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FLY ASH FROM FULL SCALE TRONA INJECTION STUDIES

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Abstract

Sodium sesquicarbonate ($\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$) and the mineral trona ($\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$) have been utilized as effective dry sorbents for SO_2 in flue gas during fossil fuel plant full-scale injection studies conducted at the Cameo Station, Unit 1, of Public Service Company of Colorado near Grand Junction, CO. Microstructural and microchemical characterization studies of fly ash samples from these studies identify decomposition features for these carbonates that relate to the development of satisfactory reaction surface areas for combination with SO_2 from flue gas. The major features are non-sulfur bearing microspheres and a mixture of fly ash and the sulfur bearing carbonate reaction products. Evidence is presented to confirm a thermal decomposition model in which particle breakup or rubbing occurs (the so-called popcorn effect) due to the build-up of carbonate decomposition gases (CO_2 and water vapor) within the carbonate. These correlate with bench top laboratory studies reported earlier.

KEY WORDS: Trona, Dry Sorbents, Sodium Sesquicarbonate, Sulfur Dioxide Sorption, Fly Ash

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Introduction

Background

A primary concern in the use of coal combustion is to effectively reduce SO_2 emission. Field evaluation of a totally dry SO_2 removal process was begun in late 1980 by Public Service Company of Colorado (PSCCO) in cooperation with Electric Power Research Institute and Multi-Mineral Corporation. Bench scale studies were reported in March 1981⁵. The use of dry sorbent injection into flue gas streams was demonstrated in full-scale studies in 1982^{3,4}.

Nahcolite (NaHCO_3 , naturally occurring sodium bicarbonate) was used in most of the testing; however, tests were also performed using two sources of trona ($\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$, naturally occurring sodium sesquicarbonate), sodium sesquicarbonate (trona analogue, $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$) and soda ash (Na_2CO_3). The tests for the use of nahcolite and of trona achieved greater than 70% SO_2 removal efficiency (target to meet New Source Performance Level) in firing low-sulfur coal. Laboratory studies were also reported in which individual particles of nahcolite and of trona were subjected to heated SO_2 and to heated air (and simulated particle residence times in the flue gas) for injection temperatures (1) in the range of 121° to 138° C of the baghouse inlet and (2) in the range of 288° to 427° C of the injection region ahead of the tubular air preheater. Microstructural and phase transformation information was presented¹.

Only a few samples of fly ash from the full scale studies were available for SEM characterization work. These samples are of trona and of sodium sesquicarbonate injection studies into the baghouse at 132° C (270° F). The objective of this study is to characterize these two dry sorbent fly ash materials utilizing scanning electron microscopy (SEM) for microstructural information and energy dispersive X-ray analysis to identify the sulfur bearing components of the fly ash. This microstructural information for the sulfur bearing components is then to be compared with the laboratory studies¹ of microstructural changes observed for trona and for sodium sesquicarbonate crystals which had been exposed to SO_2 and to air at the elevated temperatures discussed above.

Materials and Methods

Samples

Two fly ash samples from the Cameo Station injection studies were examined: the refuse material from injection of sodium sesquicarbonate into the gas stream ($\sim 132^\circ\text{C}$) in the baghouse, and the refuse material from injection of Wyoming trona into the gas stream ($\sim 132^\circ\text{C}$) in the baghouse.

Only the common fly ash constituents of quartz and mullite are seen in the X-ray diffraction patterns (refer to Figures 17 and 18 of reference 1).

Characterization details for the Wyoming trona and the sodium sesquicarbonate materials used in the injection studies are described in references 1, 3, 4 and 5. Variations of particle size studied in injection tests included 70% through 35 mesh (nominal size opening 500 micrometers) to 70% through 400 mesh (nominal size opening 38 micrometers).

Scanning Electron Microscopy and Energy Dispersive X-ray Analysis

Microstructural information was obtained using a JSM-U3 scanning electron microscope which was equipped with a high resolution energy dispersive (ED) X-ray analysis system (Tracor Northern-2000) for generating associated chemical information for the particles observed by SEM. The SEM was operated at 10 and 15 keV for photographic work, and at 25 keV for the ED X-ray studies. The sample powders were mounted onto carbon stubs utilizing a polyvinylchloride adhesive film (10% Tygon[®] tubing by weight dissolved in tetrahydrofuran). For the particles observed by SEM, the ED system confirmed the presence of sodium as an indication that the material being observed was a phase of direct interest. Other elements were monitored including sulfur as an indication that the phase being observed was representative of a sodium-bearing reaction product from the carbonates which had been exposed to SO_2 in the flue gas at elevated temperature and had subsequently reacted with the SO_2 .

The SEM samples received a silver conductive coating (300 Å; Polaron E5100 sputter coater) prior to microstructural examination. This particular coating was chosen (rather than a thin

gold film which is commonly used for SEM studies) to avoid peak overlap with sulfur (if gold had been used).

Results

The microstructural-chemical information for the two fly ash samples is organized as Figures 1-5 for the sample in which natural Wyoming trona was the dry sorbent and as Figures 6-9 in which sodium sesquicarbonate was the dry sorbent.

To show typical features for these materials, three different areas of a fly ash particle mount for the Wyoming trona injection case are seen at low and at high magnification (Figures 1A, 1B, 2A, 2B, 3A and 3B) and a fourth area of the sample shows a common form of microspheres (Figure 4A). For each of these four areas, an associated energy dispersive X-ray analysis is included for the field of view (Figures 1C, 2C, 3C and 4B). Similarly, three different areas of a fly ash particle mount for the sodium sesquicarbonate injection case are seen at low and at high magnification (Figures 6A, 6B, 7A, 7B, 8A and 8B) and a fourth area of the sample shows a common form of microspheres (Figure 9A). For each of these four areas, an associated energy dispersive X-ray analysis is included for the field of view (Figure 6C, 7C, 8C and 9B). The elemental occurrences as determined by the energy dispersive X-ray analyses are summarized in Table 1. Na and S are taken as an indication of S reaction with the carbonate phase. Ag is from the thin film conductive coating; Cl is primarily from the polyvinylchloride adhesive. The other elements are common constituents from the clays of other minerals present in the coal and now present in the fly ash phases.

SEM examination shows that the microstructural features are of three main categories: spheres (typically of the order of several micrometers in diameter and less, some with micrometer size pores; of the material in a field of view, spheres appear to represent less than 50% of the material by volume), micrometer and submicrometer coalesced fragments (porous), and larger agglomerated ash fragments and microspheres (comprises much of a fly ash sample, 50-100 micrometer diameters and less).

Table 1. Summary of ED X-ray Analyses on Fly Ash Components

SAMPLES	EDX SUMMARY									
	Na	Mg	Al	Si	S	Cl	Ag	Ca	Ti	Fe
Sodium Sesquicarbonate-1	X		X	X	X	X	X	X	X	X
Sodium Sesquicarbonate-2	X	X	X	X	X	X	X	X	X	X
Sodium Sesquicarbonate-3	X	X	X	X	X	X	X	X	X	X
Fly Ash Sodium Sesquicarbonate-4		X	X	X		X	X		X	X
Trona-1	X		X	X	X	X	X	X		X
Trona-2	X	X	X	X	X	X	X	X		X
Trona-3	X		X	X	X	X	X	X		X
Fly Ash Trona-4		X	X	X		X	X	X		X

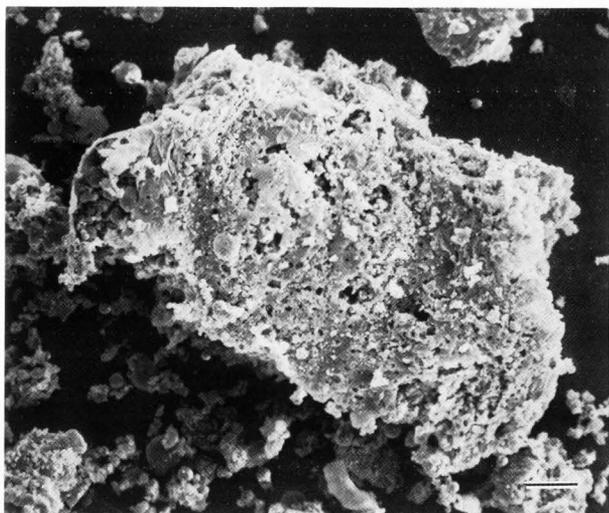


Figure 1A. Fly ash from trona flue gas injection study. Sample area 1. 15 keV. Scale bar = 30 μ m.

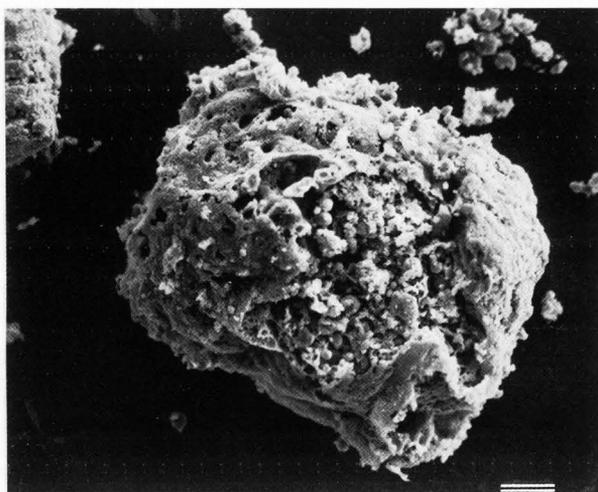


Figure 2A. Fly ash from trona flue gas injection study. Sample area 2. 15 keV. Scale bar = 30 μ m.

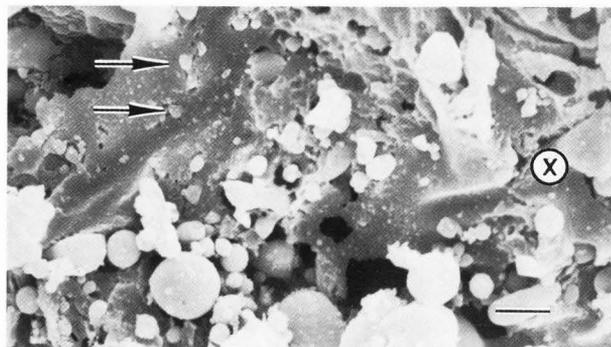


Figure 1B. Higher magnification view of area of Figure 1A. Arrows indicate regions where micrometer size spherical features are forming, prior to breaking away. An X indicates position of ED X-ray analysis. Scale bar = 3 μ m.

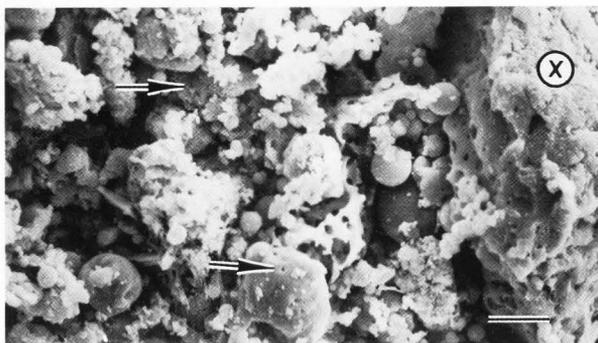


Figure 2B. Higher magnification view of area of Figure 2A. Fine particulates with highly developed microporosity (refer arrows for examples). An X indicates position of ED X-ray analysis. Scale bar = 10 μ m.

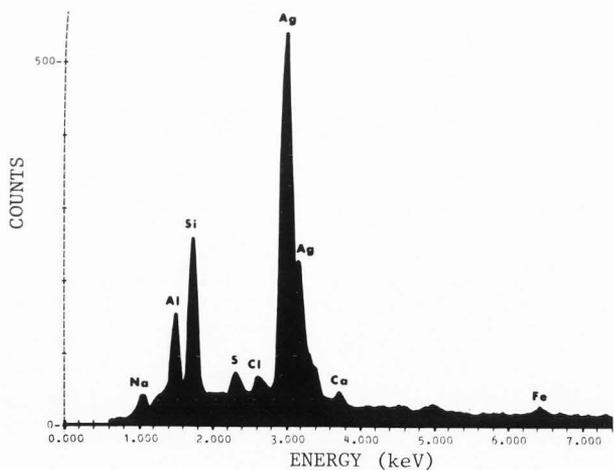


Figure 1C. ED X-ray analysis of location indicated by an X in Figure 1B. Note presence of both Na and S.

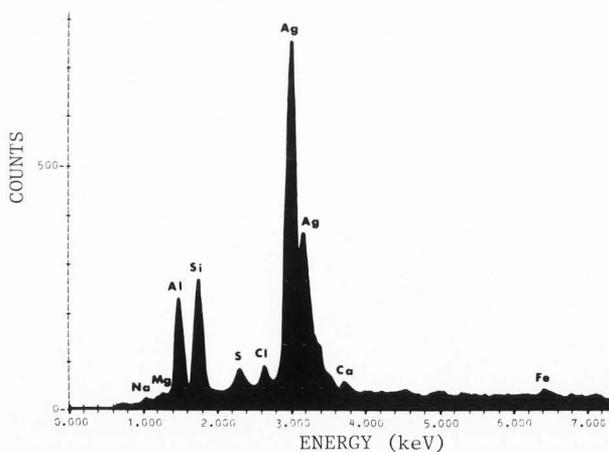


Figure 2C. ED X-ray analysis of location indicated by an X in Figure 2B. Note presence of both Na and S.

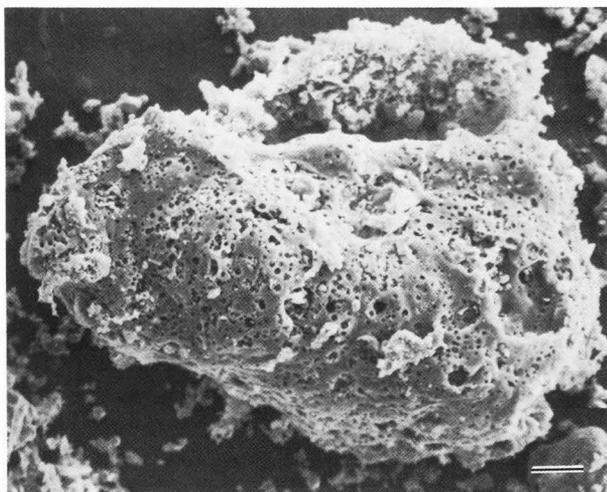


Figure 3A. Fly ash from trona flue gas injection study. Sample area 3. 15 keV. Scale bar = 30 μ m.

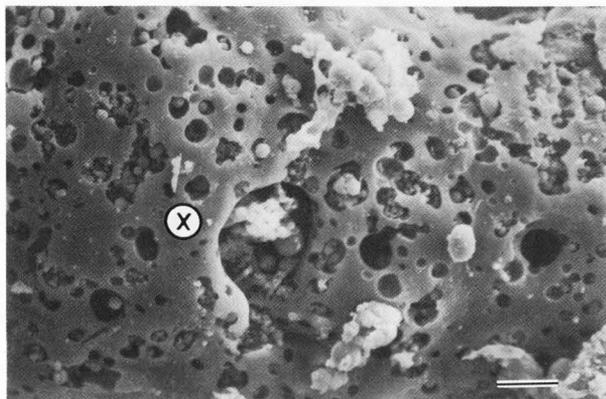


Figure 3B. Higher magnification view of area of Figure 3A. An X indicates position of ED X-ray analysis. Scale bar = 10 μ m.

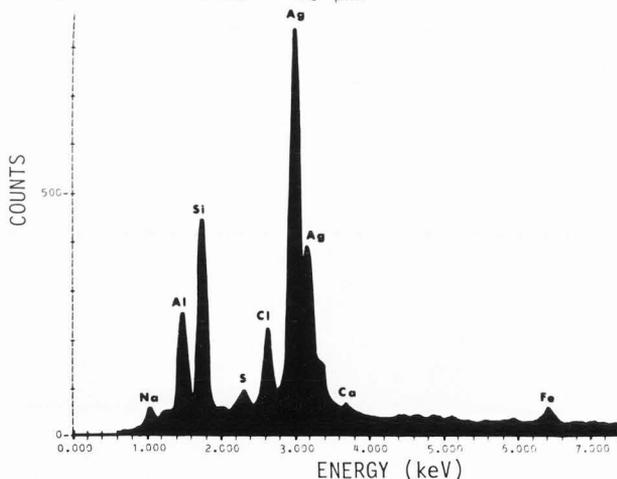


Figure 3C. ED X-ray analysis of location indicated by an X in Figure 3B. Note presence of both Na and S.

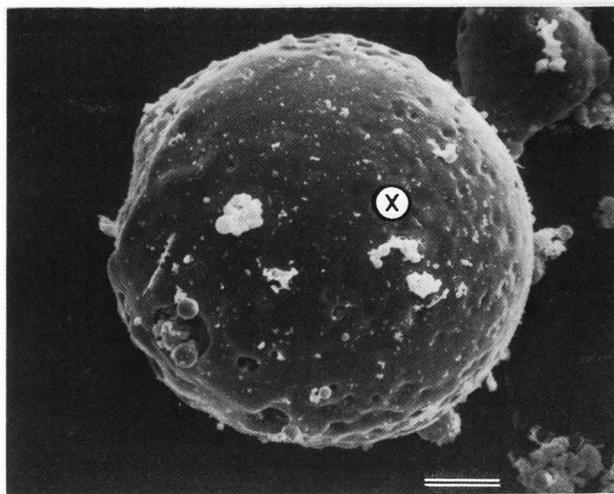


Figure 4A. Fly ash microsphere; trona flue gas injection study. An X indicates position of ED X-ray analysis. Sample area 4. 15 keV. Scale bar = 20 μ m.

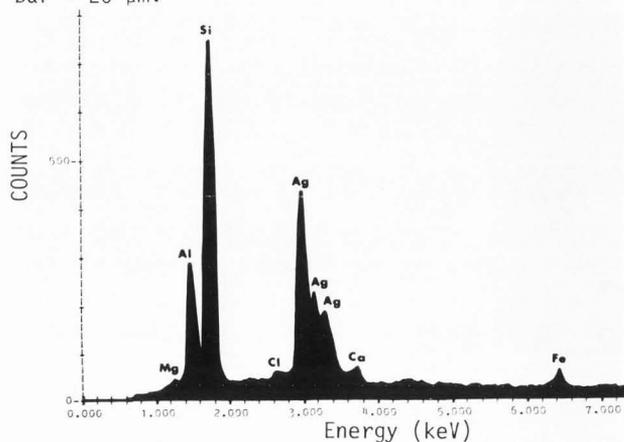


Figure 4B. ED X-ray analysis of location indicated by an X in Figure 4A. Note absence of both Na and S.

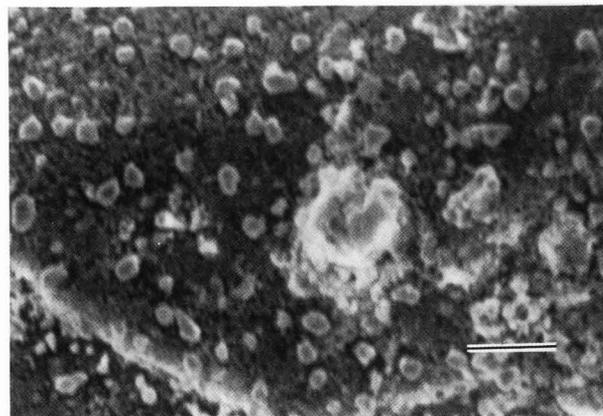


Figure 5. Wyoming trona particle which was exposed to air at 132°C (220° F) for 2 seconds. Note micrometer size particles and submicrometer size porosity. 10 keV. Scale bar = 10 μ m.

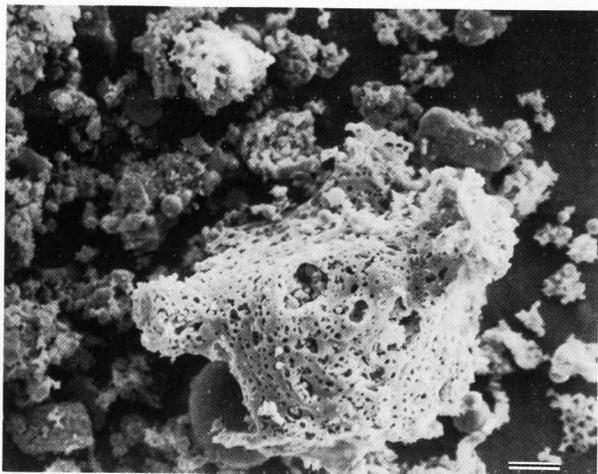


Figure 6A. Fly ash from sodium sesquicarbonate flue gas injection study. Sample area 1. 15 keV. Scale bar = 30 μm .

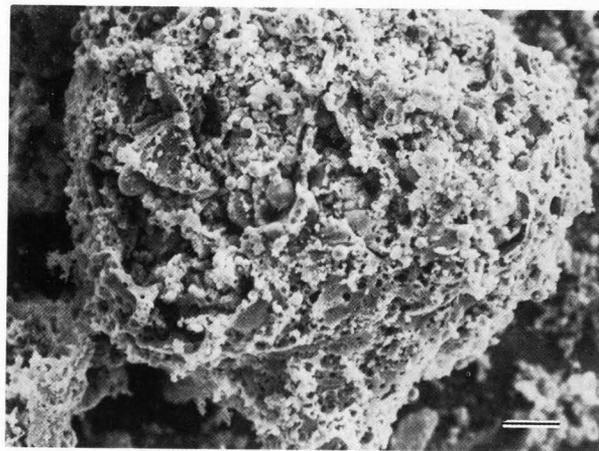


Figure 7A. Fly ash from sodium sesquicarbonate flue gas injection study. Sample area 2. 15 keV. Scale bar = 30 μm .

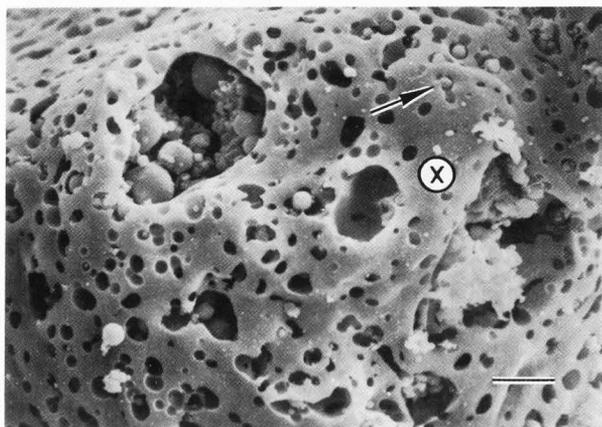


Figure 6B. Higher magnification view of area of Figure 6A. Portions of matrix are dissociating into micrometer size spherical particles (e.g., arrow). An X indicates position of ED X-ray analysis. Scale bar = 10 μm .

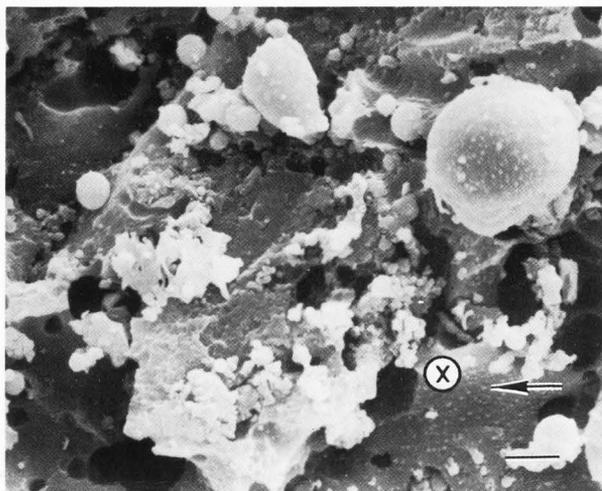


Figure 7B. Higher magnification view of area of Figure 7A. Scale bar = 3 μm . Note submicrometer size particles (arrow) on surfaces. An X indicates position of ED X-ray analysis.

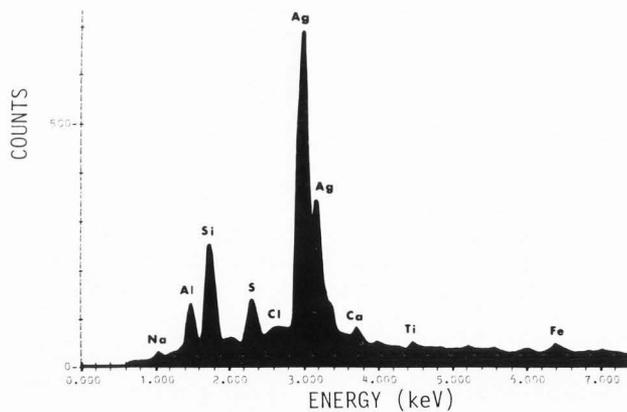


Figure 6C. ED X-ray analysis of location indicated by an X in Figure 6B. Note presence of both Na and S.

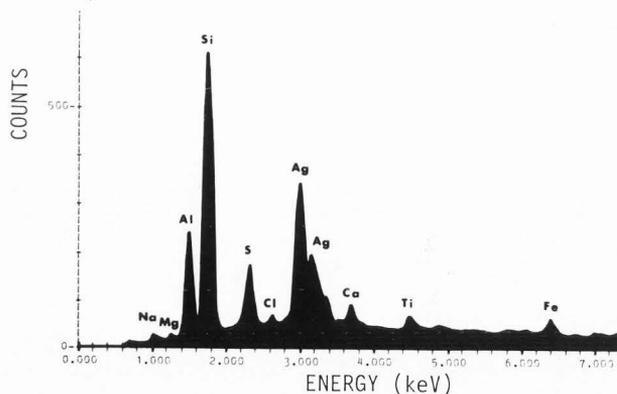


Figure 7C. ED X-ray analysis of location indicated by an X in Figure 7B. Note presence of both Na and S.

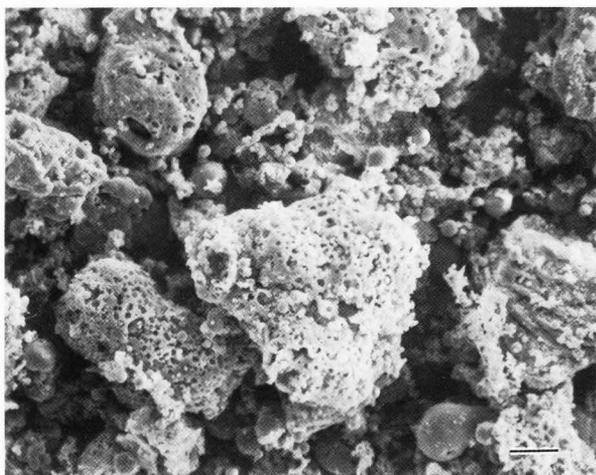


Figure 8A. Fly ash from sodium sesquicarbonate flue gas injection study. Sample area 3. 15 keV. Scale bar = 30 μm .

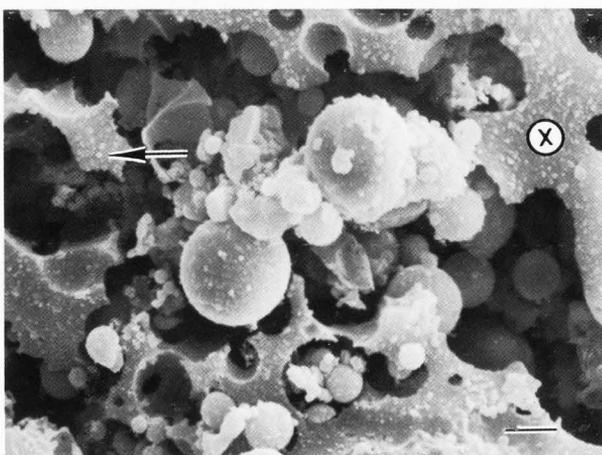


Figure 8B. Higher magnification view of area of Figure 8A. An X indicates position of ED X-ray analysis. Note submicrometer size particles (arrow) on surfaces. Scale bar = 3 μm .

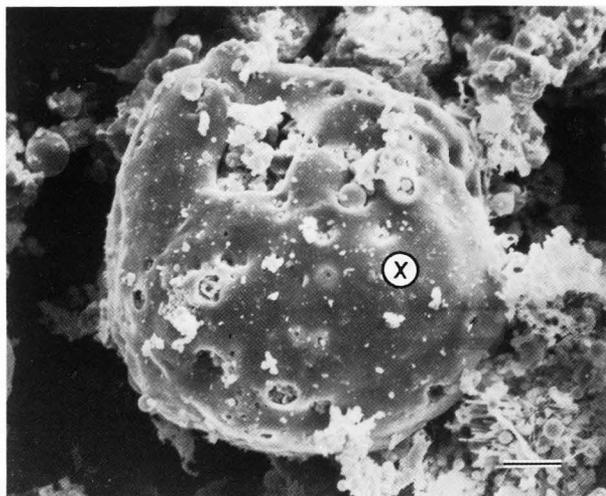
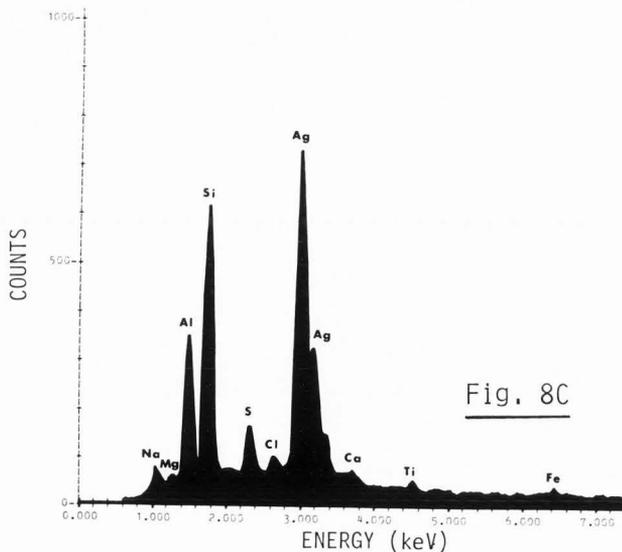


Figure 9A. Fly ash microsphere; sodium sesquicarbonate flue gas injection study. Sample area 4. An X indicates position of ED X-ray analysis. 15 keV. Scale bar = 20 μm .

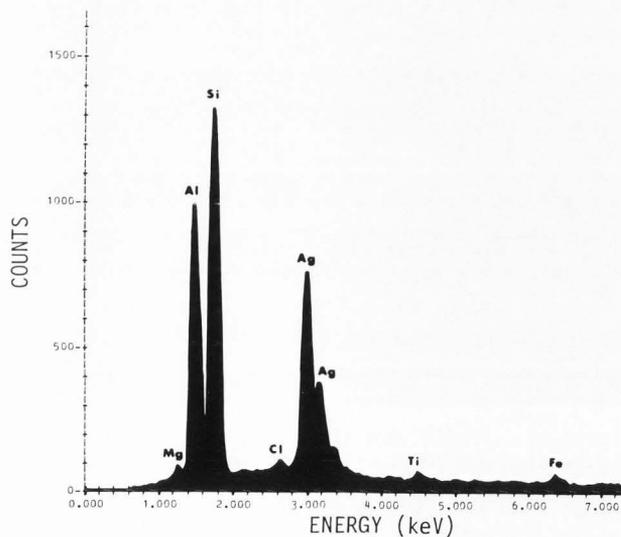


Figure 9B. ED X-ray analysis of location indicated by an X in Figure 9A. Note absence of both Na and S.

By comparison, a fragment of Wyoming trona that was subjected to hot air (at a comparable temperature, 104° C (220° F)) for two seconds is shown in Figure 5 at a high magnification. In this view we see the typical thermal decomposition or ruffling features of both trona and sodium sesquicarbonate. The material has become quite porous on a submicrometer scale. Particles from the thermal decomposition of the carbonates are both approximately spherical and micrometer size. These surface particles can fly off from the surface (described as a popcorn effect due to

Figure 8C. ED X-ray analysis of location indicated by an X in Figure 8B. Note presence of both Na and S.

the release of CO₂ and water vapor of the thermal decomposition of the carbonates^{2,6}). Additional detailed SEM micrographs of interest for the comparison are presented in reference 1 for the raw Wyoming trona (Figure 23), for the raw sodium sesquicarbonate (Figure 22), for Wyoming trona exposed to SO₂ at elevated temperatures (Figures 37-40). Note especially Figure 39a in reference 1 for examples of spherical micrometer size particles breaking away from a trona grain due to the interaction with the SO₂ gas. Similar examples are included for Wyoming trona exposed to air at elevated temperatures (Figure 35 and 36), for sodium sesquicarbonate exposed to SO₂ at elevated temperatures (Figures 32-34), and for sodium sesquicarbonate exposed to air at elevated temperatures (Figures 30 and 31). Thus, an extensive microporosity is seen to have developed and a significant component of micrometer size particle rubbing products are seen to have formed for these carbonates as a result of exposure to hot air¹, to hot¹ SO₂, and to hot flue gas (Figures 1-3 and 6-8 of this report of fly ash components from the full scale injection studies).

The microporous matrix is shown by the energy dispersive X-ray analyses (Figures 1C, 2C, 3C, 6C, 7C and 8C; summarized in Table 1) to contain both the sodium and the sulfur. The relatively large microspheres (e.g., Figures 4B and 9B, ED analyses for SEM views of 4A and 9A, respectively) are predominately mullite. No sulfur or sodium is detected on the microspheres of Figures 4A and 9A. These mullite microspheres are common components of the fly ash prior to the addition of the carbonate sorbent material.

Conclusion

Laboratory studies¹ of the carbonates being exposed just to hot air or to hot SO₂ permit general features of the development of microporosity and of a micrometer size rubbing product to be identified. On comparison with material from flue gas dry sorbent injection studies, somewhat similar features can be discerned. The microporosity of the flue gas products seems more highly developed. The sodium bearing fly ash particles directly correlate with the occurrence of the sulfur extracted from the flue gas. There is direct microstructural evidence from the flue gas particulates that the thermal decomposition or rubbing mechanism (popcorn effect) is an active feature for providing new additional surfaces for reaction with SO₂ from the flue gas. Thus, the use of dry sorbents based on these forms of carbonate is effective in the removal of sulfur from flue gas streams through the reaction with SO₂, through a degree of fine scale breakup of the carbonate matrix which provides additional reaction surfaces, as well as through the development of a microporosity associated with the thermal decomposition of the carbonate matrix.

Acknowledgements

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the Public Service Company of Colorado for providing samples of the flue gas particulates, and for support from the Iowa Power and Light Company. Technical assistance of G. Oren was appreciated.

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Discussion with Reviewers

G. B. Freeman: It would seem that mounting these fly ash products in epoxy and polishing to reveal cross sections would allow both the extent of the penetration of the sulfur reaction zone and the distribution of porosity to be examined as a function of depth into the ash products. Do you think this would be feasible and of interest?
Authors: It is feasible. Such a study would be of interest to evaluate how the thermal decomposition might be manipulated to maximize SO₂ reaction with the sorbent.

N. D. Shah: How do the results from reacted trona and sodium sesquicarbonate compare with reacted nahcolite (from Cameo sample)? If the results were not obtained for reacted nahcolite, any comments based on the information collected to date?
Authors: Samples were not available for fly ash from nahcolite injection studies. We prefer not to offer general comments on what to expect. Depending on what samples might become available in the near future for characterization, the reaction phases present in a sample could be different (i.e., sulfates or sulfites).

G. B. Freeman: In the paper, you state that only quartz (SiO₂) and mullite (Al₆Si₂O₁₃) are seen by XRD. Why is this, are no crystalline sulfates formed?

Authors: To detect a phase by X-ray diffraction, generally it must be present in amounts of the order of 1 to 5% of the material being X-rayed. We expect other crystalline phases to be present in these fly ash products based on a variety of studies including those described in reference 1. These other crystalline phases are present in amounts less than a few percent.

G. B. Freeman: The micrometer sized rubbing products which you have identified in this paper would appear to be indistinguishable from conventional pulverized coal combustion boiler fly ash. What fraction of these particles do you think are direct coal combustion products, rubbing products and combinations of both?

Authors: In the total sample, the reacted sorbent material present is less than a few percent. The particles are a mixture of fly ash and reacted sorbent; the relative fractions are undetermined.

T. Sonnichsen: The ED X-ray analyses indicate the presence of Na, S, Si and Al in close proximity if not in the same particle. Is the technique suitable for analysis of individual particles? This is of interest in that the sorbent materials were injected as discrete particles. Do they subsequently agglomerate with the fly ash materials?

Authors: Alcohol can be used to disperse the particles. The particles are a mixture of fly ash and reacted sorbent. In particular, those shown (Fig. 1A, 2A, 3A, 6A, 7A and 8A) contain a high component of reacted sorbent based on the associated presence of Na and S.

T. Sonnichsen: Would you expand on your comments concerning the similarity of the Wyoming trona and the sodium sesquicarbonate samples?

Authors: Sodium sesquicarbonate is approximately 100% $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$, whereas Wyoming trona is approximately 85% $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ and 15% other impurities (additional information is presented in reference 1).

N. Shah: Any comment about specific differences between Wyoming trona and sodium sesquicarbonate for figures 3B and 8B and for figures 1B and 6B?

Authors: They are similar. They show microporosity (on a micrometer size level), the apparent generation of microspheres (on a micrometer size level), and the presence or formation of micrometer and sub-micrometer size particles on surfaces.

N. Shah: This question may be outside the scope of this work, but it is of interest to many people. Is there anything specific about the sodium and sulfur in the reacted sorbent that would allow no release of the sulfur or alter sodium so as to make it water insoluble? The subsequent release of sulfur would be detrimental from practical considerations. One of the big problems with the dry injection process is that it results in water soluble sodium-sulfur compounds. If these compounds can be structurally changed to make them water insoluble, the process would become more popular.

Authors: Economical solutions suggested include using storage pits lined with clay (reference 4). A detailed discussion of several options is presented in the publication, Recovery, Utilization, and Disposal of Solid By-Products Generated by Flue Gas Desulfurization Systems: State of the Art and Research Needs, EPRI CS-1765, Project 1260-16, Final Report, March 1981, pages 1-1 through 8-15 (available from the Electric Power Research Institute, 3412 Hillview Avenue, Palo Alto, CA 94304).

G. Remond: Are there any average data such as differential thermal analysis (DTA) and X-ray diffraction patterns related to the microstructural and chemical information?

Authors: X-ray diffraction patterns for these specific samples are provided in reference 1 (page 610). We have not performed DTA work on these samples.