



Project Summary

Disposal of Spent Sorbent from Dry FGD Processes

P. M. Stephan, H. S. Rosenberg, and R. B. Bennett

The main by-product of a dry injection flue gas desulfurization (FGD) process for a coal burning power plant consists of a mixture of reacted sorbent and fly ash. When sodium-containing sorbents such as nahcolite (NaHCO_3) and trona ($\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$) are used to capture the SO_2 in the flue gases, the spent sorbent consists primarily of sodium sulfate (Na_2SO_4) and sodium sulfite (Na_2SO_3) which are highly water soluble and generally unsuitable for disposal in a simple landfill. A research program was undertaken to study methods of stabilizing the fly ash/spent sorbent mixtures through agglomeration and sintering. A conceptual process flow diagram and process economics were determined for a facility which would process and somewhat stabilize fly ash/spent sorbent mixtures from a dry FGD process for a 500 MW power plant burning low sulfur western coal. While the stabilization process tested successfully reduced leaching of the FGD waste/ash mixture, its projected costs (about \$41/kW and 5 mills/kWh) appear to make this process economically unattractive for a single 500 MW plant at this time. Thus, the stabilized waste would cost nearly \$88/tonne of waste disposed of, about five times the cost for conventional FGD waste.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Recent trends in SO_2 emission controls have included the use of fabric filters or

electrostatic precipitators (ESPs) for particulate control, and wet lime (or limestone) scrubbing for control of SO_2 from the boiler flue gas. Alternative FGD processes in various stages of research, development, or commercialization currently include spray drying and dry injection of sorbents into the boiler flue gas stream. Dry injection of sorbents is desirable in arid regions where water is scarce and western coal, with lower sulfur content than eastern coal, is available.

The Buell Emission Control Division of Envirotech Corporation* with support of the U.S. EPA has tested a dry FGD process at the Martin Drake Power Plant in Colorado Springs, CO. This process involves injecting nahcolite (NaHCO_3) or trona ($\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$) into a flue gas slipstream from the plant's No. 6 boiler and collecting the resulting fly/ash spent sorbent mixtures in a pilot baghouse or the baghouse at the facility.

The primary problem associated with the dry injection FGD process using sodium compounds is disposal of the spent sorbent. This reacted sorbent, containing sodium sulfate and sodium sulfite formed in the reaction with the SO_2 in the flue gases, is highly water soluble and has a high potential for leaching into ground water if disposal is via unlined landfill.

Objectives of the research program conducted at Battelle/Columbus Laboratories (BCL) were: (1) to study the sintering and leaching mechanisms of fly ash/spent sodium sorbent mixtures from a dry injection FGD process, and (2) to determine the process economics for a pelletizing and sintering facility which would handle the output of fly ash and spent sorbent from a full-scale power plant.

*Now General Electric Environmental Services, Inc.

A previous study at Battelle, sponsored by Industrial Resources, Inc. (IRI), addressed the problem of disposal of spent nahcolite from dry FGD processes. The laboratory program included glass melting studies and sintering experiments, which eventually led to development of the patented Sinterna process for consolidating and sintering material by-products containing spent nahcolite sorbent.

The Program

The laboratory research program includes pelletizing experiments, sintering experiments, use of pellets as aggregates, and an economic analysis of the process.

Pelletizing Experiments

The agglomeration technique used for the spent sorbent/fly ash stabilizing process was disc pelletizing, due to its widespread use for agglomerating a large volume of similar materials. Objectives of the pelletizing technique were: (1) to determine the pelletizer operating parameters required to produce pellets from the spent sorbent/fly ash mixtures in a satisfactory size range and with sufficient handling strength, and (2) to determine the pelletizing moisture and binder requirements for the feed material. Disc pelletizing followed by sintering of the fly ash pellets, used for many years for lightweight aggregate production, is mentioned in two recent patents as the preferred agglomeration method for fly ash waste disposal.

Disc (or pan) pelletizing involves feeding a powdered material onto a rotating disc and spraying water or another liquid onto the powder to start agglomerating the individual powder particles. The liquid acts as a binder while the powder is rolling and tumbling as it is pelletized into spheres of a narrow size distribution determined by the operating parameters and raw material variables. The operating parameters

include pan angle and depth, rotational speed, water spray and feed material rates and location, and scraper location. Raw material variables include particle shape and size distribution, compositional variability, binder type and amount, and particle surface conditions.

The initial pelletizing experiments used small batches (about 2 kg) of the fly ash/spent sorbent mixtures with and without additional binders added for green strength. These batches were pelletized in a small pelletizer, 36 cm in diameter and 16 cm deep. Pellets, 5-15 mm in diameter, were tested for strength using a hand-held spring compression device after drying or firing. The force required to break the dried or fired pellets was measured and recorded. The binders selected for comparison of their green strength contribution included calcium lignosulfonate, bentonite, hydrated lime, and limestone. Binders were added in amounts of 2-5 percent of the original batch weight.

Pilot-scale production of about 100 kg of pellets was conducted using two larger pelletizing units with different rim-height-to-diameter ratios. A deep drum pelletizer (Mars Mineral Corporation Series 20) with a rear feed screw, a diameter of 61 cm, and a rim depth of 45 cm was used initially in attempts to pelletize the fly ash/trona sorbent powder received from Envirotech from a pilot test run at the Martin Drake Power Plant in Colorado Springs. More of the trona-containing mixtures and the fly ash/nahcolite mixtures were later pelletized in a shallow disc pelletizer, 106 cm in diameter and 22 cm deep. The pellets from the later trials were dried at 150°C, fired at 925°C, and used as aggregate in the concrete and asphalt mixture testing.

Table 1 shows analyses of pure fly ash (average of several samples), the fly ash/spent nahcolite from Envirotech test 12R1,

and the fly ash/spent trona from Envirotech test 22R1 at its pilot facility at the Martin Drake Power Plant. The nahcolite was obtained from the U.S. Bureau of Mines from a deposit in Rio Blanco County, CO; the trona was from Owens Lake in California. The weight ratio of fly ash to spent sorbent was roughly 70/30 in the mixtures received from Envirotech.

Several studies have been completed on the characterization of fly ashes from coal burning power plants. TVA reports that fly ash consists primarily of the oxides of silicon, aluminum, calcium, iron, and other minor elements. Petrographic analyses indicate that fly ashes are generally 50-90 percent glass by weight; the remaining material is primarily quartz, mullite, hematite, magnetite, and carbon. The glassy phase contains a considerable amount of material known as cenospheres, which are rounded particles containing nitrogen and CO₂, comprise 5-20 percent by volume of the total fly ash, and are 20-200 μm in diameter.

The particle diameters of the fly ash/spent nahcolite received from Envirotech were 1-60 μm, with a median diameter of 15 μm, measured by sedimentation techniques. The surface area of the powder, measured in a Micrometrics Model 2205 analyzer, was 4.5 m²/g, which would be higher than that calculated from the particle size distribution, but which may be due to porosity of the nahcolite-containing particles.

To increase pellet strength, binders used included calcium hydroxide at 2 and 5 percent by weight, calcium lignosulfonate at 2 and 4 percent by weight, and bentonite at 4 percent by weight. A high calcium limestone was added to some batches because of its potential as a binder at higher sintering temperatures (as a glass network modifier and flux). These binders

Table 1. Sample Chemical Analyses^a

Description	Weight Percent													Total
	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	P ₂ O ₅	TiO ₂	Li ₂ O	LOI _{800C}		
Fly Ash from Colorado Springs Plant - Averages	66.80	4.00	17.50	4.40	1.50	0.26	1.07	1.50	0.80	0.80	0.02	-	98.65	
Fly Ash/Spent Nahcolite - Test 12R1	51.22	3.23	22.83	3.60	1.49	2.90 ^b	1.21	3.42 ^b	1.31	0.78	0.02	7.55	99.56	
Fly Ash/Spent Trona - Test 22R1	52.14	5.23	21.08	3.63	1.21	2.78 ^c	1.08	4.93 ^c	1.26	0.86	0.02	5.33	99.55	

^aAnalyses provided by General Electric Environmental Services, Inc.

^bBCL Analyses: SO₄ = 3.59, SO₃ = 0.16, Na₂O = 3.05.

^cBCL Analyses: SO₄ = 7.06, SO₃ = <0.2, Na₂O = 8.64.

were tested for strength separately and in combination with other binders in the batches.

Loads required to break the dried pellets were 5-55 newtons*; 15 newtons was the cutoff point below which pellets exhibited unacceptable breakage while rolling and tumbling through the various processing steps. Low dried pellet strength is also related to low green pellet strength (as discharged from the pelletizer), as measured by dropping pellets from various heights immediately after pelletizing to determine their initial resistance to breakage. The pellets with low dried strength (< 15 newtons) would normally break after one or two drops from a height of 20-45 cm onto a hard flat surface. Pellets with higher dried strengths usually survived multiple drops from heights up to 40 cm.

The dried fly ash/spent nahcolite pellets broke readily with moderate handling and exhibited considerable attrition loss during handling in the sample container. Most of the binders increased pellet strength at some level of addition to the basic starting mixtures; the spent trona batches had higher comparative dried pellet strength than those containing spent nahcolite. Increases in fired pellet strength indicated that some sintering and formation of glassy bonds was taking place during thermal treatment of the pellets. A 5 percent addition of calcium hydroxide [Ca(OH)₂] was used in the larger scale pelletizing tests due to its contribution to pellet strength, comparative cost, and availability, and for its possible role in the fixation of the sulfates in the mixtures. The binder also significantly reduced dusting of the pellets during handling.

Initial attempts to pelletize larger quantities of the fly ash/spent trona powder were made using the Mars Series 20 pelletizer. The pan angle was set at 73°, and the pan was operated with a rim speed of 40 to 50 m/min. The powder feed rate was 30 - 50 kg/hr and water flow rate was 7-10 l/hr. A stable condition could not be reached in this unit since the weight of the powder tumbling in the drum crushed the seed pellets.

The next attempt at pelletizing the fly ash/spent sorbent powders involved the use of the 1-m diameter disc pelletizer. The angle was set at 60°, and the rim speed was set at 70-80 m/min. The powder feed rate was 40-50 kg/hr, while the corresponding water addition was 13-16 l/hr. Pellets were formed readily in this

pelletizer, ranging from 1 to 2 cm in diameter. Nearly 100 kg of pellets were made in this unit, dried at 150°C, and then sent for testing as aggregate in concrete and asphalt mixtures.

Sintering Experiments

Temperature and heating rate most significantly influence the amount of SO₂ evolved from the spent sorbent-containing pellets during thermal processing. The development of a glassy microstructure and/or sintering of the particles in the pellets during thermal processing influence the solubility of the pellets in a liquid. SO₂ evolution during heating of the pellets was measured up to 1200°C, and leaching of sodium and sulfates from pellets in water was measured after the pellets had been heated. Most of the tests were conducted on pellets containing spent nahcolite and 5 percent lime; these were considered most representative of the material that would be processed in a full-scale operating facility using the dry injection FGD process.

Figure 1 consists of micrographs of mounted and polished sections of fly ash/spent trona pellets made on a disc pelletizer and either dried at 150°C or fired for 1 hour at 1000°C in an electrically heated furnace. The pellets dried at 150°C have distinct particle and matrix phases. In the pellets fired at 1000°C, most of the glassy particles have melted to form a glassy matrix with crystalline inclusions. The changes in crystalline content of the pellets with thermal treatment were studied by x-ray diffraction (XRD) analysis of powder from crushed pellets.

The XRD analysis results for fly ash/spent sorbent mixtures and for pellets of these compositions fired at 1000°C are shown in Table 2. Included in the table are the crystalline compounds found in the patterns, their powder diffraction file numbers, and normalized concentrations. The normalized concentrations show relative amounts of the various crystalline compounds. Best estimates for actual amounts (not shown in the table) would be based on factors for the ratio of crystalline to non-crystalline material in the samples. Petrographic examination of the powders indicates that roughly half of the material in both as-received and fired pellets is crystalline, indicating no substantial glass formation with thermal treatment up to 1000°C, although there has been substantial melting and sintering of the glassy particles at the higher temperatures.

An interesting difference occurs in the XRD analysis results for the as-received

powders. All of the sulfur in the pattern for the fly ash/spent nahcolite powder occurs as sodium sulfate; both burkeite [Na₆SO₃(SO₄)₂] and sodium sulfate are in the fly ash/spent trona sample. As expected, quartz and mullite are the major crystalline compounds in the as-received samples.

The complexity of the XRD analysis patterns for the samples fired at 1000°C indicates that several new crystalline compounds are formed during thermal treatment of the pellets, while the relative amounts of quartz and mullite decrease. The most interesting and unexpected compound to form is a complex sulfate [Na₆Ca₂Al₆Si₆O₂₄(SO₄)₂], which is present to some extent in all of the fired samples but is the major crystalline compound in the Batch A-(trona) and Batch 2a (nahcolite plus lime) compositions. Two sodium aluminosilicate compounds (albite and nepheline) are also present in major amounts in the fired samples. The crystalline compounds in the fired samples are a combination of small amounts of unreacted crystals (primarily quartz and mullite) and recrystallization products which form during cooling of the molten constituents.

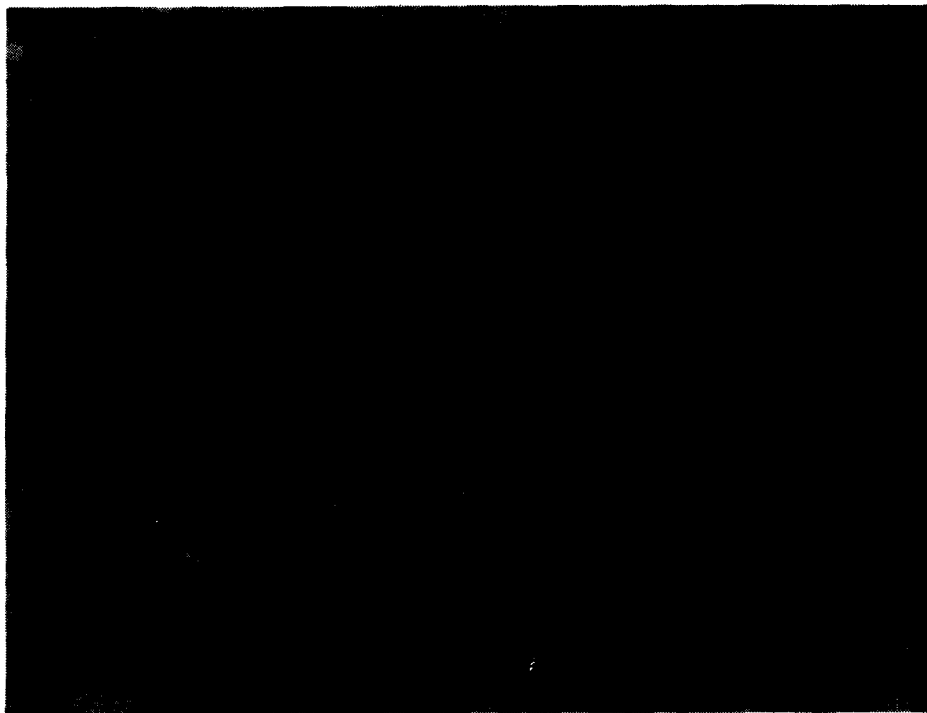
The compounds or glasses in the thermally treated pellets influence the degree of solubility or stability of the pellets under leaching conditions. Processing at high temperatures (>900°C) evidently converts most of the soluble alkaline sulfates in the pellets to less soluble compounds or absorbs them partially into the glassy matrix.

To determine the optimum time and processing temperatures to maximize sulfur retention and minimize leaching of the pellets in water, individual pellets of the various compositions made during the pelletizing studies were subjected to a controlled heating cycle during which the amount of SO₂ evolved was measured. These pellets were then leached for various times up to 1000 hours in distilled water with moderate stirring.

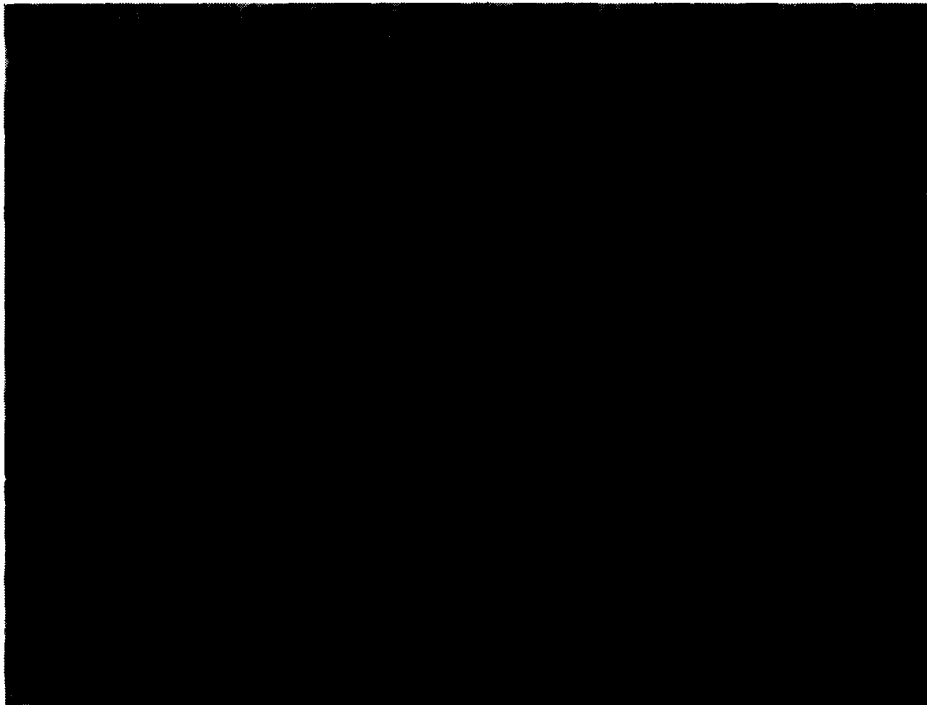
Figure 2 represents the percentage of sodium leached from pellets of Batch 2a which had been heated to different temperatures. As expected, the dried pellets exhibited the highest sodium leaching rates, up to 60 percent of the available sodium. Pellets heated to 1000°C and leached up to 100 hours had sodium leach rates of ≈ 10 percent, indicating the stabilization of the sodium through incorporation into the glassy network.

Figure 3 is a composite figure which includes the sulfates leached at 100 hours of stirring, SO₂ evolved after 1 hour of heating, and the calculated percentage of sulfur retained in the pellets after being

*1 newton = 0.225 pound-force.



a. Dried at 150°C (285X)



b. Fired at 1000°C (285X)

Figure 1. Batch A pellet microstructures (fly ash and trona).

subjected to both tests. The curves for total sulfur retained show the optimum temperature for thermal processing of the pellets. For Batch 2a (nahcolite plus 5 percent lime), the optimum temperature is near 1000°C with 50 percent sulfur retention, indicating the influence of the lime addition which increased the temperature at which there was significant SO₂ evolution during thermal processing.

Use of Pellets as Aggregates

Pellets containing fly ash, spent nahcolite, and 5 wt percent of hydrated lime were tested as aggregates in standard portland cement and asphalt mixes. Pellets fired at 150°C or fired at 925°C were substituted at 20 percent by volume for similarly sized limestone in the mixes. Both cement and asphalt mixes exhibited unacceptable leaching rates of sulfates and/or sodium. Also, in the comparative strength tests under ASTM procedures, samples made from the cement and asphalt mixes had lower than acceptable strength levels after curing.

Economic Analysis

The conceptual process flow diagram for agglomerating and sintering fly ash/spent sorbent mixtures at a power plant is shown in Figure 4. For a 500 MW power plant burning 227 tonnes*/hour of low sulfur coal with 9.7 percent ash, the fly ash collected would be 17.6 tonnes/hour, with 7.3 tonnes/hour of nahcolite injected and 1.3 tonnes/hour of hydrated lime added as a pelletizing binder. Nearly 20 percent by weight of water is needed for pelletizing.

Process equipment included two 5-m diameter disc pelletizers, a conditioning unit for lime addition and de-dusting, and a traveling grate furnace, roughly 3 m wide and 54.5 m long (based on a processing rate of 1.5 m³ m⁻² hr⁻¹).

The total process capital for this facility was estimated at \$7,102,000 (1982 \$). The addition of other direct costs and factored capital charges results in a total capital investment estimate of \$20,277,000 (\$40.55/kW of generation capacity) for the 500 kW plant.

First year revenue requirements for the facility were calculated as \$8,567,845 (1984 \$), or 3.12 mills/kWh. Levelized capital charges for the plant, assuming a 30-year life, were calculated as \$13,518,038, or 4.92 mills/kWh. Based on waste disposal of 154,000 tonnes/year of ash plus spent sorbent, the levelized annual

*1 tonne = 1000kg = 1.1025 tons

Table 2. X-Ray Diffraction Analyses for Fly Ash Spent Sorbent Mixtures

Sample	Compound	PDF No. ^a	Normalized Concentration (Wt Percent)
Fly Ash + Nahcolite	e-Quartz (SiO ₂)	5-490	45
	Mullite (Al ₆ Si ₂ O ₁₃)	15-776	40
	Na ₂ SO ₄ (Form III)	24-1132	6
	Natron (Na ₂ CO ₃ · 10H ₂ O)	15-800	5
	^b Unknown	-	2
	Magnetite (Fe ₃ O ₄)	19-629	1
Fly Ash + Nahcolite Batch 1 Fired 1000°C	Albite (NaAlSi ₃ O ₈)	20-554C ^c	30
	e-Quartz (SiO ₂)	5-490	28
	Mullite (Al ₆ Si ₂ O ₁₃)	15-776	22
	Nepheline (NaAlSiO ₄)	19-1176	7
	Na ₆ Ca ₂ Al ₆ Si ₆ O ₂₄ (SO ₄) ₂	25-802	6
	Magnetite (Fe ₃ O ₄)	19-629	2
	Na ₂ SO ₄ (Form III)	24-1132	2
	Unknown	-	2
Trona + Fly Ash Batch A Raw Powder	e-Quartz (SiO ₂)	5-490	35
	Mullite (Al ₆ Si ₂ O ₁₃)	15-776	35
	Burkeite (Na ₆ CO ₃ (SO ₄) ₂)	24-1134	18
	Na ₂ SO ₄ (Form III)	24-1132	7
	Unknown	-	3
Trona + Fly Ash Batch A Fired 1000°C	Magnetite (Fe ₃ O ₄)	19-629	1
	Na ₆ Ca ₂ Al ₆ Si ₆ O ₂₄ (SO ₄) ₂	25-802	45
	Nepheline (NaAlSiO ₄)	19-1176	18
	e-Quartz (SiO ₂)	5-490	14
	Albite (NaAlSi ₃ O ₈)	20-554C	8
	Mullite (Al ₆ Si ₂ O ₁₃)	15-776	7
	Unknown	-	7
Nahcolite + 5% Ca(OH) ₂ + Fly Ash Batch 2a Fired 1000°C	Magnetite (Fe ₃ O ₄)	19-629	1
	Na ₆ Ca ₂ Al ₆ Si ₆ O ₂₄ (SO ₄) ₂	25-802	38
	Nepheline (NaAlSiO ₄)	19-1176	25
	e-Quartz (SiO ₂)	5-490	12
	Unknown	-	12
	Mullite (Al ₆ Si ₂ O ₁₃)	15-776	6
	Albite (NaAlSi ₃ O ₈)	20-554C	3
	Na ₂ SO ₄ (Form III)	24-1132	2
	Magnetite (Fe ₃ O ₄)	19-629	1
Anhydrite (CaSO ₄)	6-226	0.4	

^aPDF = Powder Diffraction File.

^bUnknown = intensity of the strongest unidentified line in the pattern.

^cC = a calculated pattern, giving a better fit than one produced from a natural mineral specimen.

cost is nearly \$88/tonne of waste, or \$11/tonne of coal burned.

Note that SO₂ evolved during sintering of the pellets would be captured via recirculation of gases from the furnace to the power plant FGD system. The costs, both capital and operating, of removing this SO₂ are not included in these estimates.

Conclusion

Technically, results of the program are mixed in terms of feasibility or desirability of using a Sinterna-type process for disposal of fly ash/spent sodium compound mixtures from dry FGD systems. The SO₂ evolved during the processing (heating) must be balanced against the sodium sulfate leached from the processed waste, and the evolved SO₂ must be accounted for in controlling total allowable SO₂ emissions from the plant. Economically, the

process appears to be too costly for disposal of the FGD by-products from a single 500 MW power plant. The disposal cost is nearly \$88/tonne of waste, about five times greater than for conventional FGD waste.

Other options exist for disposing of waste solids from dry injection of sodium compounds into flue gas for SO₂ control. These options include disposal in lined pits with controlled runoff, or processing the material removed from the baghouse by methods similar to a double alkali process, where the spent sorbent would be dissolved in water, and then reacted with lime and converted to gypsum. Feasibility and cost estimates for these alternatives might be gained through the analysis of similar existing systems, but are beyond the scope of this study.

Acknowledgments

The U.S. Bureau of Mines supplied the nahcolite for the pilot plant experiments from their research tract near Grand Junction, CO.

The City of Colorado Springs, CO, through Ronald L. Ostrop in the Department of Public Utilities, was most helpful in providing the power plant facilities required to conduct the pilot plant dry injection experiments.

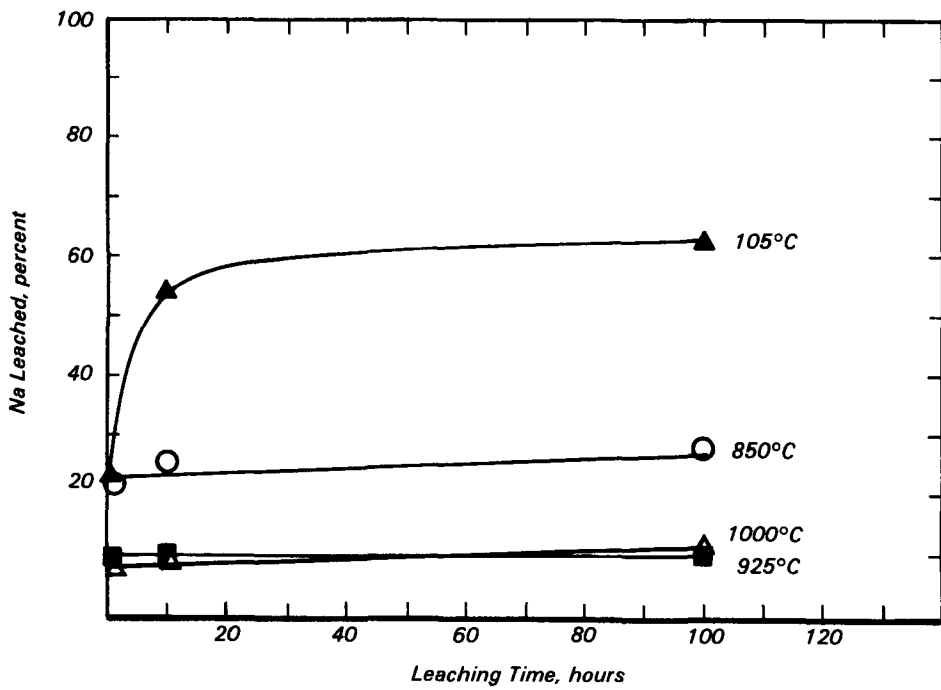


Figure 2. Percent Na leached from Batch 2a after heating at various temperatures. (Batch 2a contains fly ash and nahcolite product solids with 5 wt. percent $\text{Ca}(\text{OH})_2$ added.)

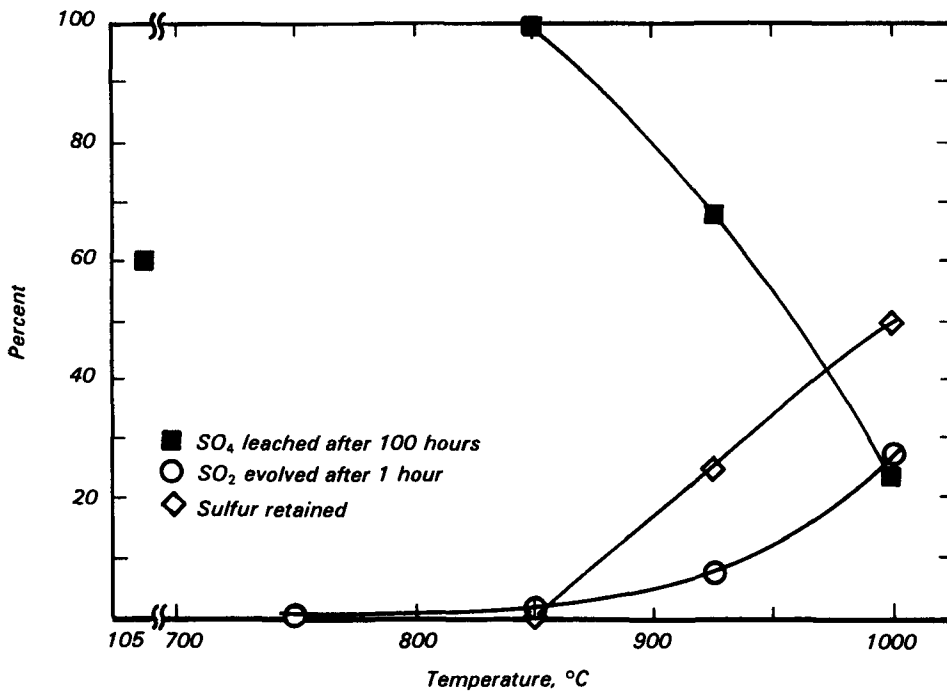


Figure 3. Sulfur retention in Batch 2a after heating and leaching tests. (Batch 2a contains fly ash and nahcolite product solids with 5 wt. percent $\text{Ca}(\text{OH})_2$ added.)

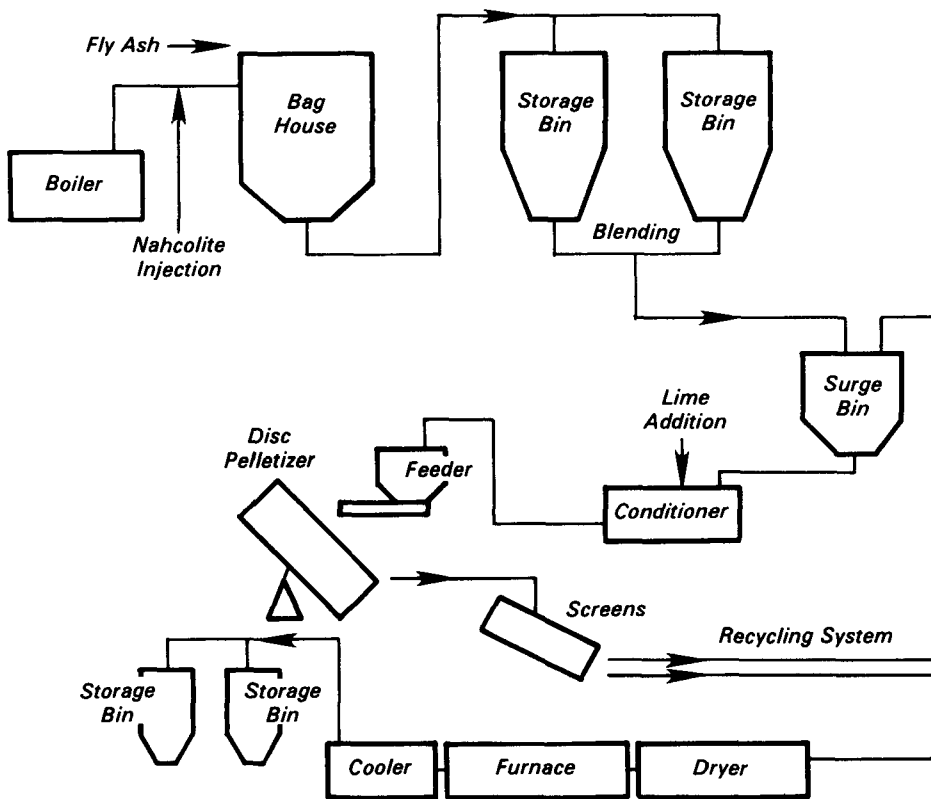


Figure 4. Process flow diagram.

P. M. Stephan, H. S. Rosenberg, and R. B. Bennett are with Battelle/Columbus Laboratories, Columbus, OH 43201.

Theodore G. Brna is the EPA Project Officer (see below).

The complete report, entitled "Disposal of Spent Sorbent from Dry FGD Processes," (Order No. PB 83-165 266; Cost: \$11.50, subject to change) will be available only from:

*National Technical Information Service
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*The EPA Project Officer can be contacted at:
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