

Field test of sodium bicarbonate and liquid CO₂ use for accelerating char bed cooling

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ABSTRACT: At the Willamette Industries mill in Albany, Oregon, USA, a full-scale trial was carried out on the use of bicarbonate (NaHCO₃) and liquid CO₂ to cool a char bed after a simulated emergency shutdown procedure (ESP). The primary objective was to obtain quantitative information on the use of these two coolants and make a side-by-side comparison of their effectiveness on the same bed. The trial provided a fully documented experience in how to use bicarbonate and liquid CO₂ to cool a char bed effectively. Videotapes show what took place as coolants were applied. Data were obtained on the extent of combustible gas formation during and after the ESP and on the effects of infiltration air on bed burning following an ESP.

Application: Short, high-volume bursts of coolant are apparently more effective than slow, steady application. Bicarbonate and liquid carbon dioxide appear to be worth the costs and the efforts involved in cooling a hot char bed after an ESP.

Since about 1995, there have been many reports of successful experiences in cooling char beds after emergency shutdown procedure, (ESPs) with sodium bicarbonate, and there have been a few reports of successful experiences with carbon dioxide. Accelerated cooling of char beds has been shown to be technically feasible and should be cost-effective for most ESPs.

Sodium bicarbonate (NaHCO₃) is a solid powder that is injected into the bed through lances, with nitrogen used as a carrier gas. As it heats up, the bicarbonate decomposes to form sodium carbonate (Na₂CO₃), CO₂, and H₂O. The decomposition reaction absorbs heat to help cool the surrounding bed. The products of the decomposition reaction act to suppress continued combustion on the char bed. The sudden expansion as NaHCO₃ decomposes helps disrupt the bed and expose hot material inside the bed to the surface, greatly enhancing heat fluxes. Suppliers are available who can provide the necessary equipment, chemicals, and knowledge.

Liquid CO₂ is injected into the bed through lances into vent holes and crevices. For effective use of CO₂, the CO₂ should be taken from the liquid layer in the storage vessel or tank truck. Furthermore, there should be a small orifice on the end of the lance tube so that the pressure drop and expansion takes place within the bed. The expansion from the liquid phase provides localized cooling and forms some dry ice that is injected into the bed. Thus liquid CO₂ provides internal cooling and acts to suppress

combustion, while the expansion generates forces that disrupt the bed. Mill personnel have carried out most of the applications of liquid CO₂ for bed cooling, with some assistance from CO₂ suppliers.

Despite the promise shown by NaHCO₃ and CO₂ as bed coolants, there has been a need for further knowledge to arrive at a consensus on procedures for using these coolants in the most effective way. The key issues are:

- How long to wait before starting accelerated cooling.
- How to get the coolant injection lances into the beds.
- How the variability in bed characteristics affects the coolant.

MILL TRIAL

In the summer of 1999, Willamette Industries indicated that it might be possible to use their old No. 4 recovery boiler for a trial of accelerated cooling after the new No. 5 recovery boiler became operational at the mill. Steps were immediately taken to secure funding for carrying out such a test and to develop a test plan that would meet mill requirements and allow the maximum amount of information to be obtained.

The test at the Albany mill took place in July 2000. It was a unique opportunity to carry out a controlled test of bed coolants. Both of the coolants were used on the same bed to compare them in terms of their effectiveness. We were able to document the way coolants are applied and make measurements on various parameters affected by how coolants work.

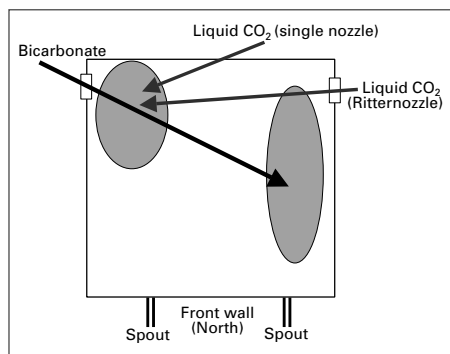
The project was sponsored by the American Forest & Paper Association's Recovery Boiler R&D Committee and the University of Toronto Recovery Boiler Research Consortium. The Albany mill provided a crew to operate the boiler while the bed was building and to monitor systems after the simulated ESP was initiated, but mill personnel did not participate directly in the bed cooling test. The University of Toronto was responsible for overall direction of the test, for making observations and measurements of the bed, and for videotaping the coolant applications. The test was carried out July 24-25, 2000.

Test description

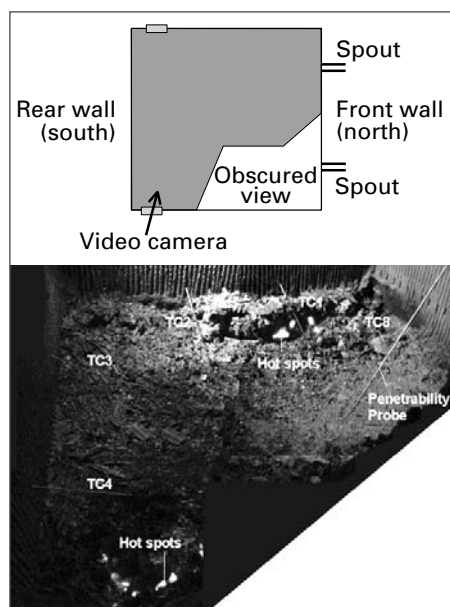
The old No. 4 recovery boiler was no longer in use, and the new evaporators and concentrators and recovery boiler were a considerable distance away. As a result, the No. 4 boiler had to work under some special operating conditions to make it possible for those involved to carry out the test.

Black liquor for the test was drawn from the old 60% storage tank, which had been filled with liquor before the test began. Green liquor formed during black liquor firing was pumped to an old green liquor clarifier that was used as a storage tank. When either the black liquor tank became empty or the green liquor clarifier became full, it would have a negative economic impact on the mill if we continued to operate the No. 4 recovery boiler. This constraint effectively bounded the period when black liquor could be burned in the boiler.

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1. Overhead view of where coolants were applied.



2. Composite of bed before coolants were applied.

The No. 4 recovery boiler was brought up on auxiliary fuel over a 9 h period before black liquor firing was initiated. To build the bed, we operated the boiler on black liquor for 6 h, after which the bed had formed and stabilized. The green liquor had accumulated to a point where the old clarifier was full, and the No. 4 recovery boiler could not continue to operate without the other recovery boiler being shut down. Since the bed height had remained relatively constant over the last hour or so of operation, it was apparent that little would be gained by continuing to operate the furnace even for any moderate length of time. The decision was made to initiate the simulated ESP at this time.

The emergency shutdown procedure was carried out with the normal ESP sys-

tem on the No. 4 recovery boiler, except that the rapid drain valves were not opened. After the ESP, the bed was observed and probed, and measurements were made of the composition of the gases coming from the bed. The bed that was formed was relatively small, and it continued to burn after the ESP. The furnace draft was quite high after the ESP, especially during the first hour and fifteen minutes, and this draft increased the intensity of bed burning. The bed was left undisturbed for 8 h after the ESP before coolants were applied. **Figure 1** shows the locations where coolants were applied to the bed.

The first coolant used was liquid CO_2 , which was applied to the bed on the left-hand side of the furnace through a lance inserted through the liquor gun port on the rear wall. The nozzle had a single orifice in the end, which directed the flow straight into the bed. The first application period lasted about an hour, of which about 30 min actually involved CO_2 introduction. A total of 650 lbs of CO_2 was used in this first application.

Bicarbonate was then introduced into the bed on the right-hand side of the furnace through a lance inserted through a manhole door on the left wall. The standard procedures that had been developed by Southland were used to apply the bicarbonate. The bicarbonate injection began 9 h after the simulated ESP and lasted about 55 min. Eight bicarbonate canister loads were injected during this period for a total amount of about 2800 lbs. When the bicarbonate injection was completed, the right half of the bed was cool.

After the bicarbonate was applied, we began a second period of injecting liquid CO_2 into the bed on the left-hand side. This period began about 10 h after the simulated ESP. The CO_2 lance was inserted through the manhole door on the right-hand wall, which offered better access to the bed along the left wall. A different nozzle, a Ritter nozzle, was used to direct part of the CO_2 flow radially outward. The flow rate of CO_2 with the Ritter nozzle was more than twice that of the previous attempt. Liquid CO_2 was applied for about 36 min, and the total amount used was about 1850 lbs. When this second application was completed, the left half of the bed was cool.

CHAR BED CHARACTERISTICS

The char bed had formed from char accumulating on the side walls and sloughing off, and the bed was low, relatively high in carbon, and porous. Right after the ESP, the bed was U-shaped from side to side with a trough down the middle of the furnace. Air infiltration was substantial and was aggravated by the strong draft. Consequently, the bed continued to burn, mostly in front of spouts and along side walls where thermocouple probes came in through air ports. The bed burned most markedly during the first 75 min after the ESP, but some bed burning continued throughout the cooling period. Visual observations suggest a bed volume shrinkage of 30%-50% during the eight hours between the ESP and the start of coolant applications.

When we started adding coolant, the bed contained some high areas and mounds with hot and burning char underneath. Although some hardening of the bed surface took place as the bed cooled, no hard, impenetrable crust had formed. **Figure 2** is a composite picture of the bed in the morning, shortly before coolants were applied. The right side is at the top, and the spout (front) wall is on the right. The ridge along the right wall is clearly evident, as is the mound in the left rear (southeast) quadrant. A few hot spots can be seen. A large portion of the bed was essentially at floor level and consisted mainly of char and smelt pieces.

Bed temperatures

Bed temperatures were measured with eight thermocouple probes inserted through primary air ports immediately after the ESP. The temperature data provided evidence of continued burning and shrinkage of the bed during the period between the ESP and the start of coolant applications. The data are consistent with the sensing parts of the probes being buried within the char bed after the ESP and becoming exposed to the active burning area as the bed continued to burn. This evidence is consistent with the videos showing the bed during this period.

The temperature data also show the extreme locality of the temperature field in a cooling or burning char bed. In some cases, probes only 25 cm apart recorded

very different temperatures. The temperatures being measured did not respond to coolant applications, even when the coolants were introduced close to the probes.

BED COOLING RESULTS

Bicarbonate

Sodium bicarbonate was injected into the bed on the west half of the hearth (the right-hand side) through a lance inserted through the mandoor on the east side. The lance was fabricated in 5 ft sections that could be assembled as the lance was inserted into the furnace. The bicarbonate lance was able to reach all actively burning areas of the west-side char bed through the one east-side mandoor. The lance ended in a bevel-tipped nozzle with radial ports. A hand-operated on-off valve located at the top of the lance was opened to start injecting a charge.

The lance was connected through a flexible hose to a canister containing the bicarbonate. Each canister contained a charge of 350 lbs of bicarbonate. The canister was on a wheeled cart that also contained a nitrogen gas cylinder. The nitrogen gas was used as a carrier to inject the bicarbonate powder into the bed. One cylinder of gas was used up in propelling each 350 lb charge. A picture of a cart being loaded and prepared for action is shown in **Fig. 3**.

The bicarbonate was brought to the mill site in 50 lb plastic pails and was loaded into the canisters as cooling proceeded. Three canister-containing carts were used. As each canister was emptied, it was taken to the loading site for refilling, and a fresh nitrogen cylinder was installed. Three men were involved in this operation, two loading the canisters and preparing the cart, and the other one transporting the carts from the boiler to the loading site and back.

One person manned the lance and actually applied the bicarbonate to the bed. The approach is similar to fighting a fire with dry chemical. Hot spots are located, and the lance is brought to the hot spot and inserted under the bed surface to the extent possible. The valve is opened, and the bicarbonate striking the bed helps to disrupt it and allow further penetration. The lance is then worked along the bed, continuing to disrupt it and put out the fire. There is a good deal

of art in making maximum use of the injected chemical, and experience in applying the chemical is beneficial. Once injection has started, the idea is to take advantage of the bed disruption and move the lance along to cover a wider area of the bed than just the initial entry point.

Bicarbonate was effective in breaking up the bed, allowing the coolant to reach the burning char beneath the surface. A residual powder (bicarbonate and carbonate) was left behind to help prevent the cooled char from reigniting. **Figure 4** is a series of pictures showing how well the bed can be disrupted with bicarbonate.

Eight canister loads were injected into the bed over 55 min, and it took about 3 min to deliver each load, for an average injection rate of about 120 lb/min. The total amount of bicarbonate used was about 2800 lbs, which was enough to cool the bed on the west half of the hearth.

The first three charges were injected with very little waiting time between them, since all three canisters were loaded before the cooling application began. After that, the cycle time for loading and transporting canisters determined the rate at which bicarbonate could be injected. Based on the rate of bicarbonate addition during the latter part of this test, we estimate that it would normally be possible to apply bicarbonate to a bed at a rate of about 2800 lb/h, or about eight charges per hour.

The disrupted bed and the injected powder flying around did impede visibility within the furnace while the injection was taking place, but the atmosphere inside the furnace cleared rapidly after each injection stopped. Visibility problems were less severe than had been expected and did not constitute a serious problem for applying the bicarbonate effectively. The stack opacity did increase each time the bicarbonate was injected.

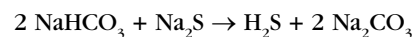
Measurements of stack CO₂ during bicarbonate application indicated that not all of the bicarbonate decomposed, which is not surprising if we consider that an excess of bicarbonate in an area that had already cooled down would not decompose. There was no correlation between the individual applications of a



3. Workers preparing the lance and the canisters for injecting bicarbonate.

canister load of bicarbonate and the CO₂ in the stack.

The stack TRS during the bicarbonate cooling period did correlate with the periods when coolant was actively being applied. The peak values of TRS reached were about 22 ppm, which was significantly higher than the maximum values reached during liquid CO₂ application. The TRS released during bicarbonate injection is probably the result of the reaction between bicarbonate and sulfide in molten smelt:



Bicarbonate was effective in cooling the bed, with 2800 lbs of bicarbonate being used to quench all hot spots on half of the boiler in about 55 min. The entire bed could probably have been cooled with bicarbonate in less than 2 h if that had been desired. This bed was not a difficult one to cool in that it was relatively small and easy to penetrate. The test did demonstrate, however, that bicarbonate was effective on a hot, porous, actively burning bed. The good results obtained with bicarbonate in this cooling test confirm the successful experiences obtained at a number of mills, as reported through BLRBAC.

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4. Pictures of the second bicarbonate application.

Liquid CO₂

There were two separate applications of liquid CO₂ during the test, carried out by the two representatives of Airgas Carbonics who participated in the test. **Figure 5** shows photos of the liquid CO₂ storage tank and the injection lance used in this bed cooling test.

The first application of liquid CO₂ was into a hot spot in the mound on the southeast (left rear) quadrant of the hearth. The mound was too close to the manhole access door on the east side that they originally planned to use, and there was not a good angle to get to that mound through that man-way. As a result, the probe insertion point was moved to

the liquor gun opening on the south (rear) side of the boiler, but it was still difficult to reach the half of the mound closest to the corner. An I-beam, 8 ft up and several feet away from the boiler, made it difficult to maneuver the 25-ft long injection lance. A 5 ft section of the lance was removed to give the two workers more maneuverability. CO₂ was injected for 14 min, then the 5 ft section of the lance that had been removed was added back on for the lance to reach the northernmost section of the mound. Then CO₂ was injected for 15 min more. The injection pressure was 300 psig at the CO₂ storage tank. The total amount of CO₂ applied during this first application was about 650 lbs.

The injection procedure entailed three steps:

1. Pressurize the injection system with CO₂ vapor for 60 s.
2. Introduce liquid CO₂ and vapor together for 10 s.
3. Close the CO₂ vapor valve for full liquid CO₂ injection.

The nozzle used in this first CO₂ application was a 5/32 in. orifice in the center of the plug face of a 1 in. stainless steel pipe plug. The design flow for this nozzle was 40 lb/min, but the actual flow was considerably less, at 23 lb/min. The CO₂ flow was less than the design flow rate because of vaporization in the hose and lance upstream of the orifice, which led to two-phase flow through the orifice, limiting the liquid CO₂ flow rate.

When the lance was placed into a hot spot, the injection pressure from the expansion of CO₂ broke the bed surface and threw the molten material and char into the air, where they were further cooled by radiation and by the air flow in the bed. There was no noticeable kick-back on the CO₂ lance. Some CO₂ snow formed (dry ice) and was observed on the surface of the bed. Videotapes of the action in the bed during this first injection period show some disruption of the bed, but a lot of the CO₂ injected appeared to just flow through the bed. The coolant was somewhat effective in breaking up the char bed crust and blanketing a small area with dry ice, but some burning was still evident not too far from the injection point. At one point, there was a layer of dry ice on the bed just above a burning hot spot visible below it.

The injection lance was made up of three sections of 1 in., schedule-80 stainless steel pipe, two of them 10 ft long and one 5 ft long. The sections were connected by 1 in. stainless steel couplings. The nozzle was screwed onto the end of the lance. A 120 ft length of flexible hose rated for CO₂ service connected the lance to a 6 ton liquid CO₂ storage tank located just outside the recovery boiler building. It was difficult to maneuver the lance because of its weight and length, and the pipe bowed, making it difficult for the one maneuvering the lance to place it and penetrate the mound.

The second application of liquid CO₂ was carried out after Southland had finished applying sodium bicarbonate to the bed on the west side (near the right-hand wall) of the hearth. The lance was inserted through the man-way door on the third floor on the right side of the furnace. The lance was assembled as it was inserted into the furnace. It took all 25 ft of the available pipe length to reach the mound on the hearth on the opposite side. A different nozzle, the Ritter nozzle, was used in this second application. This nozzle, as shown in **Fig. 6**, had a 5/32 in. orifice on the front face and six 5/64 in. orifices evenly spaced radially around the plug (one in each hexagonal face). As mentioned, the liquid CO₂ flow with this nozzle was considerably greater. The design flow was 80-90 lb/min, and the actual average flow during the application period was 52 lb/min.

In the second application, liquid CO₂ was applied to the bed continuously for 36 min. The total amount of CO₂ applied was about 1850 lbs. The CO₂ was much more effective during this second application. The increased flow, coupled with the radial velocity component, resulted in much more disruption of the bed material in the mound. Burning embers were showered around as the bed broke up. Most of the visible hot spots were put out in the first 5-10 min of injection. Holding the nozzle in the same position and rotating the lance 90° back and forth seemed to help break up the bed and allow the lance to penetrate below the surface. After a minute or so of concentrated application in this manner, the lance could be pushed forward 6-10 in. No significant kick-back of the lance was felt during the application.

Figure 7 shows pictures of the bed disruption action during this second application. While the action of the coolant is much more readily observed in the videotapes, the effectiveness of the higher flow rate and the radial nozzles is clearly evident in these pictures. The high pressure radial spray was highly effective in breaking up the bed and blanketing the area with dry ice.

Access to the hot spots on the bed was a problem for liquid CO₂ injection. The available lance was only 25 ft long, and the man-way was located about 16 ft above the hearth. The weight of the 25 ft lance made it difficult to maneuver it, and a longer lance would have been even more difficult to handle.

The lance used for applying liquid CO₂ in this test was heavier than it needed to be. The use of schedule-80 pipe and 1 in. diameter was conservative. A 3/4 in. schedule-40 pipe could be used instead and still withstand the pressure and flow. This change would reduce the weight of the lance and make it possible to use a longer or more maneuverable lance. Aluminum mid-sections for the lance could make it even lighter, but it is not certain that aluminum would have the strength required at the low temperatures reached during exposure to liquid CO₂.

Visual observations indicated that the CO₂ injection eliminated the hot spots within minutes of direct contact with the CO₂. The hot spots and glowing areas of the bed were less dense and were more easily penetrated by the lance. Once a relatively cool crust forms, it is much more difficult to penetrate it with the lance. Consequently, it would be advantageous to apply liquid CO₂ to a hot bed as early as safely possible.

The estimated values for CO₂ out the stack were greater than the amounts of liquid CO₂ applied. This increase probably arises from CO₂ formed by continued bed burning and possibly from delayed release of CO₂ from bicarbonate applied earlier. Stack TRS also increased slightly when liquid CO₂ was applied. The average value was 2.5 ppm for the first liquid CO₂ application and 5.6 ppm during the second liquid CO₂ application, as compared to 1.8 ppm before any coolants were applied.



5. Liquid CO₂ storage tank and lance.

Liquid CO₂ was quite effective in cooling the bed, especially during the second application. Inexperience in handling the injection probe and problems with access to some areas of the bed were factors that contributed to the relative ineffectiveness of the CO₂ addition during the first application. During the second application, the hot spots on the left-half of the bed were effectively cooled in about 40 min.

OTHER INFORMATION

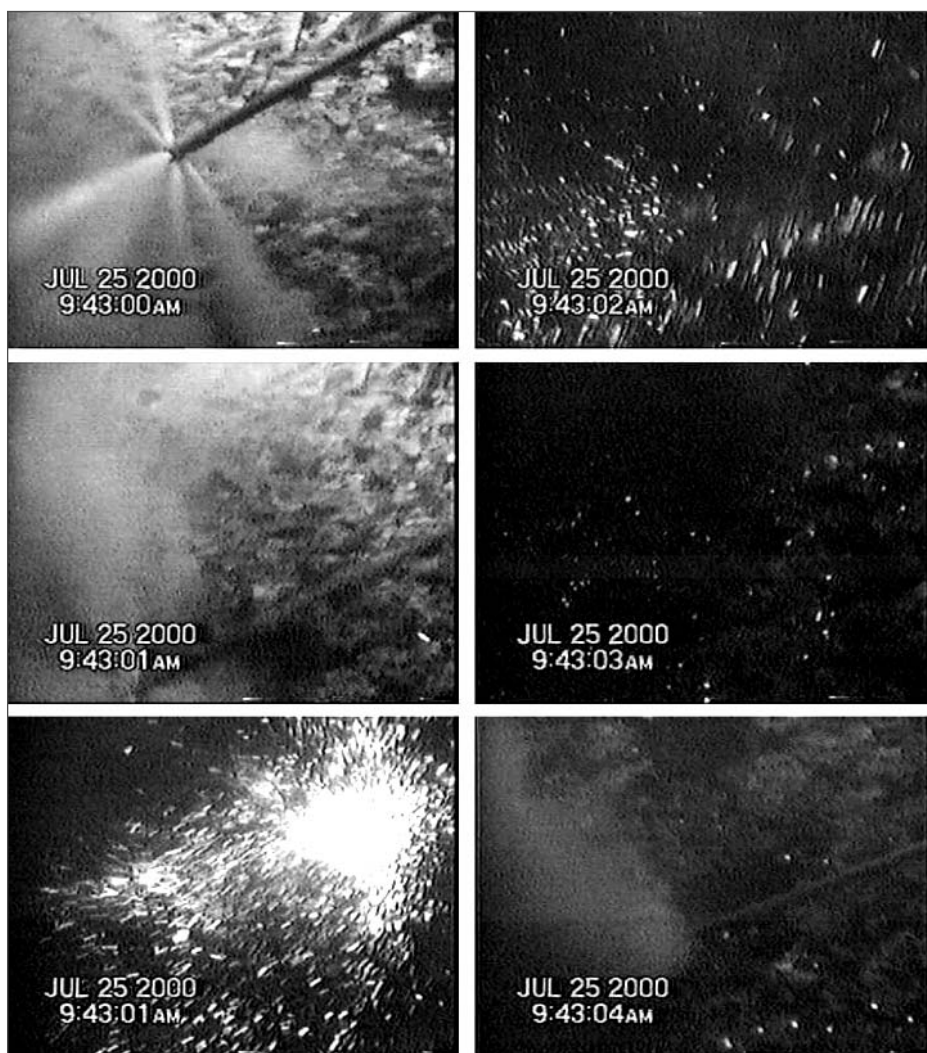
Concentrations of CO, VOC, and TRS in the flue gases were measured during the test. The data showed a rapid displacement from the combustion gas in the stack before the ESP to essentially pure air in 3 or 4 min after the ESP. There was a peak in CO concentration in the first few minutes after the ESP. The concentration reached its maximum in about 3 min, then fell off to a low, steady value by 15 min after the ESP. The highest value for CO reached at any time was only 700 ppm, which is about double the value that existed before the ESP was initiated. There was no clear indication of a rise in TRS. The measured concentrations of total hydrocarbon were zero throughout the period spanning the ESP.

Thus, measurements showed that the char bed gave off only minor amounts of

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6. The Ritter nozzle used in second liquid CO₂ application.



7. Pictures of bed disruption action during the second CO₂ application.

combustible gas right after the ESP and that the gas quickly stopped coming off the bed. Continued pyrolysis and char combustion did not produce significant amounts of combustible gas. During the period when these measurements were

taken, the draft on the boiler was strong (in excess of 10 in. H₂O), and the amount of air infiltration was high. How much these air flows affected the measured results is difficult to estimate, but it is safe to say that the volume of air moving over

the bed would have had to be reduced by a factor of 100 to get CO concentrations of 5%-7%, which could be in the explosive range.

The test showed the consequences of continued contact between air and the char bed after an ESP. Intense combustion can take place if air jets impact the bed. Even if forced air below the liquor guns is stopped, infiltration air can have detrimental effects on bed burning. To keep infiltration air from coming in contact with the bed, it is important to minimize draft in the lower furnace after an ESP. However, steps taken to minimize air to the lower furnace, such as closing the primary air damper (or both the primary and secondary air dampers) and shutting down forced draft fans, can actually aggravate bed burning by infiltration air if the ID fan is not also slowed down. It may be worthwhile to deliberately supply some forced air at higher levels in the furnace to provide the necessary flow for the ID fan.

CONCLUSIONS

The test confirmed that both bicarbonate and liquid CO₂ can work effectively to cool beds quickly. It was not possible to reach an ultimate judgment on the relative merits of the two coolants. There were no significant problems in applying either coolant to a hot, porous, actively burning bed, and there was no indication that cooled portions of the bed reheated and re-ignited after the we stopped applying the coolant.

It is advantageous to begin applying coolants as early as possible, consistent with safety considerations about possible smelt-water contact in an actual ESP. Early application of coolants to the hot burning bed is likely to increase the amount of coolant needed. It is also advantageous to use large quantities of coolants at higher rates to achieve better penetration and more rapid and widespread cooling. The economics of accelerated bed cooling are such that in almost all cases, the cost of using more chemical is far overshadowed by the savings brought about by shortening the cooling time.

Proper techniques are important in using coolants effectively in char beds. Lances should be constructed to make them easy to handle and manipulate. Furnace access points need to be identi-

fied and assessed in terms of the ability to maneuver lances to specific locations on the bed. Those who handle the lances need to be able to recognize the locations of hot spots and determine when enough coolant has been applied in a particular region.

The atmosphere within the furnace was dirtier when bicarbonate was applied than when liquid CO₂ was applied, as the stack opacity data confirmed. However, the bicarbonate dust was contained within the furnace and did not contaminate the area surrounding the furnace. The dusty atmosphere cleared rapidly when the injection of bicarbonate stopped, and the dust did not interfere with the effective application of bicarbonate. Refilling canisters with bicarbonate is dusty work and is best done at a distance from the furnace.

Thermocouple probes did not generally respond to coolant applications, even when they were located fairly close to the point where coolant was being introduced.

Measurements of combustible gas rising from the bed after the ESP showed that the minor amounts stopped quickly.

Continued pyrolysis and char combustion did not produce significant amounts of combustible gas. Considerable bed burning from infiltration air was observed. The test clearly showed the consequences of continued air-bed contact and demonstrated the need to maintain a balanced draft in an ESP. **TJ**

ACKNOWLEDGEMENTS

We are most grateful to Willamette Industries and the Albany mill for making the No. 4 recovery boiler available for use in the test. Support from the American Forest and Paper Association Recovery Boiler Committee was critical to the success of this test. We acknowledge the University of Toronto's Research Consortium, "Improving Recovery Boiler Performance, Emissions and Safety" for allowing us to carry out the test as part of the consortium program.

Southland Fire and Safety Equipment, Inc. provided equipment and personnel for carrying out cooling with sodium bicarbonate. Airgas Carbonics provided equipment and personnel for carrying out cooling with liquid CO₂. Weyerhaeuser Company assisted with

gas analysis, data acquisition, and liquor sampling and analysis. Babcock & Wilcox Co. provided a special IR camera for monitoring the bed. RWDI made measurements of the flue gas flow and estimated the amount of air infiltration. Representatives from International Paper, Westvaco, and Boise Cascade assisted with test observations and data acquisition. Several University of Toronto students assisted in data collection, analysis, and interpretation.

The results of this study also appeared in: Tran, H., Kawaji, M., and Grace, T., "Accelerated Bed Cooling Test at the Willamette Industries Albany Mill" report to American Forest and Paper Association Recovery Boiler Committee, Pulp & Paper Centre, University of Toronto, Toronto, Ontario, Canada, January 2001.

Received: June 25, 2001
Accepted: January 6, 2002

This paper is also published on TAPPI's web site <www.tappi.org> and summarized in the January *Solutions!* for People, Processes and Paper magazine (Vol. 86 No. 1)

INSIGHTS FROM THE AUTHORS

Cooling of char beds after emergency shutdowns can take days, with production curtailed in the meantime.

An earlier study of bed cooling concluded that little could be done to speed up the cooling process. Empirical development of cooling techniques showed promise, but there was a need to understand how they work and what limitations there might be. Accelerated bed cooling was beginning to be practiced commercially but there was little technical information available about it.

Once a recovery boiler became available for a test (a highly unusual event), the most critical need was to put together a test team that would embody the experience of suppliers who had been cooling char beds, provide the necessary measurement capability for following what happened during the test, and interfacing with the Albany mill. The AF&PA Recovery Boiler Committee provided the key support to make this test happen.

We were surprised at how easily the bed burned where infiltration air struck the bed. A hot smelt pooled formed by the spouts as a result of air rushing in through the spout openings.

From this study, mills that have not had direct experience with accelerated bed cooling can see how it works. It can provide the mill with critical information on how to do accelerated cooling if they choose to do it themselves.

The primary need now is to disseminate the information on accelerated cooling to the industry. A video is being prepared that will help do this. A final report to AF&PA Recovery Boiler Committee will also make the findings widely known.

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Tran



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