:

1. Reaction of sodium bicarbonate in flue gas stream to calcine the sodium bicarbonate into sodium carbonate (soda ash). This step is not required with wet sodium carbonate (soda ash) scrubbing.

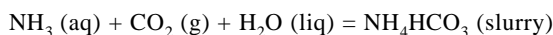


2. Reaction of sodium carbonate with sulfur dioxide and oxygen to produce sodium sulfate.

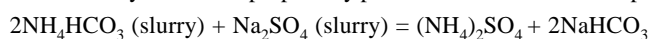


3. Sodium sulfate feedstock preparation is chemically accomplished by pH adjustment of the solution. The addition of sodium carbonate (soda ash) to the sodium sulfate solution complexes the harmful heavy metals into carbonates i.e. lead carbonate (PbCO_3). These metal complexes are filtered out of the brine before further processing. This step is critical to ensure product purity for both the sodium bicarbonate and the fertilizer co-product. The solubility of sodium sulfate in water makes the removal of heavy metals both technically and commercially viable.

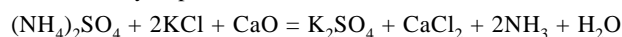
4. Production of ammonium bicarbonate is achieved with the mixing of ammonia and carbon dioxide in water slurry.



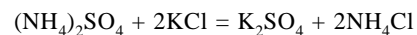
5. Reaction of ammonium bicarbonate with sodium sulfate produces a sodium bicarbonate crystal and ammonium sulfate solution. The challenges to the process were the stoichiometric conversion efficiency and the efficient separation of sodium sulfate from ammonium sulfate to produce a high quality ammonium sulfate fertilizer. Process development by AIRborne has led to a commercially viable and proprietary procedure for this crucial step.



6. As an option, potassium sulfate fertilizer can be made by reacting ammonium sulfate with potassium chloride (potash) and calcium oxide (lime) to produce potassium sulfate and recycle ammonia. This will eliminate the need for the ammonia feed stock, which is costly to procure and more difficult to store.



7. Optional Step: The potassium sulfate fertilizer can also be made in a reaction of ammonium sulfate with potash to produce potassium sulfate and ammonium chloride. This step does not allow for the ammonia recycle. The ammonium chloride would be granulated and sold as a commercial fertilizer in the nitrogen fertilizer market.



The AIRborne process can be operated in a dry, wet or combined scrubbing configuration.

The Fertilizer Products

Fertilizer must be properly formulated before it is accepted in today's markets. This means that product granules should be predominantly within the 5-10 mesh size range, round, free flowing, uniform, durable and meet commercial grades.

Both ammonium sulfate and potassium sulfate presented formulation difficulties in meeting industry standards in the past. Currently they are compacted products and as a result, product quality is low. AIRborne has acquired and developed new technology for a highly efficient means of pan granulation that produces top quality premium granular product. See Figure 6.

Ammonium sulfate is now used primarily as a source of sulfur, although at one time, before the advent of urea, it played a significant role as a nitrogen source. Currently, most ammonium sulfate is produced as a bi-product of caprolactam production. It is typically 10-14 mesh crystal and difficult to blend with other fertilizers. In contrast, AIRborne's granular ammonium sulfate is completely blendable and a premium product.

Potassium sulfate is a premium potash fertilizer. The premium pricing arises from the high costs to manufacture it from regular potash (potassium chloride) and a sulfate source. Potassium sulfate is also higher valued because it also contains sulfate sulfur which is readily available for plants. In the case of the B&W/AIRborne FGD process, the economics of producing potassium sulfate are significantly better than current calcium-based FGD processes.

AIRborne has formed a marketing alliance with Potash Corporation of Saskatchewan, the world's largest fertilizer company,



Figure 5 AIRborne granular fertilizer products.

to market the fertilizer product from our FGD process. Potash Corporation has extensive operations and infrastructure throughout North and South America and market connections around the world. This arrangement will ensure that fertilizer product from B&W/AIRborne FGD units will find an attractive market.

The Economics of B&W/AIRborne FGD

Comparisons of the B&W/AIRborne process and the LSFO/SCR systems are shown in Table 1.

The information in Table 1 is based upon a 600 MW coal-fired electric power plant. The cash flow is positive for the utility company for a B&W/AIRborne installation.

The industry standard process is lime/limestone for SO_x and an SCR for NO_x. Table 1 also contains the operating cost data for this process. The cash flow is negative for this type of installation. The capital costs for the B&W/AIRborne system for SO_x and NO_x abatement are comparable but slightly less.

In addition to the individual process economics, Table 1 also contains a comparison between the two types of processes. The benefits of the B&W/AIRborne process are readily apparent, with less capital requirements and a substantial operating profit versus a cost on the LSFO/SCR system.

All the assumptions for the B&W/AIRborne system, LSFO, and the SCR system are included in the Appendix 1. Detailed financial comparison information is included in Appendix 2.

SO_x and NO_x Recovery Percentages

It has been well established by Bennett (Reference 4), Verlaeten et al (Reference 2) of Solvay and Lowell et al (Reference 1) that the use of sodium-based sorbents reduces NO_x as well as SO_x.

The extent of the SO_x reduction is 95+ % for dry sodium bicarbonate with 98+ % reduction of SO₂ using a wet sodium carbonate solution. The extent of the NO_x reduction is 40~95+ % depending on conditions.

Demonstration Project

B&W and AIRborne are in the process of designing a combined demonstration plant to confirm the performance of the FGD system, regeneration plant, and fertilizer production all together. The scale of this demonstration is to produce 3 tons/day of sodium bicarbonate (i.e. scrub approx. 1 tpd of SO_x). The program will evaluate and optimize all aspects of the process for scale up to commercial size. Additional testing will include NO_x and mercury removal and optimizations of both.

Conclusion

AIRborne has developed an environmentally sound pollution management system that can realize economic returns. AIRborne has formed alliances with Babcock & Wilcox along with Potash Corporation to implement the technology in the marketplace.

The Advantages of the B&W/AIRborne Process:

1. High SO₂ removal efficiency with a smaller proven scrubber system.
2. Regeneration of reagent for re-use in scrubber system avoiding disposal issues.
3. High NO_x and oxidized mercury removal.
4. Production of a variety of fertilizers for assured market success.
5. Fertilizer co-product transported, stored, and marketed by Potash Corporation, a world leader in the fertilizer business.
6. Dramatically improved economics (produce more valuable fertilizer) with higher sulfur, lower cost fuels.
7. Pollution abatement will now create additional operating revenue to the utility.

Table 1
Summary Technology Financial Comparison for High-sulfur Coal-fired Utility (All \$US M)

	Install a LSFO system and add SCR unit for NO _x recovery	Install an AIRborne Potassium Sulfate/ Ammonium Chloride for SO _x and NO _x recovery
Capital		
B&W/AIRborne Process	141.0	141.0
LSFO/SCR Alternative Processes	147.0	
Incremental Capital Cost (Savings) for B&W/AIRborne System (6.0)		
B&W / AIRborne Operating Cost Advantage		
Operating Cost LSFO/SCR System (profit)	(0.9)	
Operating Revenue generated by B&W/AIRborne (profit)	(37.0)	
Total Operating Cost Saving by B&W/AIRborne Technology	36.1	

Appendix 1

Assumptions for Sample Flue Gas Purification Cost/Benefit Study

Power Station MW Capacity	600
Coal Sulfur Percentage	3.40%
Heat Rate	10,500 Btu/kWhr
Coal HHV	12,000 Btu/lb
SO ₂ % recovery requirements by B&W/ATI	98%
NO _x % recovery requirements by B&W/ATI	85%
Capacity Factor of Power Plant	80%
SO _x Recovery % for LSFO	95%
NO _x % Recovery for SCR	85%
NO _x Operating Season (Months)	5

**Appendix 2
Detailed Financial Information**

	Cost Assumptions	Install a LSFO system and add SCR unit for NO _x recovery	Install an AIRborne Potassium Sulfate/ Ammonium Chloride for SO _x and NO _x recovery
Technology Financial Comparison for High-sulfur Coal			
Capital Costs			
LSFO System	150 \$/kWe	90,000,000	
SCR System	95 \$/kWe	57,000,000	
Sodium Scrubber	60 \$/kWe		36,000,000
Dry Sodium Bicarbonate feed and Sodium Sulfate collection system	7 \$/kWe		4,200,000
Sodium Carbonates Regeneration Plant	91\$/kWe		54,600,000
Fertilizer Plant	78 \$/kWe		46,100,000
Total Capital Requirement		147,000,000	140,900,000
\$/kWe Capital Cost		245	235
FGD/NO _x Systems Operating Costs			
NO_x Operating Costs	5 months	3,800,000	200,000
SO_x Operating Costs			
O&M Labor	41.72 \$/hr	1,300,000	1,600,000
Maintenance	1.00%	1,500,000	900,000
Power	.033 \$/kWhr	2,300,000	2,200,000
Pressure Drop		900,000	500,000
Steam	\$3.50 / klb	1,700,000	
Sorbent Costs	12.00 \$/ton	2,100,000	
CO ₂	10.00 \$/ton		1,600,000
Landfill	10.00 \$/ton	3,300,000	
Operating Costs for SO _x		<u>13,000,000</u>	<u>6,900,000</u>
Operating Costs for SO_x and NO_x		16,800,000	7,100,000
Fertilizer Plant Operating Costs and Revenue			
Fertilizer Inputs			
Ammonia	220 \$/ton		14,100,000
Potash	105 \$/ton		29,500,000
Binder	106 \$/ton		1,000,000
Granulation Royalty	.61\$/ton		300,000
Operating Costs			
Electrical	.033 \$/kWhr		1,200,000
Steam	\$3.50 / klb		6,900,000
Maintenance	1.00%		500,000
Labor	41.72 \$/hr		800,000
Fertilizer Sales			
Potassium Sulfate & Nitrate	205 \$/ton		(60,700,000)
Ammonium Chloride	110 \$/ton		(19,400,000)
Total Fertilizer Profits			(25,700,000)
Fuel Costs, SO_x and NO_x Equalization			
Incremental Fuel Costs	10 \$/ton	(18,400,000)	(18,400,000)
Cost Equalization for SO _x Recovery	200 \$/ton	700,000	
Total Cost Equalization		(17,700,000)	(18,400,000)
Total Operating Costs/year (Profit)*	\$/year	(900,000)	(37,000,000)
Total Annual Operating Costs (¢/kWhr)		-.022	-0.881

* Utility and AIRborne to share this operating profit.

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4. Robin Phinney, AIRborne Technologies Inc.
5. Robert Bennett, AddChem Systems
6. Gary Derald, Dirdal Rand Technologies

References

1. P.S. Lowell, J. G. Noblett Jr., C. M. Snow and H. K. Koleini, EPRI Symposium, Scottsdale, Arizona, November 19-21, 1985.
2. J. Verlaeten, G. G. de Soete, L. Ninane and J. M. Bondel of Solvay and IFP.
3. R. G. Hooper, NaTec Resources, CRSS/IRI Project.
4. Robert Bennett and Eric Darmstaeder, NaTec Resources, ASME 1991.
5. Arm & Hammer Bicarb Bulletin, 1987.
6. NaTec Resources, Inc. National Energy Strategy, 1990.
7. Robert Bennett, A Nastri, NaTec Resources, 1990.
8. Tim Sonnichesen, ASME Conference 1987.

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