Composition of recovery-boiler dust and its effect on sintering

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ABSTRACT *Dust from the recovery boiler can form tough deposits on tube surfaces, even when flue-gas temperatures are too cool to melt the dust. Such deposits are formed by sintering between the dust particles. There are currently no theories for predicting the sintering of the heterogeneous salt mixtures in recovery boiler dust. This paper describes the results of sintering tests performed for a number of sodium–potassium–carbonate– sulfate–chloride salt mixtures with broadly varying composition. Dust pellets were placed in a furnace and exposed to different temperature/time cycles. The degree of sintering was determined by measuring the compression strength of the pellets. The presence of both chloride and potassium significantly increased the sintering tendency of the dusts. These components increase the tendency to form deposits on the superheater by decreasing the first melting point of the mixtures. However, this does not explain their influence in the relatively low-temperature (400° C), solid-state sintering case studied here. The presence of SO_2 in the gas phase increased sintering of dusts that contained high levels of carbonate.*

KEYWORDS
Ash
Boilers
Flue gas
Fly ash
Furnaces
Heat recovery
Heat transfer
Recovery furnaces

The formation mechanisms of superheater fireside deposits in recovery boilers have been investigated in detail during the past decade (*1–4*). These studies show how the chemical and thermal properties of recovery-boiler fly ash influence the formation of superheater fireside deposits.

The main components in recovery-boiler fly ash are Na_2SO_4 and Na_2CO_3, with smaller amounts of potassium and chloride salts. Salt mixtures such as these melt in stages when they are heated. Backman *et al.* (*1*) developed a model, based on the melting behavior of the fly ash, for predicting the fouling of the superheaters in a recovery boiler. Their work introduced two important indices, the temperature of a fly ash at which it is molten enough to stick to a surface (T_{15}), and the temperature at which the fly ash is so molten it flows (T_{70}).

Very little work, however, has been published on fouling and fireside deposits in the cooler regions of the flue-gas channel, where temperatures do not exceed the threshold for generation of sticky fly ash (T_{15}). Deposit formation in these cooler regions cannot be explained by the stickiness of the fly ash. There must be some other formation mechanism at work.

Backman *et al.* (*5*) discussed the role of acidic sulfates on deposit formation in the economizer section of the recovery boiler's flue-gas channel. However, these acidic sulfates are formed under a very narrow range of conditions and are found rarely, if at all. Tran *et al.* (*6*) briefly discussed the sintering of fly ash in the boiler-bank region of the recovery boiler, where temperature is considered to be the main factor in sintering.

This paper describes results of sintering tests performed for several sodium–potassium–carbonate–sulfate–chloride salt mixtures with widely varying composition. The results were obtained using a recently developed test method for evaluating sintered deposits (*7*). The method is based on a technique introduced in 1956 by

Barnhart and Williams (*8*), who measured the compression strength of sintered, cylindrical pellets of coal ash in an attempt to predict the fouling tendency of coal ash. The method—later modified by Attig and Barnhart (*9*) and again by Gibb (*10*)—is still used by Babcock & Wilcox to predict the fouling tendency for new types of coal (*11*).

Sintering

The word "sintering" is commonly used to describe a variety of densification mechanisms for solid powders. According to Kingery *et al.* (*12*), sintering is the process by which dust or small particles agglomerate to form a dense body. In their view, agglomeration can take place through any of several mass-transfer mechanisms. They identify three types of sintering:

- **Solid-state sintering**, where the mass transfer takes place by means of surface diffusion, lattice diffusion, boundary diffusion, or through the surrounding gas phase. In some cases, the sintering mechanism for mass transfer through the surrounding gas phase is referred to as "gas-phase sintering."
- **Sintering by viscous flow**, where sintering occurs because of a viscous material. This type of sintering correlates strongly with the viscosity of the material and occurs only in siliceous systems.
- **Sintering via a liquid phase**, where mass transfer takes place through a reactive liquid.

All these sintering processes are highly dependent on particle size and temperature, with smaller particle sizes and higher temperatures giving increased sintering rates. The sintering of recovery boiler dusts is mainly solid-state sintering.

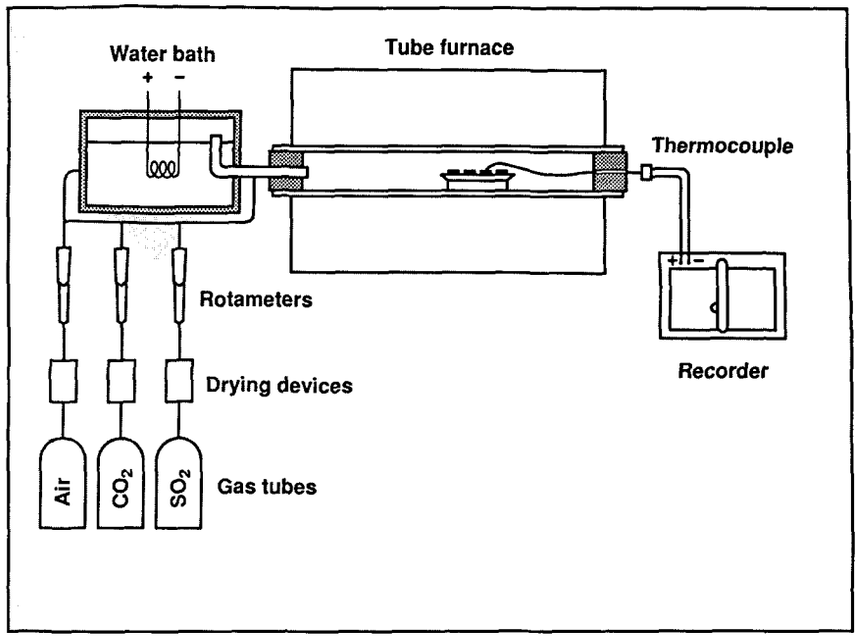
Experimental

The objective of our research was to learn how different chemical compounds affect the sintering tendency of the salt mixtures typically found in recovery boilers. The tests were carried out on synthetic mixtures prepared in the laboratory and on fly ash collected from flue gases.

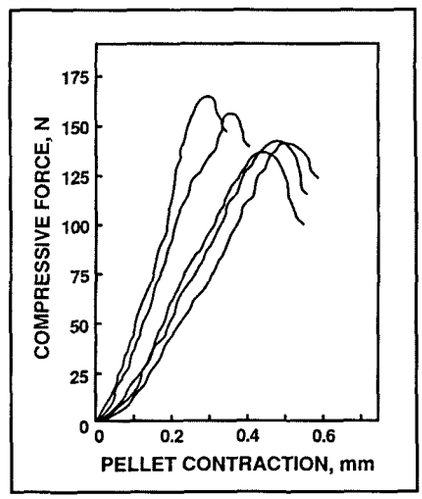
For the synthetic samples, the testing procedure involved selecting and mixing the desired compounds. To achieve a homogeneous bulk composition in the mixture, the compounds were melted at 900°C in air. The solidified slag was crushed and screened to a mean particle size of 100 μm, which was achieved by passing the crushed slag through a 149-μm sieve and a 62-μm sieve. The dust remaining on the 62-μm sieve was collected. (Particle-size distribution was measured later using a standard laser particle sizer.) This melting-milling-screening stage allowed us to control both the chemical composition and the particle size of the dust, each a key parameter influencing sintering tendency.

The synthetic dust was then pelletized. Four pellets were made for each test. The cylindrical pellets, which were 10.0 mm in diameter and about 10.5 mm in height, were made by pressing the dust in a die. The influence of pellet-making pressure on sintering tendency was minimized by using the lowest die pressure that would guarantee pellet integrity during handling. Compacting pres-

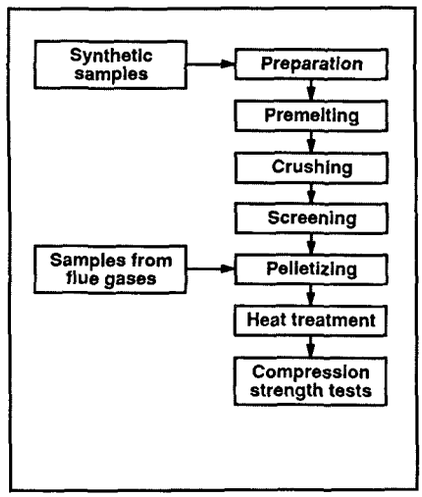
1. Tube furnace where cylindrical pellets were sintered



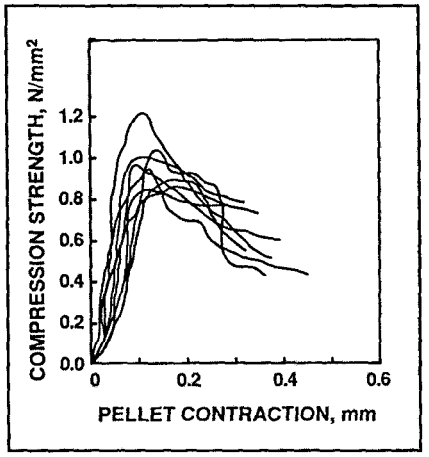
2. Typical curves from pellet-compression tests



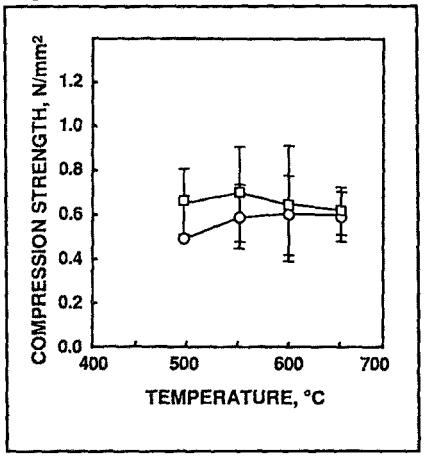
3. Summary of sintering test method



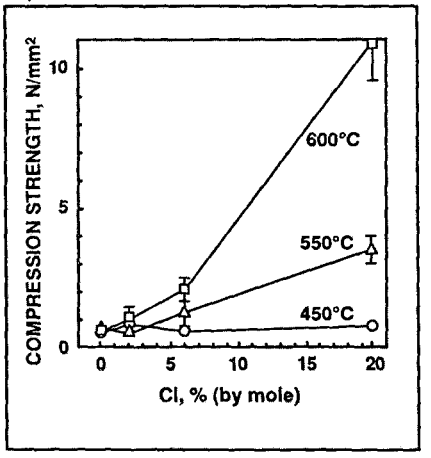
4. Compression strength of eight pellet samples prepared from the same synthetic dust. Pellets were sintered at 600°C in dry air for 4 h. Data scatter is within acceptable range, indicating test results are reproducible.



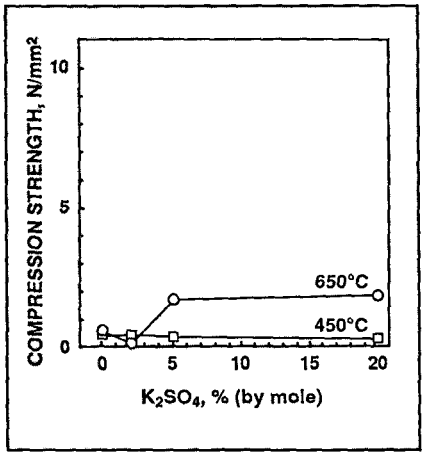
5. Compression strength of two sets of pellet samples prepared from synthetic dusts with the same chemical composition. Each set of pellets was prepared and sintered separately. For each trial, four pellets were sintered at each temperature for 4 h in dry-air atmosphere. Data scatter is within acceptable range, indicating that sample preparation is reproducible. The vertical lines represent the calculated standard deviation with three degrees of freedom.



6. Compression strength of synthetic-dust pellets as a function of chloride content at three furnace temperatures. The vertical lines represent the calculated standard deviation.



7. Compression strength of synthetic-dust pellets as a function of potassium content at two furnace temperatures.



sure also was maintained at a constant level to eliminate possible variation in sintering response from pressure fluctuations.

The pellets were sintered by exposing them to different temperature/time cycles in a tube furnace under a controlled gas atmosphere. The experimental apparatus is shown in **Fig. 1**.

Sintered pellets were crushed in a standard compression-strength testing device that measured the force needed to break the pellet. The pellet's compression strength was considered to be a measure of the degree of sintering.

Figure 2 depicts five typical compression-strength test curves. Each curve represents the results of compression testing for a different pellet. The figure shows that the force increases up to the point where the pellet breaks. After this, the compression force decreases, while the pellet slowly breaks down. The maximum force is taken as a measure of the degree of sintering. To convert the force readings to strength values, we measured the dimension of each pellet, calculated the cross-sectional area of the pellet, and divided the compression force by the cross-sectional area.

Figure 3 is a brief summary of the test procedure.

Before the systematic runs were started, an eight-pellet reproducibility test was carried out. The results in **Fig. 4** show that the scattering of the compression strength varied within an acceptable range. Reproducibility was further checked by repeating the entire process of sample preparation. The results in **Fig. 5** show that reproducibility of sample preparation was acceptable.

Preliminary testing showed that if the average compression strength of the four sintered pellets did not exceed 1 N/mm², no sintering had occurred. If the average strength exceeded 4 N/mm², significant sintering had taken place.

Dusts collected from operating recovery boilers also were tested to provide a basis of comparison for the results obtained with the synthetic dusts. The procedure for testing boiler dusts was slightly different, with the cylindrical pellets formed directly from the collected fly ash. Premelting, crushing, and screening were not carried out.

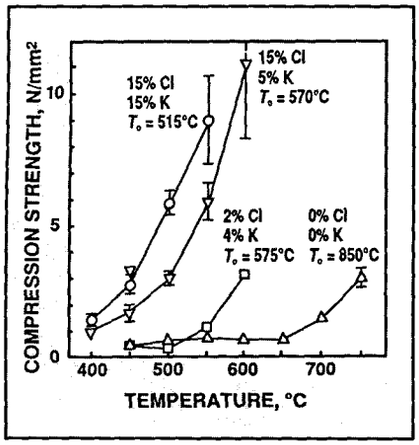
Results

The influence of chemical composition on the sintering tendency of recovery-boiler dust was investigated by testing 20 synthetic dusts. The primary variables were the chloride and potassium contents. These compounds cause deposit problems in the superheater area by decreasing the solidus temperature of the dust.

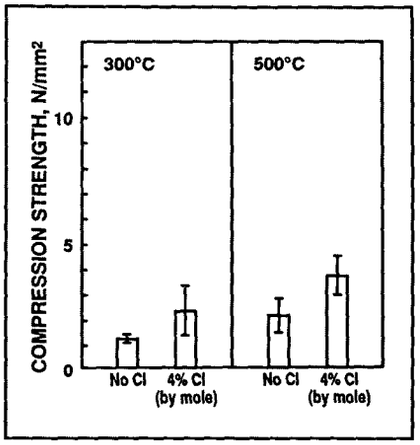
As a first step, synthetic dusts with different amounts of chloride were tested. Four synthetic dusts with increasing amount of Cl were heat treated for 4 h in a dry-air atmosphere at 450°C, 550°C, and 600°C. The results in **Fig. 6** show that sintering increased when the chloride content exceeded 5% (by mole) at temperatures of 550°C or higher.

A similar test was performed for potassium. **Figure 7** shows that sintering increased only slightly when the temperature was raised to 650°C. Increasing the potassium content in the dust apparently does not have a large effect on sintering.

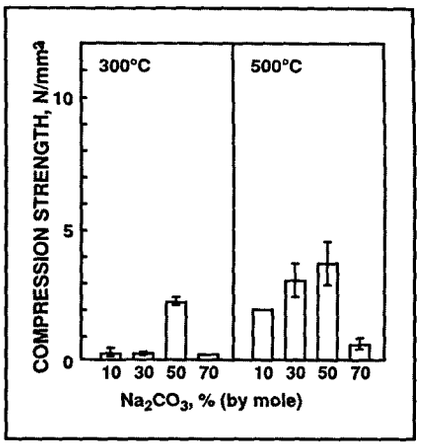
8. Compression strength of synthetic-dust pellets as a function of furnace temperature for dusts with different concentrations (% by mole) of chloride and potassium. T_0 indicates the first melting temperature of each dust. The vertical lines represent the calculated standard deviation.



9. Compression strength of pellets made from two synthetic dusts sintered at 300°C (4 h, dry-air atmosphere) and 500°C (4 h, dry-air atmosphere). For both dusts, Na_2SO_4/Na_2CO_3 = 1. One dust has no chloride, while the other contains 4% Cl (by mole). The vertical lines represent the calculated standard deviation.



10. Compression strength of pellets made from four synthetic dusts sintered at 300°C (4 h, dry-air atmosphere) and 500°C (4 h, dry-air atmosphere). All four dusts contain 4% Cl (by mole) and different ratios of Na_2SO_4/Na_2CO_3. The vertical lines represent the calculated standard deviation.



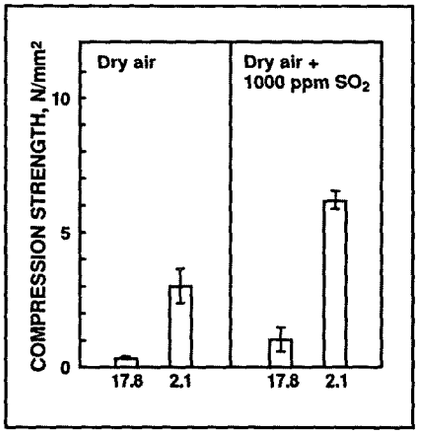
The most remarkable effect is achieved in dusts containing both chloride and potassium. **Figure 8** shows that a synthetic dust containing 15% Cl (by mole) and 15% K (by mole) starts to sinter at 400°C, while a dust with no Cl or K needs 700°C to reach the same degree of sintering. Each dust was subjected to differential thermal analysis to ensure that the sinterings were carried out at temperatures below the first melting points (T_0) of the dusts. T_0 for each dust is listed in Fig. 8.

To determine how the molar ratio of Na_2SO_4/Na_2CO_3 affects sintering, one synthetic sample was made with an increased amount of carbonate compared with other dusts tested. No relevant changes could be detected at first. However, sintering increased when the sulfate/carbonate ratio was increased to 50/50 and 4% Cl (by mole) was added, as seen in **Fig. 9**. This increase was not detected when potassium was substituted for chloride or when neither was present. The sintering of a synthetic dust with a normal sulfate/carbonate ratio, and no Cl or K, can be seen in Fig. 8.

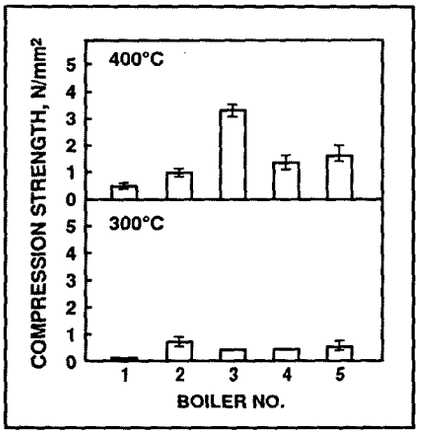
It is also interesting to note that when the content of sodium carbonate was increased beyond 50% (by mole), sintering decreased rather than continuing to increase. These results are presented in **Fig. 10**.

To study how SO_2 in the gas phase affects sintering, two synthetic dusts with different amounts of Na_2CO_3

11. Compression strength of pellets made from two synthetic dusts sintered in two different gas atmospheres at 500°C for 4 h. Both dusts contain 2% Cl (by mole) and 4% K (by mole). The numbers on the *x*-axis represent the molar ratio of Na_2SO_4/Na_2CO_3 for each dust. The dust with a 17.8 ratio contains 5% Na_2CO_3, while the dust with a 2.1 ratio contains 30% Na_2CO_3. The vertical lines represent the calculated standard deviation.



12. Compression strength of pellets made from dusts collected from five recovery boilers. Pellets were sintered at 300°C (4 h, dry-air atmosphere) and 400°C (4 h, dry-air atmosphere). The vertical lines represent the calculated standard deviation.



I. Chemical composition of dusts collected from four recovery boilers

Boiler No.	Chemical composition, % (by weight)				
	Na^+	K^+	Cl^-	CO_3^{-2}	SO_4^{-2}
1	31.4	2.4	0.8	3.8	61.6
3	31.2	3.3	0.9	2.4	62.2
4	31.7	3.2	0.9	9.4	54.8
5	32.1	3.6	2.1	4.4	57.8

were sintered at 500°C for 4 h. One dust contained 5% Na_2CO_3 (by mole), and the other dust contained 30% Na_2CO_3 (by mole). **Figure 11** shows that the dust with 5% Na_2CO_3 did not sinter even when SO_2 was added in the gas phase. (The mean strength in both cases was approximately 1 N/mm^2 or less, indicating that no significant sintering occurred.) SO_2 had a much greater influence on the sintering of the dust containing 30% Na_2CO_3 (by mole). This can probably be explained by the sulfation reaction between SO_2 in the gas phase and the Na_2CO_3 in the dust. Apparently, when the Na_2CO_3 particles are sulfated, they form necks with neighboring particles.

Five different dusts collected from operating recovery boilers also were studied. Results are shown in **Fig. 12**. If the sintering strengths of the collected dusts are compared with their chemical composition, presented in **Table I**, it can be seen that the general trend is for an increase in sintering strength as the K and Cl concentrations are increased. However, the Cl and K concentrations in the dust do not correlate well with the sintering strength. According to the chemical analysis, Dust 5 should sinter the most, but it has only the second-highest sintering strength. The greatest sintering is detected in Dust 3, which has Cl and K contents in the mid-range.

These results show that Cl and K content in the dust are not the only important variables affecting the tendency to sinter. Particle size is known to be an important variable in sintering, and the particle sizes of the collected dusts were not controlled.

In some cases, the measured sintering tendency of the dust could be connected to operator perception of dust-deposit problems. However, the severity of deposits is affected by many other variables, including boiler design, load, soot-blowing system, etc. Given the multitude of variables affecting deposit formation, it is possible that a dust with a strong sintering tendency will not be a problem in a particular boiler.

Conclusion

A novel method for testing the tendency of materials to sinter was applied to several sodium-potassium-carbonate-sulfate-chloride salt mixtures with broadly varying composition. The method involves measuring the compression strength of sintered cylindrical pellets made of screened, synthetic dusts.

The sintering tendency of synthetic dusts was shown to be dependent on the chloride and the potassium content of the dust. Chloride increased sintering when the amount exceeded 5% (by mole) and the sintering temperature exceeded 550°C. Potassium did not affect the sintering at 450°C or 650°C, even if the amount was raised to 20% (by mole). When chloride and potassium were both present, sintering occurred at temperatures as low as 400°C.

The sintering tendency for dusts containing chloride and Na_2CO_3 increased with increasing Na_2CO_3 content up to 50% (by mole). At Na_2CO_3 contents above 50% (by mole), the sintering tendency decreased. The presence of SO_2 in the gas phase increased the sintering if the dust contained high amounts (30% by mole) of Na_2CO_3.□

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