

JÚLIO CÉSAR TORRES RIBEIRO

SMELT SPOUT CORROSION IN A RECOVERY BOILER

Dissertação apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação do Mestrado Profissional em Tecnologia de Celulose e Papel, para obtenção do título de *Magister Scientiae*.

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APROVADA: 14 de Junho de 2010.

Prof. Jorge Luiz Colodette
(Co-Orientador)

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Prof. Marcelo Cardoso
(Orientador)

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A Deus, acima de tudo, e aos meus PAIS pelo amor, compreensão e apoio em todos os dias de minha vida.

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A todos vocês, muito obrigado.

BIOGRAFIA

Júlio César Tôrres Ribeiro, filho de Pedro Américo Ribeiro e Juracy Tôrres Ribeiro, nasceu aos 5 dias de novembro de 1969, na cidade de Belo Horizonte, Minas Gerais.

Concluiu o segundo grau científico em 1987 no Colégio Municipal Marconi, em Belo Horizonte, MG.

Cursou Engenharia Mecânica no período de 1988 a 1992 pela Universidade Federal de Minas Gerais.

Em fevereiro de 1993 iniciou suas atividades profissionais na setor de celulose e papel como engenheiro trainee da Celulose Nipo-Brasileira S/A - CENIBRA, onde atualmente ocupa o cargo de coordenador de recuperação e utilidades.

Cursou MBA em gestão empresarial no período de 1998 a 2000 no programa de pós-graduação da FIA-USP, na cidade de São Paulo, SP.

Cursou pós-graduação *lato sensu* em Tecnologia de Celulose e Papel no período de fevereiro de 2001 a fevereiro de 2003 pela Universidade Federal de Viçosa.

Atua como membro do Sub-comitê de Segurança em Combustão do Comitê Brasileiro de Segurança em Caldeiras de Recuperação, CSCRB, desde 2002.

No período de 2004 a 2006 atuou como vice-coordenador da Comissão de Recuperação e Energia da ABTCP e como coordenador no ano de 2007.

Em Agosto de 2008 iniciou o curso de Mestrado Profissional em Tecnologia de Celulose e Papel pela Universidade Federal de Viçosa, com defesa da dissertação em Junho de 2010.

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RESUMO

RIBEIRO, Júlio César Tôres, M.Sc., Universidade Federal de Viçosa, Junho de 2010. **Smelt spout corrosion in a recovery boiler**. Orientador: Marcelo Cardoso. Co-orientadores: Jorge Luiz Colodette e Cláudio Mudado Silva.

Acidentes com Bicas de *Smelt* são reportados pelo *Black Liquor Recovery Boiler Advisory Committee, BLRBAC*, e constituem uma preocupação real de segurança sob o ponto de vista operacional. Tipicamente o *smelt* escorre através de bicas refrigeradas a água da fornalha para o tanque dissolvedor e uma falha pode levar a explosões pelo contato água-*smelt*. Este trabalho estuda um caso real onde condições severas de corrosão culminaram com a falha em serviço de uma de seis bicas em uma caldeira de recuperação na CENIBRA. A falha resultou em grande volume de água de resfriamento entrando na caldeira e em contato com *smelt* ao redor da abertura da bica, mas felizmente não ocorreram explosões água-*smelt*. Uma elaborada investigação foi conduzida para se determinar as causas da falha da bica. Conclui-se que a falha foi causada por fluxo insuficiente de água de resfriamento para a bica de *smelt*, que, por sua vez, foi causada por uma seqüência de eventos que ocorreram após uma falha geral no sistema de geração de energia elétrica da fábrica. O estudo do evento levou ao desenvolvimento e implantação de procedimentos operacionais e de manutenção que tem por objetivo assegurar fluxo de água de resfriamento adequado para as bicas de *smelt* para prevenção de falhas recorrentes.

ABSTRACT

RIBEIRO, Júlio César Tôrres, M.Sc., Universidade Federal de Viçosa, Junho de 2010. **Smelt spout corrosion in a recovery boiler.** Advisor: Marcelo Cardoso. Co-advisors: Jorge Luiz Colodette and Cláudio Mudado Silva.

Smelt Spout accidents are reported by Black Liquor Recovery Boiler Advisory Committee, BLRBAC, and constitute a real safety concern from the operational point of view. Typically smelt flows through water cooled spouts from furnace to the smelt dissolving tank and a failure can lead to smelt-water contact explosions. This work studies a real case where severe corrosion led to an in-service failure of one of the six spouts on a recovery boiler at Cenibra. The failure resulted in a large amount of cooling water entering the boiler and contacting smelt around the spout opening, but fortunately no smelt-water explosion occurred. An extensive investigation was conducted to determine the causes of the spout failure. It was concluded that the failure was caused by insufficient cooling water flow to the smelt spout, which, in turn, was caused by a sequence of events that occurred after a general black out of an electrical energy system at the mill. The experience has led to the development and placement of operating and maintenance procedures that ensure adequate cooling water flow to smelt spouts to prevent future failures.

1- INTRODUÇÃO GERAL

De acordo com os dados da Associação Brasileira de Celulose e Papel - BRACELPA, o Brasil é o quarto produtor mundial de celulose do mundo desde 2008, com 12.697 mil tsa, estando atrás apenas dos Estados Unidos, Canadá e China. No ano de 2009, um ano de intensa crise econômica, a produção cresceu 6% atingindo a marca de 13.461 mil tsa, enquanto em outros países de grande expressão ocorreram reduções de produção em função de demanda e custos de produção (BRACELPA, 2010a). Para os próximos anos espera-se incrementos de produção cada vez maiores em função dos maciços investimentos em empreendimentos do setor.

Na mesma velocidade em que novos empreendimentos são postos em marcha cresce a contribuição do setor no superávit comercial brasileiro. De acordo com BRACELPA (2010a) as exportações de celulose contribuíram positivamente na balança comercial com US\$ 3,643 Bilhões em 2008, resultado 30,5% superior ao atingido em 2007. Também, conforme esperado, o setor emprega grandes volumes de mão-de-obra, estimados em 114.000 empregos diretos e 500.000 indiretos (BRACELPA, 2010b).

A tecnologia de extração de celulose é muito bem estabelecida e dominada por fornecedores de equipamentos e produtores de celulose. Existem vários processos industriais de extração de celulose conforme o produto final desejado, porém o processo de produção mais amplamente utilizado no mundo é o processo *Kraft*, responsável por 67% da produção mundial de celulose (TRAN, 2010). *Kraft* é uma palavra de origem germânica que significa forte e foi utilizada para designar o processo em função da polpa de alta resistência produzida. O processo *Kraft* foi descoberto por Dahl, em 1879, porém a sua ampla utilização só foi possível após o desenvolvimento da caldeira de recuperação química por Tomlinson, na década de 1930 (TRAN, 2010). Além de sua versatilidade, caracterizada pelo grande número de espécies de madeira que podem ser processadas, o processo *Kraft* possui um eficiente ciclo de recuperação de produtos químicos, responsável por níveis de recuperação de até 97% nas fábricas modernas. Considera-se que a viabilidade econômica e ambiental de uma fábrica de celulose é sustentada pelo ciclo de recuperação química, na medida em que elevada carga orgânica, originada do cozimento da madeira, é incinerada na caldeira de recuperação. Este processo fornece, em casos específicos, até mais de 100% das demandas de energias térmica e elétrica necessárias ao pleno funcionamento da unidade industrial.

A caldeira de recuperação química é um equipamento extremamente complexo que gera vapor a partir da combustão do licor preto forte. Trata-se de um reator químico que

passou por muitos aperfeiçoamentos desde o seu surgimento na década de 30, porém a essência do processo de combustão permanece a mesma. O processo de combustão do licor se dá em um leito de fundidos, no fundo da fornalha, composto essencialmente de sais de sódio e enxofre e carbono. A massa de fundido, também denominado *smelt*, em função das reações químicas envolvidas, é naturalmente mantida entre 750 e 850°C e é removida de dentro da fornalha através de seu escoamento pelas bicas de fundido, ou, como mais comumente denominadas, bicas de *smelt*. Usualmente as bicas de *smelt* possuem um sistema de refrigeração a água, podendo este ser pressurizado ou à vácuo, que é responsável por manter a sua integridade em operação.

A possibilidade de contato água-*smelt* é uma das grandes preocupações na operação de uma caldeira de recuperação. Apesar dos rígidos controles de fabricação, instalação e operação, sempre existe a possibilidade de um vazamento de água no sistema de refrigeração. Devido à grande energia concentrada na massa de fundido, o contato água-*smelt* normalmente é catastrófico e responsável pela grande maioria das explosões em caldeiras de recuperação. Baseado na estatística consolidada pelo BLRBAC (2009b) verifica-se que no período de 1980 a 2009 ocorreram 31 explosões em caldeiras de recuperação nos Estados Unidos, sendo que 21 causadas pelo contato água-*smelt*. Em outra avaliação, realizada por Grace (2010), verifica-se que de um total de 28 explosões de caldeiras de recuperação por contato água-*smelt*, cinco ocorreram devido a vazamentos em bicas, sendo três de moderada a elevada magnitude.

A operação segura das caldeiras de recuperação sempre foi um tema muito discutido e estudado nos países onde a indústria de celulose e papel se instalou ao longo dos anos. Em um passado remoto, muitas mortes ocorreram em função de explosões em caldeiras de recuperação causadas por falhas operacionais, de projeto e/ou de materiais. A criação de comitês de segurança, compostos por profissionais da indústria, foi uma das maneiras encontradas para se estudar os problemas e desenvolver mecanismos de prevenção à falhas. O trabalho destes comitês, dentre os quais destaca-se o *Black Liquor Recovery Boiler Advisory Committee (BLRBAC)*, é caracterizado por intensa colaboração entre empresas, especialmente no tocante a troca de informações sobre os acidentes ocorridos e na elaboração de recomendações de operação segura.

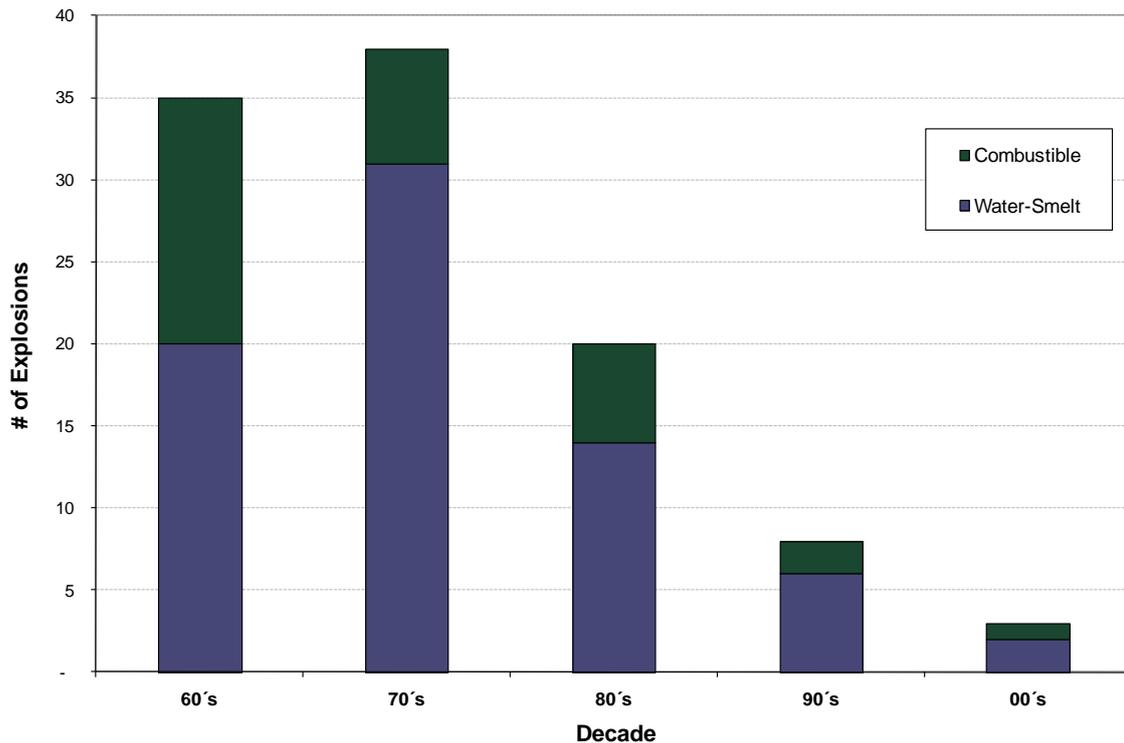


Gráfico 1 - Estatística de explosões com caldeiras de recuperação nos EUA.
Fonte: BLRBAC, 2009b.

Não obstante as questões de operação segura, a parada não programada de uma caldeira de recuperação devido a uma explosão pode significar a parada de toda a fábrica por vários dias ou até meses, além de demandar elevado capital na recuperação da capacidade produtiva da mesma. Tal situação pode chegar a comprometer a continuidade e saúde financeira de todo o empreendimento.

Este trabalho, baseado em uma situação real vivenciada em uma fábrica de celulose brasileira, tem por objetivo estudar o mecanismo de falha por corrosão a alta temperatura de uma bica de *smelt* em serviço. Trata-se de uma ocorrência rara e de grande complexidade, o que pode ser comprovado pela quase total inexistência de literatura sobre o assunto. Uma das alternativas na condução do trabalho, especialmente devido à escassez de literatura, foi a consulta a metalurgistas e especialistas em corrosão.

Foi exatamente este caráter inédito da ocorrência, e de grande importância prática sob vários aspectos, incluindo segurança patrimonial, pessoal e econômica, que motivou o desenvolvimento deste trabalho. Espera-se que outras fábricas e fornecedores de equipamentos possam usufruir dos resultados aqui demonstrados de maneira a subsidiar modificações e melhorias de projeto proporcionando melhoria nas condições operacionais e de segurança das caldeiras de recuperação.

2- ARTIGO : SMELT SPOUT CORROSION IN A RECOVERY BOILER

SMELT SPOUT CORROSION IN A RECOVERY BOILER

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ABSTRACT

Severe corrosion led to an in-service failure of one of the six spouts on a recovery boiler at Cenibra. The failure resulted in a large amount of cooling water entering the boiler and contacting smelt around the spout opening, but fortunately no smelt-water explosion occurred. An extensive investigation was conducted to determine the causes of the spout failure. It was concluded that the failure was caused by insufficient cooling water flow to the smelt spout, which, in turn, was caused by a sequence of events that occurred after a general black out of an electrical energy system at the mill. The experience has led to the development and placement of operating and maintenance procedures that ensure adequate cooling water flow to smelt spouts to prevent future failures.

INTRODUCTION

Celulose Nipo-Brasileira S.A. (Cenibra) is a 1.2 million ADMT/year bleached eucalyptus kraft pulp mill located near the city of Ipatinga, 250 km south of Belo Horizonte, Minas Gerais State, Brazil. The mill has two pulp production lines and three recovery boilers. The #1

recovery boiler (RB) was built in 1976. It has a firing capacity of 1800 tonnes (t) of BL ds/day but is presently in a standby condition. The #2 RB was built in 1992 and presently burns 2700 t BL ds/day at 72% solids. The #3 RB, the newest and largest of the three, started up in 2006 and burns 3500 t BL ds/day at the same solids. These boilers produce superheated steam rated at 65 bars and 450°C, and they were all supplied by CBC, a Mitsubishi Heavy Industries branch in Brazil.

The mill electrical power is supplied by two turbo-generators, 40 and 60 MW, and by the grid, 9.5 MW. The generators operate in island mode and are not directly connected to the grid. The mill had never had an Emergency Shutdown Procedure (ESP) since its startup in 1976, until February 2008, when one of six smelt spouts of the #2 RB failed (Figure 1). This spout #5 was severely corroded that water was leaking out and so coming into contact with molten smelt. Figure 2 shows a large hole at the spout lip (front end) and multiple layers of large perforations along the inlet and outlet cooling water tubing on the furnace side (rear end) of the spout.

The ESP occurred seven days after a total mill-wide power failure that disrupted operations. Although the incident did not lead to a smelt-water explosion fortunately, the severity of the problem and the potential damage it might have caused prompted the mill to conduct an extensive investigation to determine the causes of the spout failure. This investigation involved documentation of the sequence of events, analysis of relevant process data, non destructive testing of all smelt spouts and metallurgical analysis of corroded and non-corroded section of the failed spout. The paper discusses the smelt spout system, the key findings of the investigation, the connection between the power failure and the smelt spout leak, the underlying reasons the failure occurred and the steps taken to prevent a recurrence in the future.

SMELT SPOUT SYSTEM

The #2 RB originally had only 5 smelt spouts. The sixth smelt spout (spout #6) was added in order to handle the increased smelt flow after a major retrofit of the boiler in 2004 to increase its firing capacity from 2050 t BL ds/day to 2700 t BL ds/day. At that time, all six smelt spouts were relocated to new positions.

The spouts were supplied by the same boiler manufacturer, CBC. They are made of carbon steel with no weld overlay and inserted into the boiler (Figure 2A). All three recovery boilers use the same type and model of spouts which are essentially the same as the original design that was used in 1976. Over the years, the mill has been following BLRBAC operation procedures to discard all smelt spouts and replace them with a new set of spouts every year regardless of their condition [1]. They have always been found to be in good condition after one year in service with no excessive thinning or corrosion. This specific set of the #2 RB smelt spouts had been in service for ten months at the time of the incident.

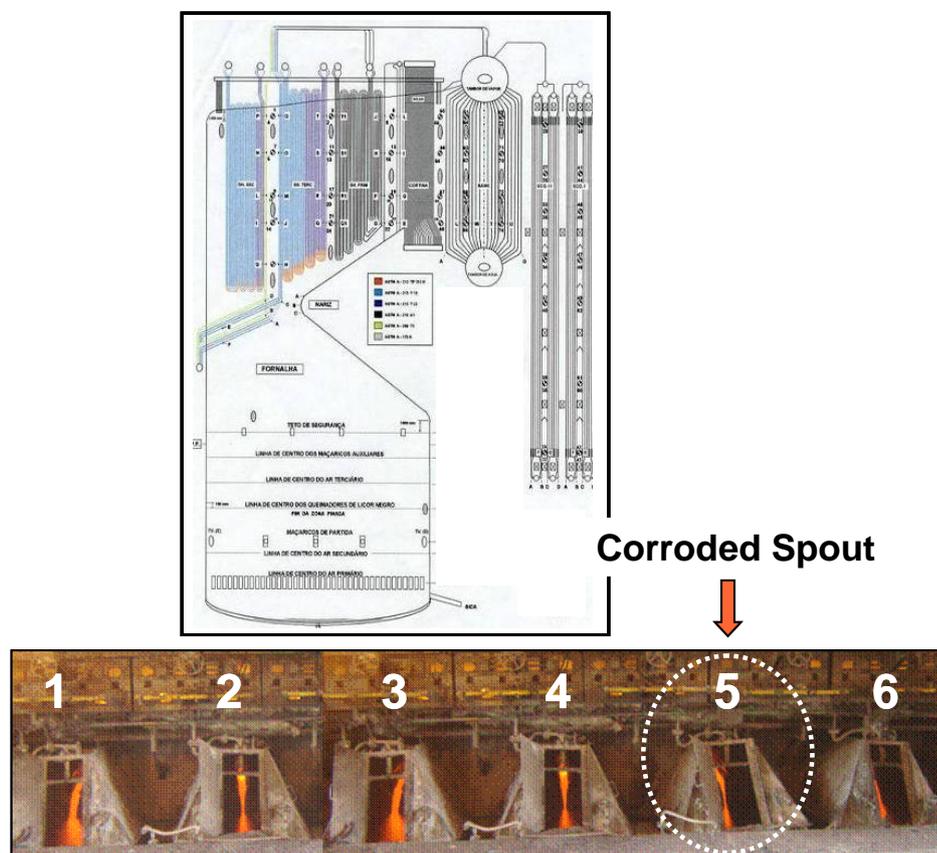


Figure 1. Schematic drawing of the #2 recovery boiler and smelt spout identifications.

The smelt cooling water system is a typical pressurized, closed loop system using high-quality treated water, as shown in Figure 3. The main components are a head tank, piping to and from the individual smelt spouts, hand valves, a collection tank, and dual recirculation water pumps to transfer the cooling water back to the head tank. There are no flowmeters on the lines to the individual spouts. Although visual verification of cooling water flow could be done through glass doors installed on individual spout pipelines, but it was usually not done, since the glass doors were small and often dusty, and were mounted in a obscure position that was difficult to

access. Monitoring through DCS the cooling water temperature discharging from each spout with a thermoprobe was the primary means for verifying their proper operation.

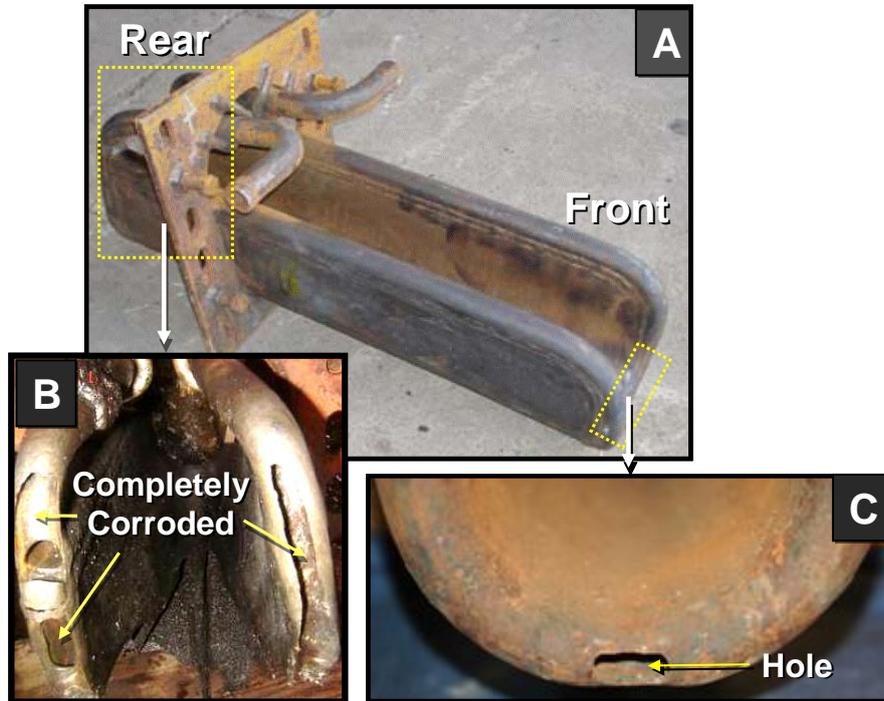


Figure 2. Large perforations at the rear end and a hole at the front lip of the severely corroded Spout #5.

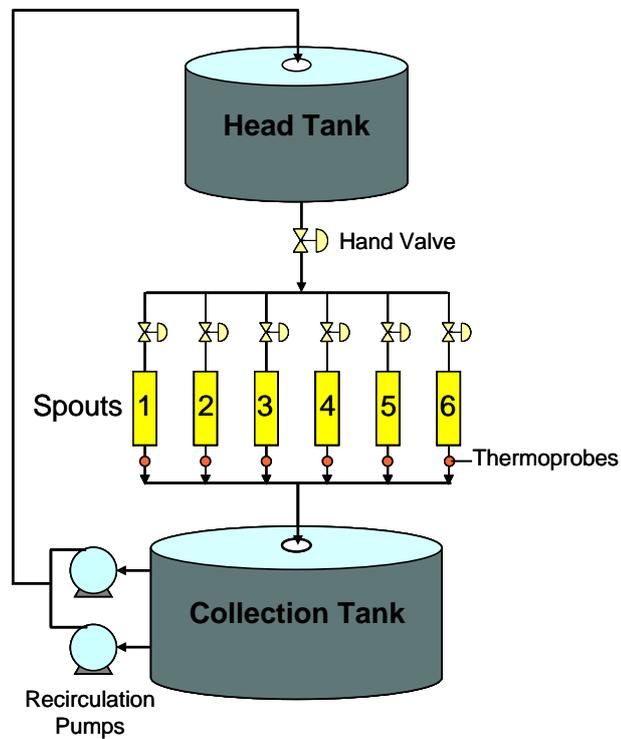


Figure 3. #2 RB smelt spout cooling water system

There is a hand valve (normally wide open) in the main cooling water line leaving the head tank. This main line is divided into six smaller lines, one to each spout with a separate shutoff valve to isolate the cooling water to that spout in the event of a spout leak. Since the system at the time of the incident did not have the capability of adding firewater to the head tank in the event of a power failure, the loss of electrical power means that the recirculation pumps were unable to continue delivering water to the head tank, which would eventually run out of cooling water.

SEQUENCE OF EVENTS

February 11, 2008 (Black Out)

The #2 RB was operating normally that day until 9:02 PM when a general electrical power blackout occurred due to a short circuit in the turbo-generator #1. The short circuit caused most emergency systems to fail, including the grid power and backup diesel generators. The mill had no electrical power for 71 minutes. The power failure caused the boiler to trip, but smelt continued to flow out of the furnace for some time after the boiler trip.

The loss of power also caused both recirculation pumps to stop, thereby shutting off the return cooling water flow to the head tank. In order to preserve cooling water flow for a longer time during the black out, a boiler operator partially closed the hand valve on the main line from the head tank. He thought that he closed it halfway, but there is no way to tell if it was actually the case, since the hand valve had no marks to indicate the degree of closure. It was not known how much cooling water was flowing to each spout at that time, since there were no flowmeters and it was difficult to check visually.

Figure 4 shows the trend data for the cooling water temperatures from individual spouts and the amperages of the recirculation pumps for the period before and after the blackout. Before the blackout, the cooling water temperature from all six spouts appeared to be normal, $70 \pm 3^{\circ}\text{C}$. After the black out, however, the cooling water temperature of spout #5 behaved erratically and was much lower than those of other spouts. This indicates that something had happened to spout #5, although it was not noticed at the time because the boiler was down.

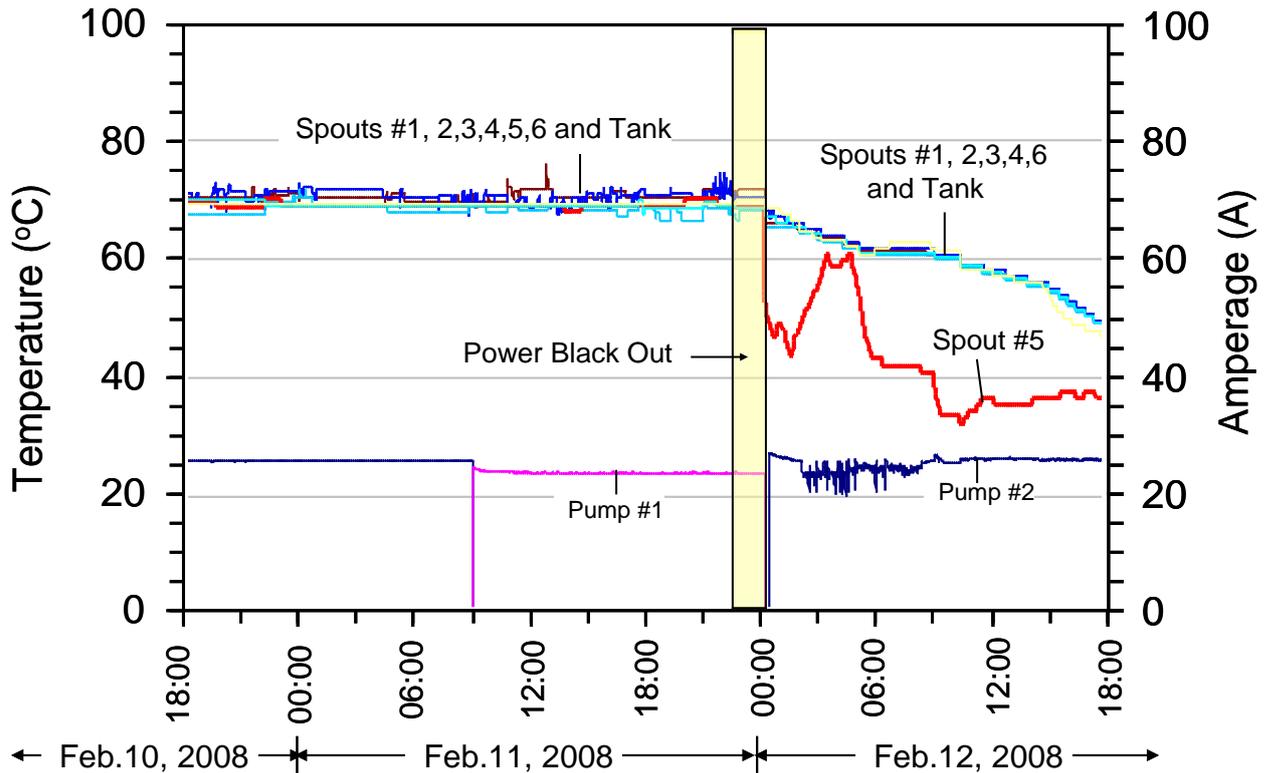


Figure 4. Cooling water trend before and after the blackout period

February 16, 2008 (Boiler Startup)

The mill #1 production line was down for five days while the turbo-generator #1 was fixed. Only the #3 RB was operated during this period. The #2 RB was started up on February 16, 2008 at 3:10 AM and began burning black liquor at 9:40 AM. During this period, an unusually low and erratic cooling water temperature was noted on spout #5 as can be seen in Figure 5. This was the first time that the abnormal behaviour of spout #5 was noted on the DCS, even though it had occurred 5 days earlier. The boiler operator asked for maintenance and was told that the thermocouple in the thermoprobe was bad and needed to be replaced. The thermocouple was checked after the ESP and was found to be normal; no replacement was made.

February 18, 2008 (ESP)

Because of the inconsistent temperature trends and the apparently bad thermocouple, the DCS personnel called on another boiler operator to check spout #5 out. When passing in front of spout #5, the operator saw small explosions inside the furnace, and smelt was dark and

stopped flowing. As he started cleaning the spout with a steel lance, thinking it was a common jelly-roll smelt situation, he noted suddenly that water was flowing down the spout trough and that the bed was dark near the spout area. Thinking the water was from a leak on spout #5, the operator shut off the cooling water valve to stop the water flow to that spout. The water, however, kept flowing out from the furnace even after the valve had been closed. The operator then saw the water was sizzling and rumbling inside the furnace and it appeared to come from a primary air port tube nearby. He immediately called for an ESP, which was initiated at 3:29 AM on February 18, 2008.

The boiler was firing 1800 t BLds/d when ESP was initiated. The sequence of events shows that the boiler had been burning black liquor with spout #5 operated at an usually low cooling water temperature for nearly 2 days before the ESP.

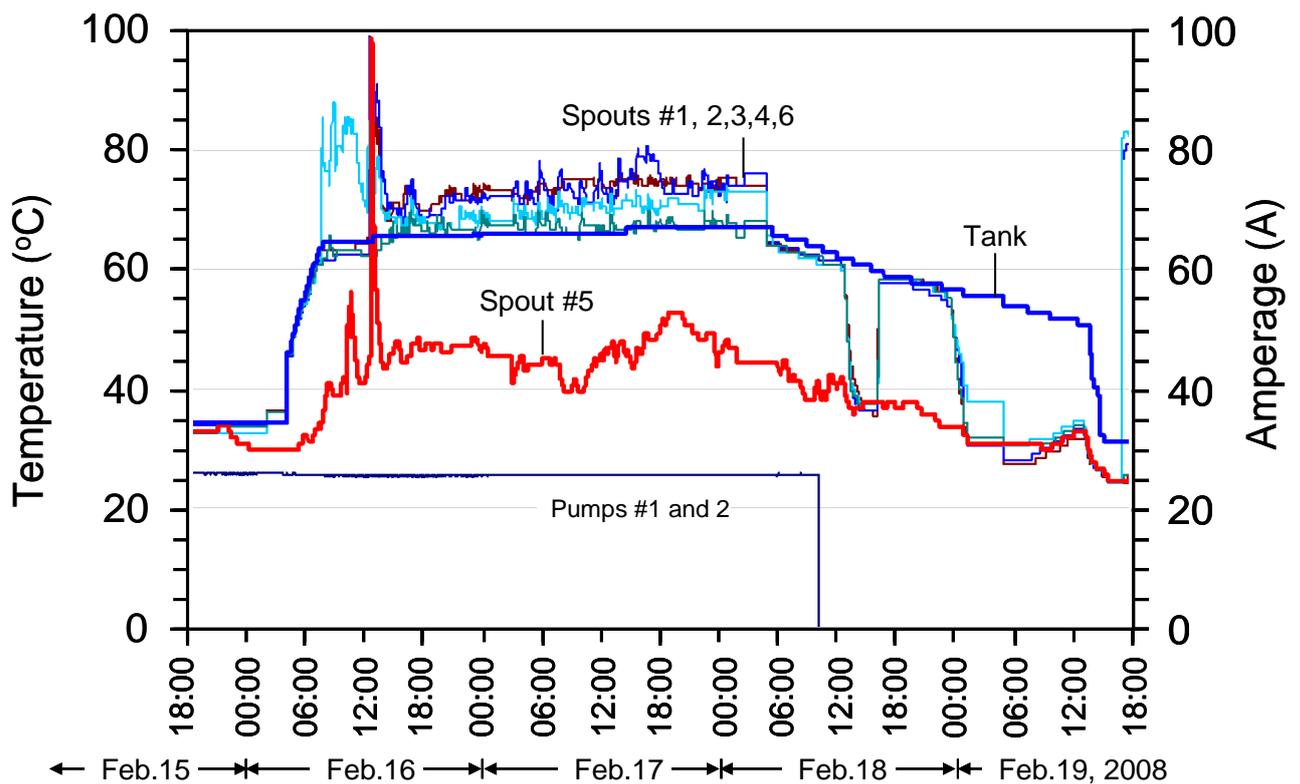


Figure 5. Cooling water trends on restart of #2 recovery boiler

February 19, 2008 (Damage Inspection)

An initial inspection at the smelt spout floor about 12 hours after the ESP showed water running down the trough of spout #5 from within the furnace as well as from a hole at the

spout lip (Figure 6). From a mandoor one floor above the spout floor, a pool of water could be seen around spout #5 (Figure 7). A close look at the rear end of the spout revealed that the inlet and outlet of the cooling water tubing and the trough were completely corroded through, and some water still remained on the trough (Figures 7, 2B, and 8B).

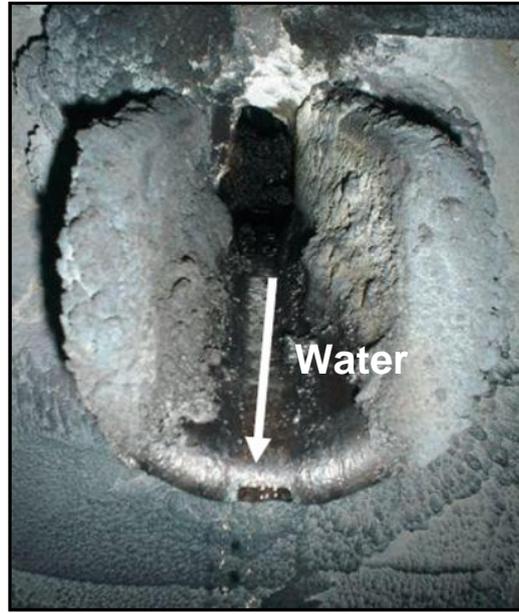


Figure 6. Water running out of spout #5 from inside the furnace, 12 hours after ESP.

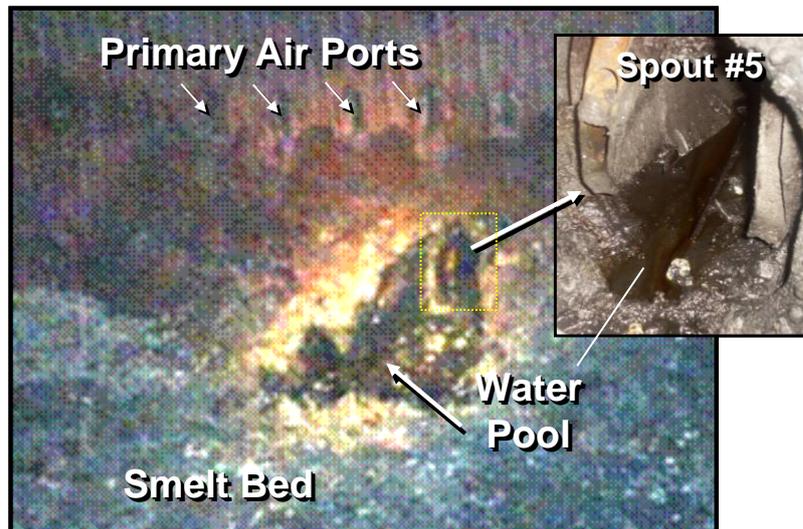


Figure 7. Water pool accumulated on frozen smelt bed at the spout #5 opening. Box photo shows extensive damage to the cooling water tubing and water on spout trough

THE INVESTIGATION

The investigation included a review of event chronology, operator interviews, trend analyses of the #2 RB and its spout cooling system operating data, operating procedures of emergency systems, and metallurgical evaluation of corroded and non corroded spouts. The main focus was on determining the causes of spout failure and devising operational and equipment modifications to avoid a repeat occurrence.

A thorough inspection was conducted on the spout cooling system, particularly the water lines shown in Figure 3. It was discovered during the inspection that the individual valve identifications were reversed between spouts #3 and #5, although the identification swap had probably been there since the boiler upgrade in 2004. This means that when the operator closed the water valve to spout #5 just before the ESP, he, in fact, shut off the cooling water to spout #3. This explains why water continued to enter the furnace through spout #5 even though the valve was closed. This also means that spout #3 passed through the ESP with no water cooling.

Non destructive dye-penetrant tests, thickness measurements and visual inspection were performed on all spouts and waterwall tubes near spout openings. The results showed that waterwall tubes were intact and that spout #1, 2, 3, 4 and 6 were in excellent condition with no signs of thinning, cracking or internal deposits. On spout #5, however, in addition to large perforations along the cooling water tubing at the rear end of the spout, there appeared to be a defect in the weld that joined the inlet cooling water tube and the outlet tube as can be seen on figures 8A and B.

A large section of spout #5 (corroded) and a section of spout #3 (not corroded) were also sent to an external laboratory, Nalco Company, in Naperville, IL, USA for metallurgical analysis.

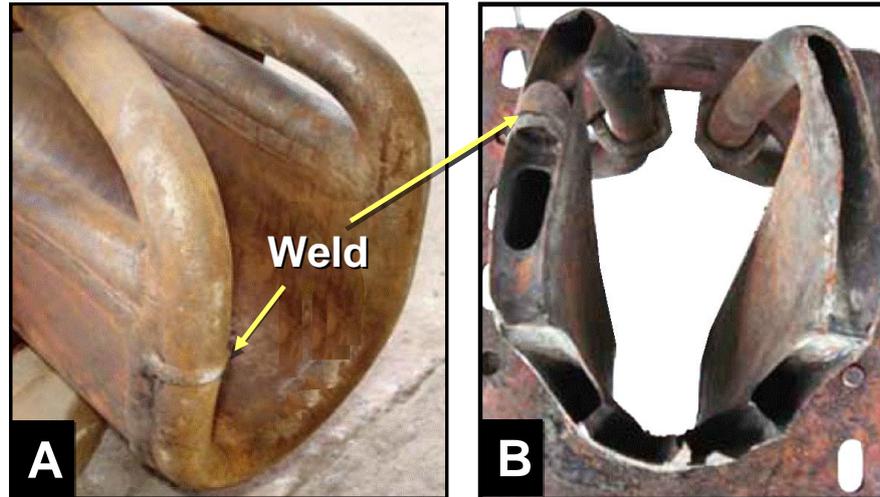


Figure 8. (A) Weld connecting the cooling water tube to the spout at the rear end of a good spout. (B) Suspected "defect" on the weld joining the inlet and outlet cooling water tubes of spout #5

The metallurgical analysis by Nalco revealed that the metal loss of spout #5 was mainly from the external surface (Figure 9). In the areas of severe wastage and along the bottom of the trough, the metal surface was smooth with signs of gouging, resulting presumably from the erosion-corrosion action of molten smelt flowing over the spout surface (Figure 10). The analysis also revealed that the wastage on spout #5 was mainly on the furnace side where heat input is greatest, suggesting a strong temperature dependence of corrosion rates. The microstructure consisted of spheroidized carbides in a ferrite matrix (Figure 11), suggesting that the metal temperature must have exceeded 540°C (1000°F) for a period of time.

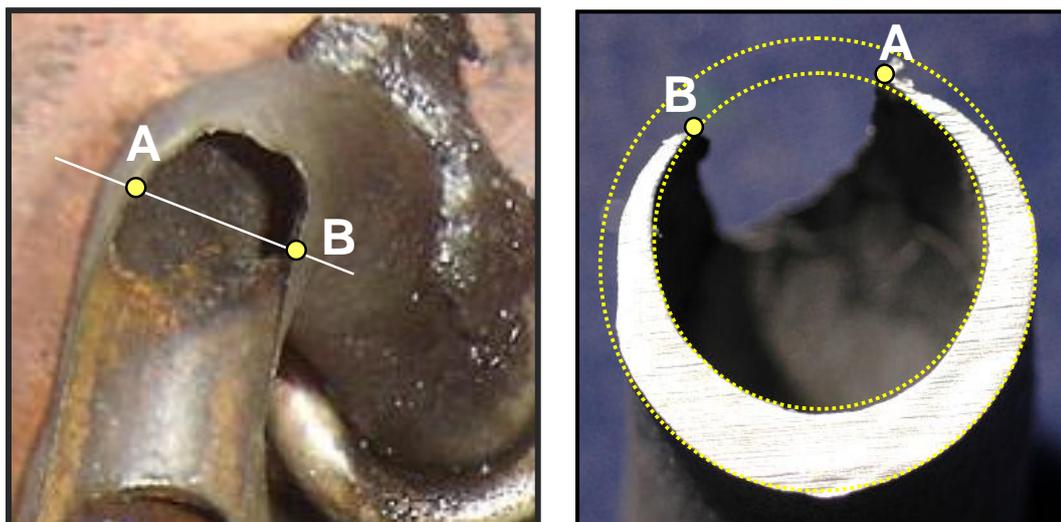


Figure 9. Cross section through a perforation on the cooling water tubing of spout #5 showing severe external metal loss. Broken circles are contours of original tube surfaces. The difference in original tube thickness is due to bending.

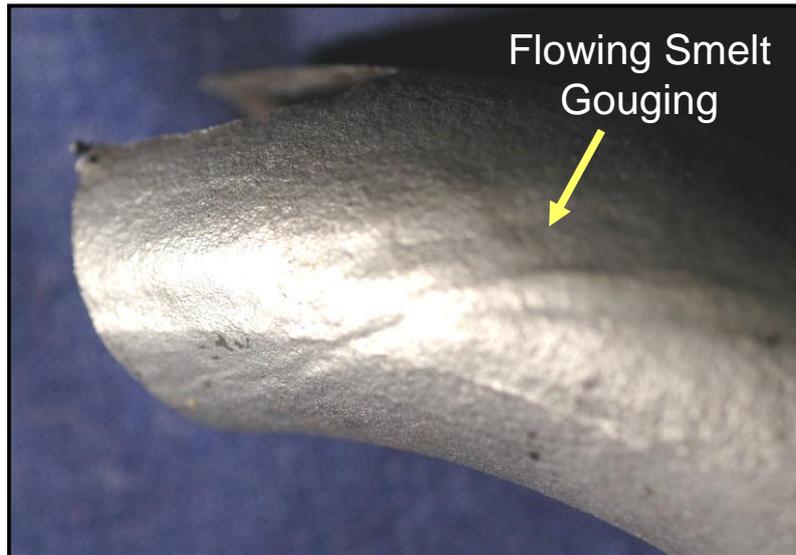


Figure 10. Smooth surface of spout #5 with signs of gouging by molten smelt.

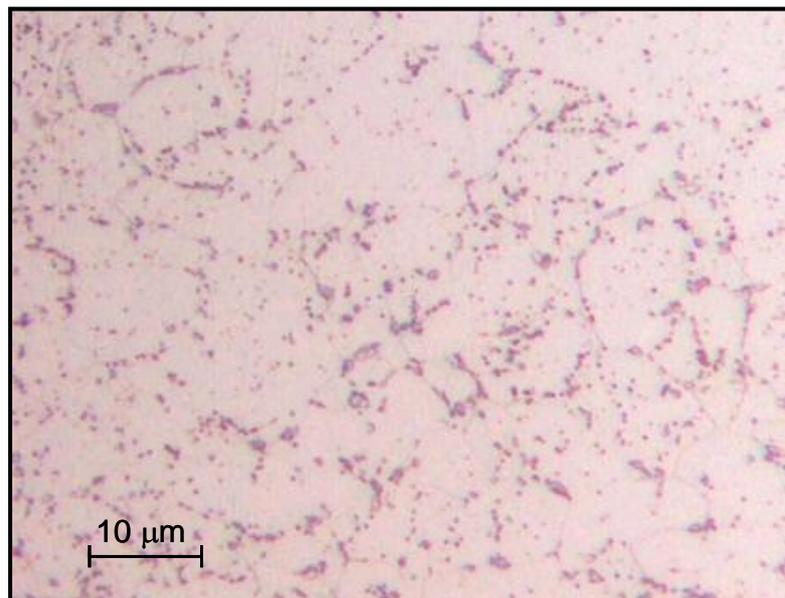


Figure 11. Microstructure of the metal near the corroded area of spout #5

Some shallow depressions were also found along the bottom of some cooling water passages. The patterns, however, were characteristic of those caused by idle time oxygen pitting. This type of corrosion is generally superficial and is unlikely to be the contributing factor in the failure of spout #5.

Although some wastage was also observed along the bottom of the trough of spout #3, the extent was insignificant and was expected of a smelt spout that has been in service for 10 months. The internal surface was covered with only a thin and dense layer of oxides (Figure 12), as opposed to thick layers of deposits and oxides observed on the internal surface of

spout #5. This implies that spout #3 did not experience significant overheating, despite the fact that it had its cooling water flow cut off just before the ESP and would have been exposed to smelt flow for some time while the ESP was in effect.

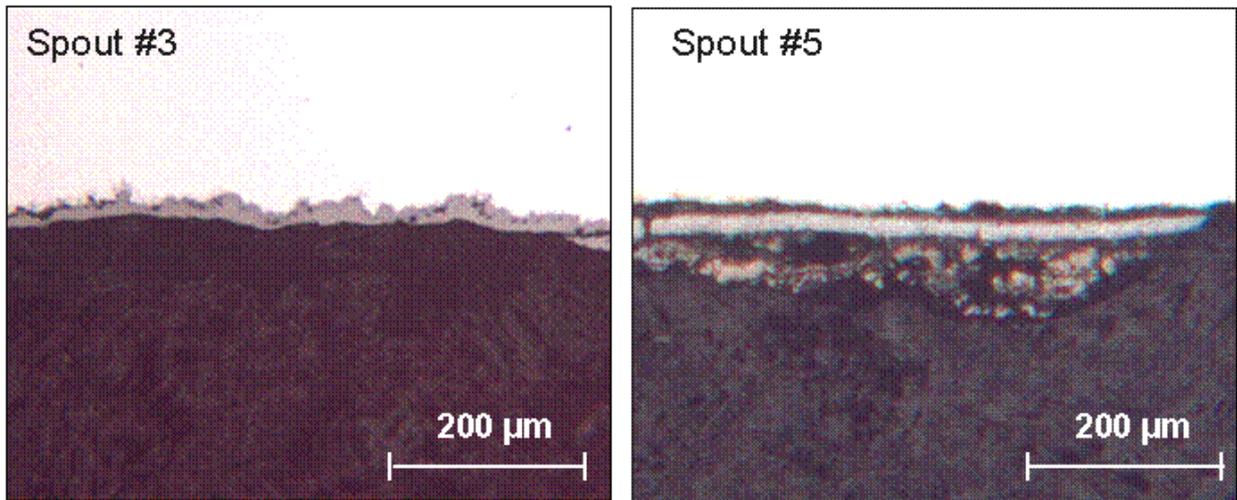


Figure 12. Internal surface of Spout #3 (left) and Spout #5 (right)

INTERPRETATION OF RESULTS

Causes of Failure

It was apparent from the investigation that the failure of spout #5 was caused by excessive overheating of the spout metal surface and the subsequent aggressive attack by flowing smelt, and that the loss of cooling water to that spout was the main reason for the overheating. Some of the overheating occurred during the black out period as indicated by the low cooling water temperature from spout #5 after the black out. Overheating also occurred after the boiler was restarted and was on liquor for nearly 2 days before the ESP. It is unclear, however, which period was more damaging to the spout: during the black out or during the startup after the ESP.

Spout #3 operated during the ESP without any cooling water flow and did not experience significant overheating. This, along with the fact that the duration in which all smelt spouts in the #2RB were exposed to molten smelt following the boiler trip (due to power black out) was about the same as that following the ESP, suggests that the main damage to spout #5 did not occur during the boiler trip. However, the cooling water temperature trend data in Figures 4 and 5 definitely shows that spout #5 was at a much lower cooling water temperature than

other spouts and the collection tank. While it is not known what caused the low cooling water temperature of spout #5 during the power blackout, the data suggests that spout #5 did experience enough damage that it impaired the cooling water flow through that spout.

The suggested “defect” found in the weld of spout #5 (Figure 8) may play a role in its failure. It is possible that the sudden temperature change in the boiler due to power blackout may have caused the weld to fail, resulting in a small crack through which cooling water leaks out to the furnace. This, in turn, reduces the cooling water flow to the spout, causing it to overheat, and hence, to corrode. As the crack becomes larger, more water leaks out and less passes through the spout, aggravating the problem further.

The leaked water begins to accumulate in the furnace near the spout when there is more of it there than it can vaporize. It forms a pool of concentrated smelt solution (saturated green liquor) which pours out the boiler through the spout. This concentrated smelt solution can also be detrimental to the spout (carbon steel) for two main reasons: i) it contains corrosive $\text{Na}_2\text{S}_2\text{O}_3$ as a result of partial oxidation of Na_2S in the solution, and ii) it cannot vaporize easily due to boiling point rise and thus can remain as liquid at a temperature as high as 180°C [3]. Some smelt solution entered the interior of spout #5 where it re-crystallized to form deposits, leading eventually to complete clogging of cooling water passes, as shown in Figure 13.



Figure 13. Crossed section of spout #5, showing smelt deposits locking cooling water passage.

The clogging, in turn, impaired the cooling water flow, forcing it to partially by-pass the spout and flow directly to the outlet tube. This could be one of the reasons for the lower cooling water temperature of spout #5 compared to other spouts. There are two other possible reasons for the low cooling water temperature. One is the lower flow rate and temperature of molten smelt flowing over the spout because of the cooling effect of leaked water. The other is that due to the reduced flow rate of the cooling water from spout #5, the water level in the pipe line was low, and so, the thermoprobe might not be able to “touch” the water to provide proper temperature readings (Figure 14).

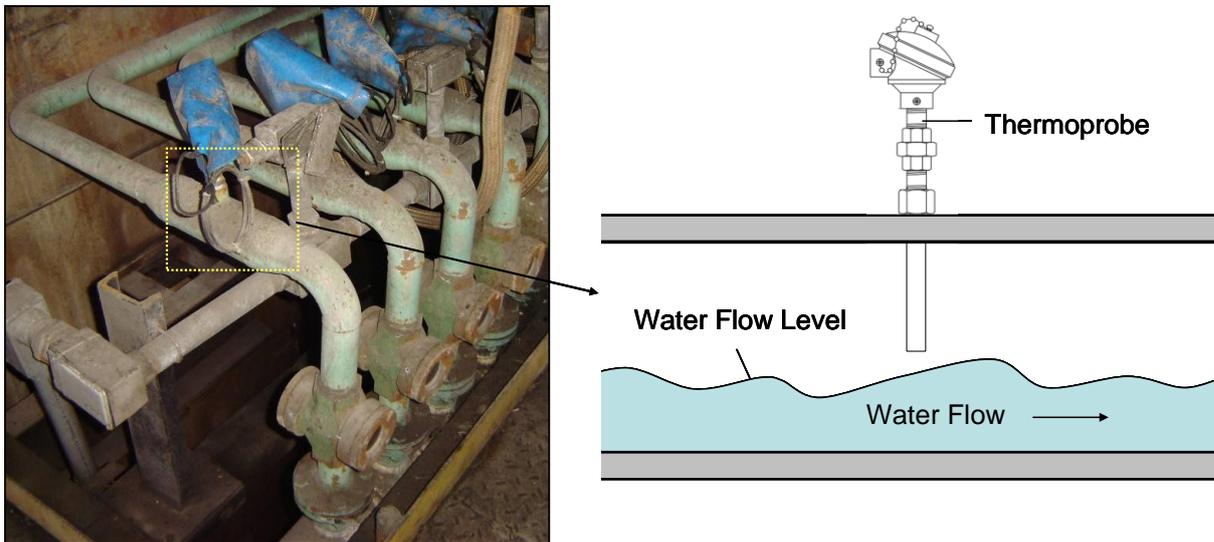


Figure 14. Thermoprobe and suspected water level in the cooling water pipe line during the time of reduced flow rate.

If the low cooling water temperature in spout #5 was real (not a result of faulty temperature reading), it may also contribute to the severe corrosion at the front lip of spout #5 (Figure 2). As shown in Figures 4 and 5, it varied between 40°C and 50°C, which is well below the minimum temperature of 60°C that a smelt spout must be kept above in order to avoid dew point corrosion caused by condensation of water vapour from the dissolving tank [3].

In any event, what really important here is the fact that the cooling water flow to spout #5 remained impaired when the boiler was restarted. Overheating of spout #5 would occur, resulting in massive corrosion damage to the spout.

Impact on Smelt-Water Explosion

The constant drainage of the leaked water from the furnace through the spout prevented accumulation of a large amount of water inside furnace. The smelt around the spout opening

would solidify and serve as a barrier, isolating the water and preventing it to be in direct contact with molten smelt. Furthermore, since all six spouts are located underneath a large nose arch (Figure 1) and since the boiler had been down due to power blackout, the likelihood of falling slag and deposits forcing molten smelt to be in contact with water is small. All of this may help explain why no smelt-water explosion occurred in this incident.

PREVENTIVE MEASURES

Based on the investigation results, preventive measures have been devised and implemented in order to prevent a recurrence of the problem. As summarized in Table 1, the main strategy is to provide effective means for more closely monitoring the cooling water system and help operators to inspect water flow at smelt spout floor more readily. Continuous operator training for handling emergency situations is also one of the important preventive measures. As the last option, water from the mill firefighting system was connected to the upper tank in order to keep the cooling water system operative during a black out and failure of the others emergency systems.

Table 1. Main Countermeasures implemented after the Incident

Actions	Before the Incident	After the Incident
Inspection of new smelt spouts	<ul style="list-style-type: none"> - Keep complete records of each set of spouts (design and fabrication data). - Perform dye-penetrant tests before installation. - Perform a hydrostatic test on each spout after installation to ensure no leakage 	<ul style="list-style-type: none"> - Same as before the incident, with improved testing and commissioning procedures - Pay more attention to spout welds - Check connections between spouts and their cooling water lines to ensure no mislabeling
Cooling water flow measurement	No	- A flowmeter installed on each spout line
Head tank level indicator	No	- Installed
Emergency power and water supplies to the cooling system	<ul style="list-style-type: none"> - Grid and diesel generators - No emergency water supply 	<ul style="list-style-type: none"> - Grid and diesel generators - Water from firefighting system
Cooling water inspection at the spout floor elevation	- Through on-line glass ports (these ports were in an obscure location, not easily accessible)	- An acrylic box was installed. Inspection ports are now easy to access
Operator training	Yes	- Retrained
Operating procedures	Yes	- Revised

CONCLUSIONS

An extensive investigation was conducted to determine the causes of severe corrosion that led to in-service failure of spout #5, one of the six smelt spouts in the #2 recovery boiler at Cenibra. The results show that the failure was caused by insufficient cooling water flow to spout #5, causing it to overheat and to severely corrode. The insufficient cooling water flow was, in turn, caused by a sequence of events that occurred after a black out of an electrical energy system at the mill.

Due to the loss of operating data during the power black out, however, the investigation could not positively determine what actually caused the cooling water flow to decrease in the first place. The theory of a suspected weld defect that may have caused the spout to fail as a result of large temperature change during the boiler trip is not unreasonable, considering the fact that this is the first time the problem occurred in 32 years of the mill's operation history and that spout #5 was the first failure of some 250 smelt spouts that have been used to date.

The experience has led to the revision of existing emergency procedures and the development and placement of operating and maintenance procedures that ensure adequate cooling water flow to smelt spouts to prevent future failures.

ACKNOWLEDGEMENTS

The investigation could have not been possible without the concerted effort and cooperation of many people at Cenibra: recovery boiler operators, DCS operators, process engineers and mill management. The authors wish also to acknowledge NALCO Company for its great assistance with metallurgical and chemical analyses and Dr. Thomas M. Grace for his valuable comments on the problem.

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3- CONCLUSÕES GERAIS

A falha da bica de *smelt* #5 ocorreu em função de refrigeração deficiente, o que ocasionou o superaquecimento do metal. Segundo Nalco (2008a) o superaquecimento do metal atingiu temperatura superior a 540 °C, o que propiciou o início de um acelerado processo de erosão e corrosão pelo fluxo de *smelt* fundido.

A refrigeração deficiente originou-se de uma seqüência de eventos deflagrada após uma ocorrência de completa falta de energia elétrica na unidade industrial, seguida da falha de sistemas de segurança auxiliares.

Devido ao avançado estado de degradação do material e à perda dos dados operacionais durante o período de falta de energia, não foi possível determinar com total certeza a seqüência inicial do mecanismo de falha, ou seja, o que determinou a redução do fluxo de água de resfriamento. Uma falha pré-existente na solda de conexão da linha de água de refrigeração, agravada pelos eventos durante o período de falta de energia, é a hipótese mais provável para explicar o início da falha.

Apesar da gravidade da ocorrência e da constatação visual do contato água-*smelt* não ocorreram explosões.

O desenvolvimento do trabalho propiciou a implementação de novos instrumentos e equipamentos, bem como a revisão e elaboração de novos procedimentos de operação e manutenção que tem por objetivo garantir a adequada refrigeração das bicas de *smelt*, especialmente em situações de emergência.

Os resultados e conclusões aqui apresentados são uma fonte de referência para quaisquer caldeiras de recuperação química que possuam sistema de refrigeração pressurizado para bicas de *smelt*.

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APÊNDICE - SLIDES

Smelt Spout Corrosion in a Kraft Pulp Mill

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Universidade Federal de Viçosa – UFV , Viçosa, MG, Brazil
June, 14th, 2010



Presentation Outline

- **Introduction**
- **Objectives**
- **Relevance**
- **Smelt Spout Failure Event**
- **Methodology**
- **Results**
- **Conclusions**

Introduction

- **Brazilian Pulp and Paper Industry**
- **Cenibra Pulp Mill**
- **Kraft Process introduction**

Brazilian Pulp and Paper Industry

- 4th world pulp producer – 13,46 MM Adt – 2009
- “State of the Art” Mills – Low costs and huge productions, mainly of *Eucalyptus* Kraft Pulp
- Pulp production is growing, even during economical crisis – 6% in 2009
- Positive contribution to Trade of Balance – 3,643 Billion US\$ in 2008. A 30,5% increase over 2007 trade balance
- Intensive use of man labor – Estimated direct and indirect jobs near 614.000.

BRACELPA, 2010a/b

Cenibra Mill

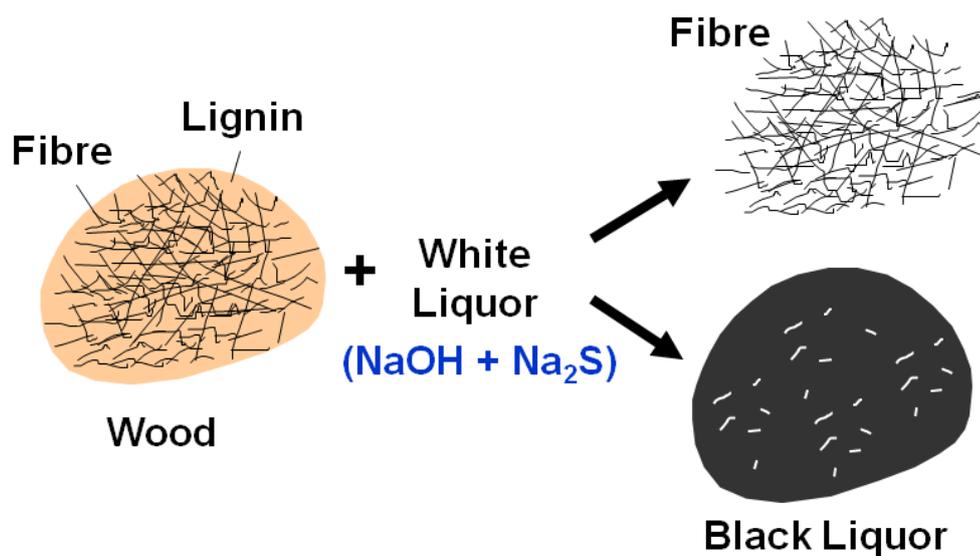
- Owned by JBP and managed by Oji Paper, Itochu, JBIC and others
- Started up in 1976, producing 0.26 million adt/year of eucalyptus kraft bleached pulp
- Currently two production lines, producing 1.2 million adt/year
 - Plans to reach 2 to 2.3 million adt/year with the 3rd production line

Kraft Pulping Process

- Most important chemical pulping process
- Global kraft pulp production: 130 million metric tons/year (67% of total)
- Kraft Pulping chemicals
 - Aqueous solution of NaOH and Na_2S
 - As opposed to only NaOH in the soda pulping process
- Rapid growth only after the development of the Tomlinson recovery boiler in the 1930's

TRAN, 2010

Kraft Pulping Process

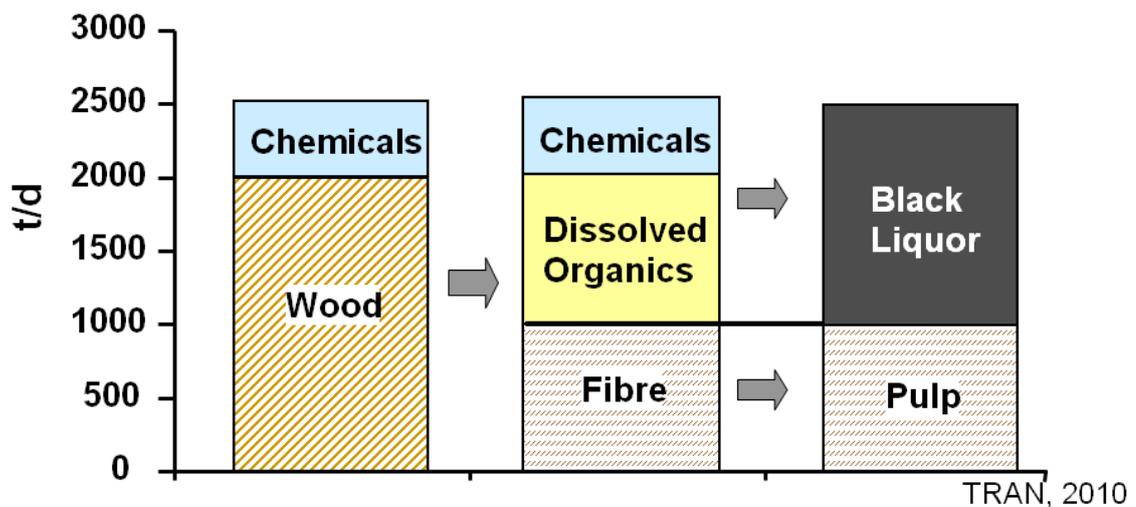


TRAN, 2010

A 1.000 t/d Kraft Pulp Mill

produces 1.500 t/d BL d.s.

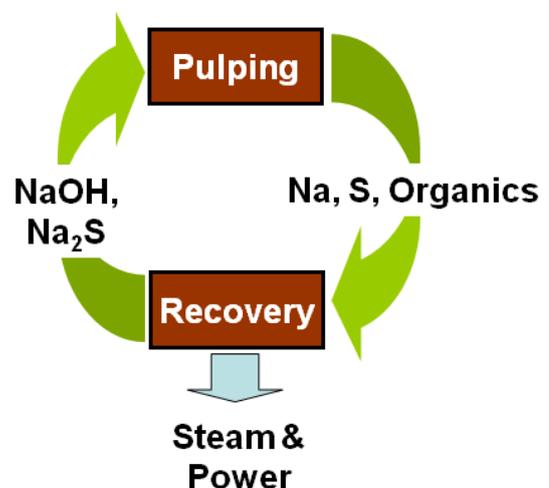
8.000 ~ 10.000 t/d weak black liquor



Kraft Recovery Process

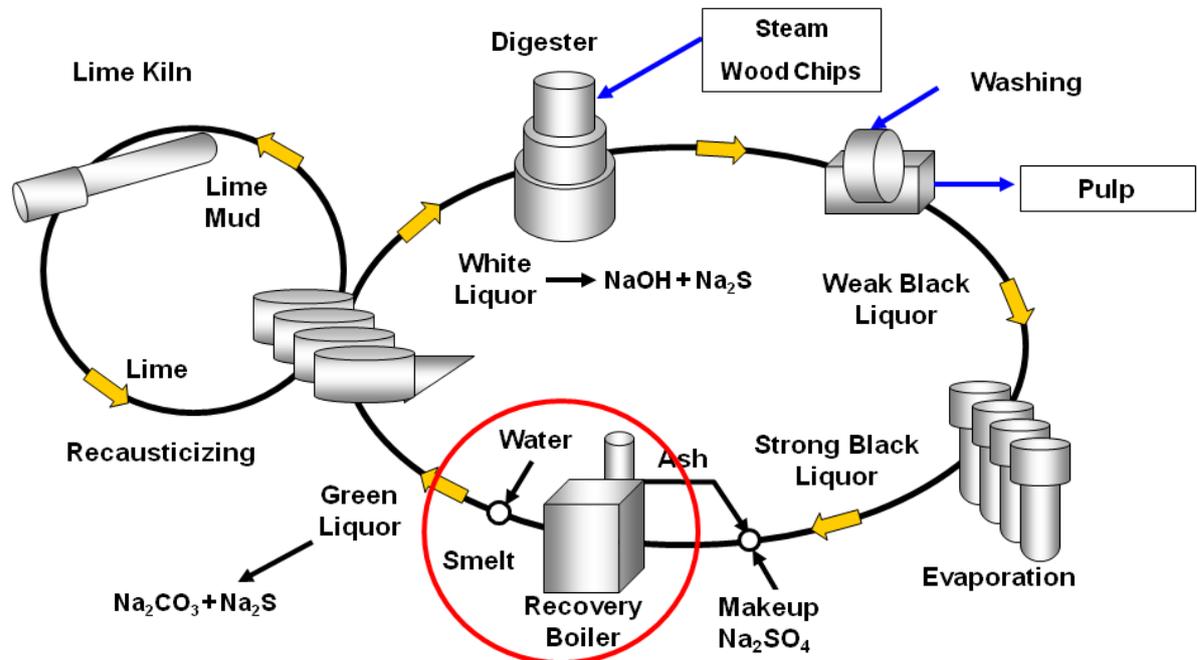
A Closed Cycle Process with 3 Main Functions:

- Eliminate the “waste” material (black liquor)
- Recover pulping chemicals (NaOH and Na₂S)
- Generate steam and power

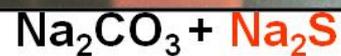
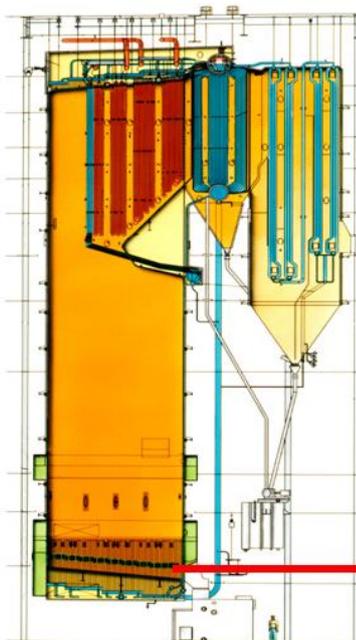


TRAN, 2010

Kraft Recovery Process



Smelt flow through spout



800°C (1470°F) TRAN, 2010

Objectives

Main Objectives

- **Identify the failure mode of a in service Smelt Spout in a Recovery Boiler based on a real upset event**
- **Establish recommendations and preventive measures in order to avoid new occurrences**

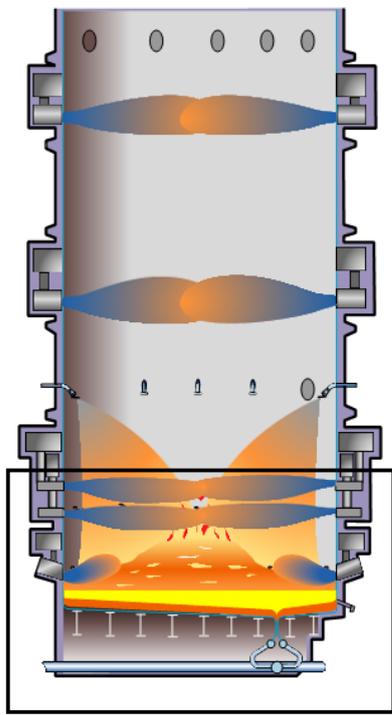
Relevance

- Smelt Spout Corrosion in a Kraft Pulp Mill
- Recovery Boiler Explosions – Brief review

Smelt Spout Corrosion in a Kraft Pulp Mill

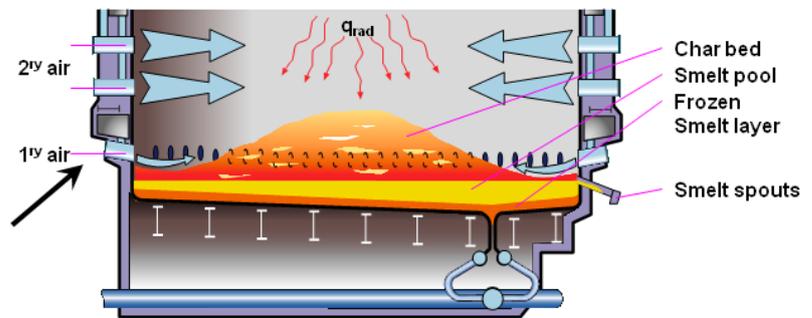
- Based on a real upset event on a recovery boiler
- Rare event → need of understanding
- Smelt-water contact lead to an explosion
 - Safety issues → Share experience with other mills and manufacturers
- Lack of literature
- Scientific and practical approach

RB Furnace and BL Composition



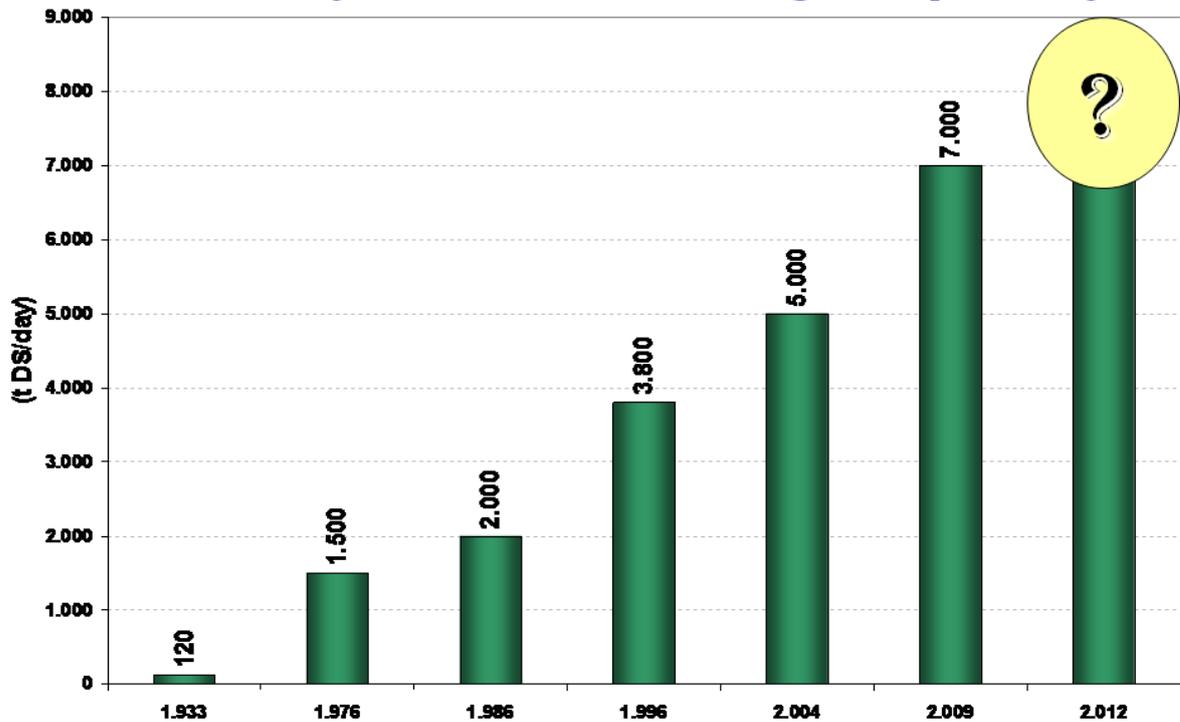
BL Composition	Typical	Range
Solids content, %	72	65 – 85
HHV, MJ/kg	13.9	12.5 – 15.5
C, wt% d.s.	33.9	30 – 40
H	3.4	3.2 – 4.0
O	35.8	34 – 38
Na	19.6	17 – 22
S	4.6	3.6 – 5.6
K	2.0	1 – 3
Cl	0.5	0.1 – 4

TRAN, 2010



TACLA, 2002

Recovery Boilers Firing Capacity



Adapted from METSO POWER, 2009

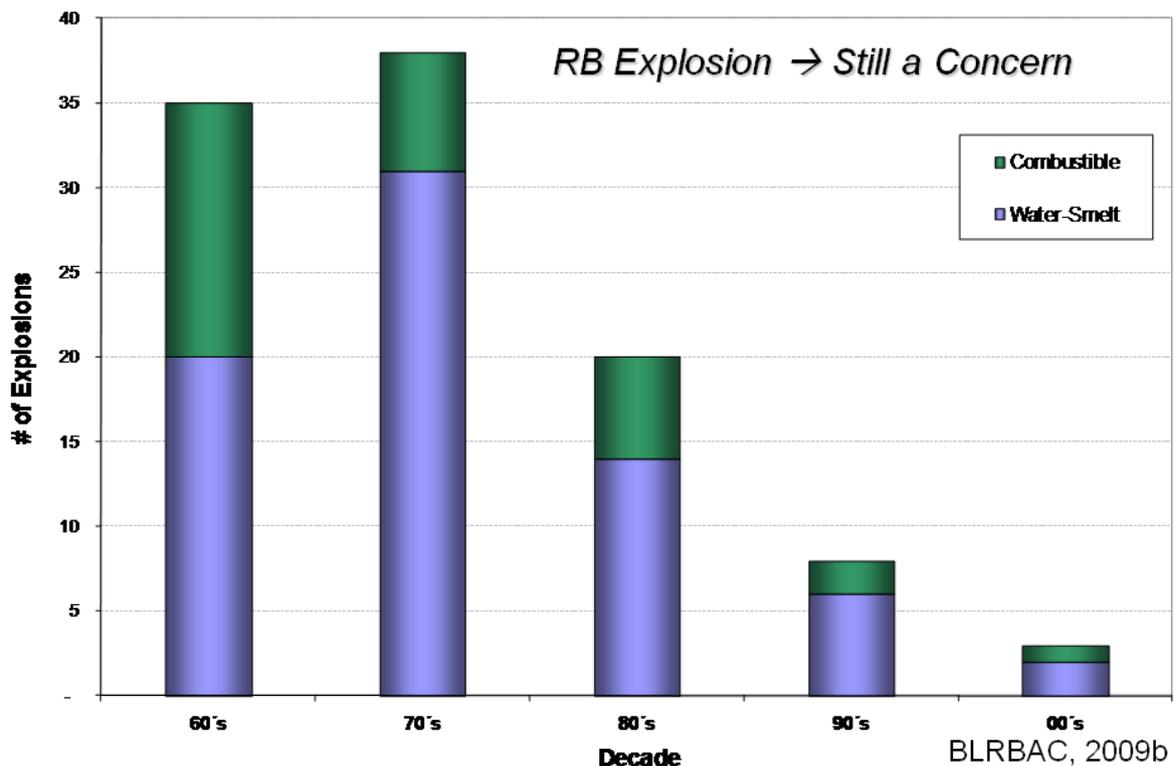
Water-Smelt Contact Potential Catastrophe

- A major recovery boiler explosion is a catastrophic event at a kraft pulp mill
- Risk of injury or death
 - Fatalities in $\approx 5\%$ of explosions
 - Serious injuries in another 5%
- Cost of repair
 - Depends on explosion magnitude
 - ? US\$ Millions
- Loss of production and Profit
 - Mill stopped for days or months
 - Losses of US\$ 1.000.000 a day, based on a daily production of 3.000 adt. (Estimated. Basis 2010)



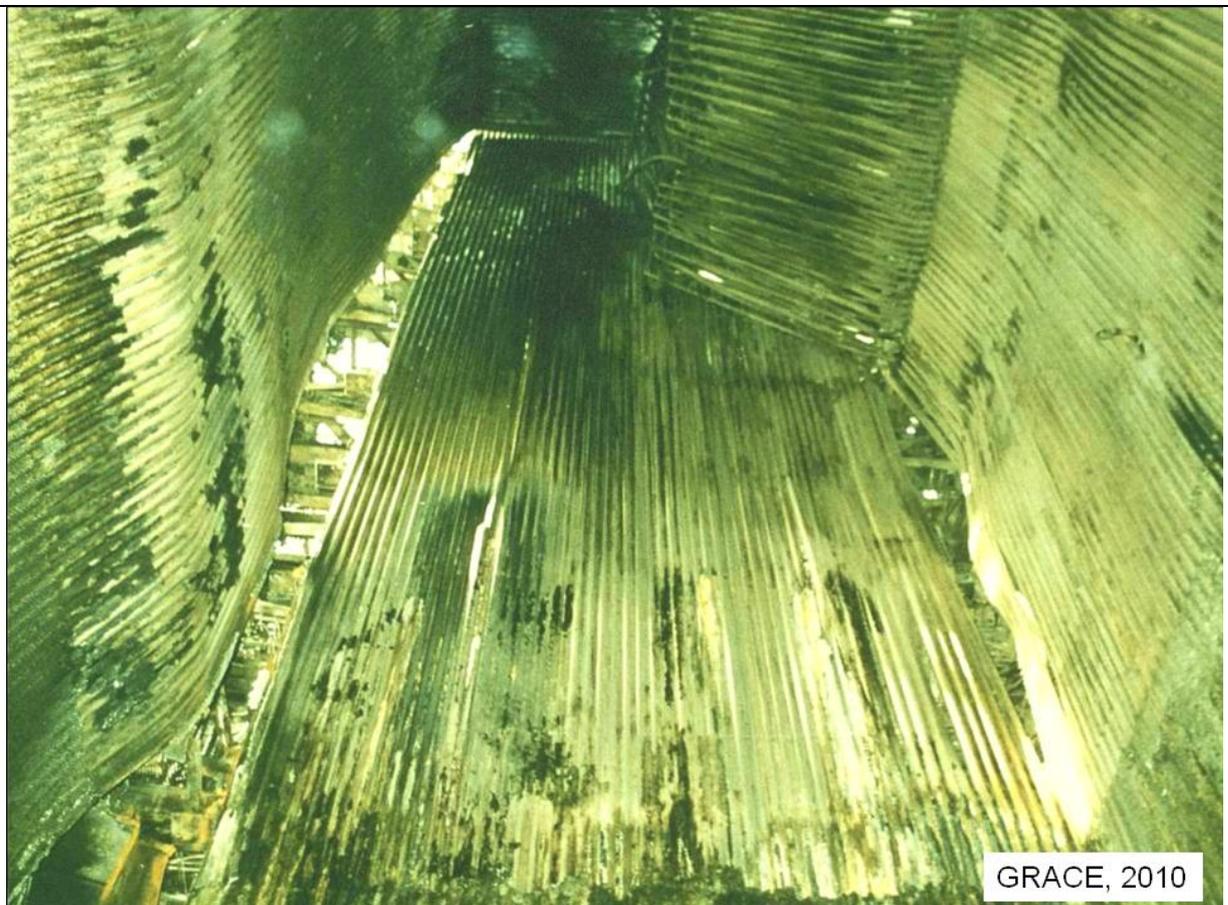
GRACE, 2010

Recovery Boiler Explosions - USA



RB Explosions Statistics – USA

- **Smelt-Water Contact ~ 70%**
 - Due to extremely rapid steam generation
 - Mainly due pressure parts failure
 - Five reported explosions involving smelt spout leaks. (GRACE, 2010)
 - Non-combustible in nature
- **Combustible Gas Explosions ~ 30%**
 - Accumulation of air-fuel mixture within the explosive concentration range
 - Ignition source



GRACE, 2010

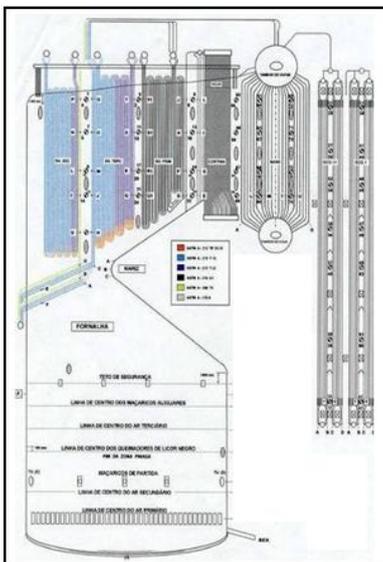


GRACE, 2010

Smelt Spout Failure Event

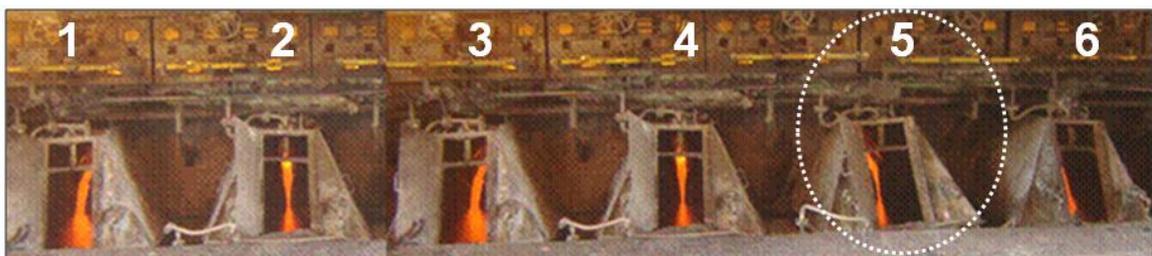
Recovery and Utilities

- One of three recovery boilers
 - RB#1 (1976): 1800 tds/day @ 72% (stand by)
 - RB#2 (1992): 2700 tds/day @ 72%
 - RB#3 (2006): 3500 (4200) tds/day @ 72 (80)% (3rd line boiler)
- Supplied by CBC, a MHI branch in Brazil.
- Never had a real ESP since the mill start up in 1976
 - First ESP performed in February 2008 due to RB#2 smelt spout failure
- Mill Power supply
 - Two Turbo-generators – 100 MW + Grid – 9,5 MW

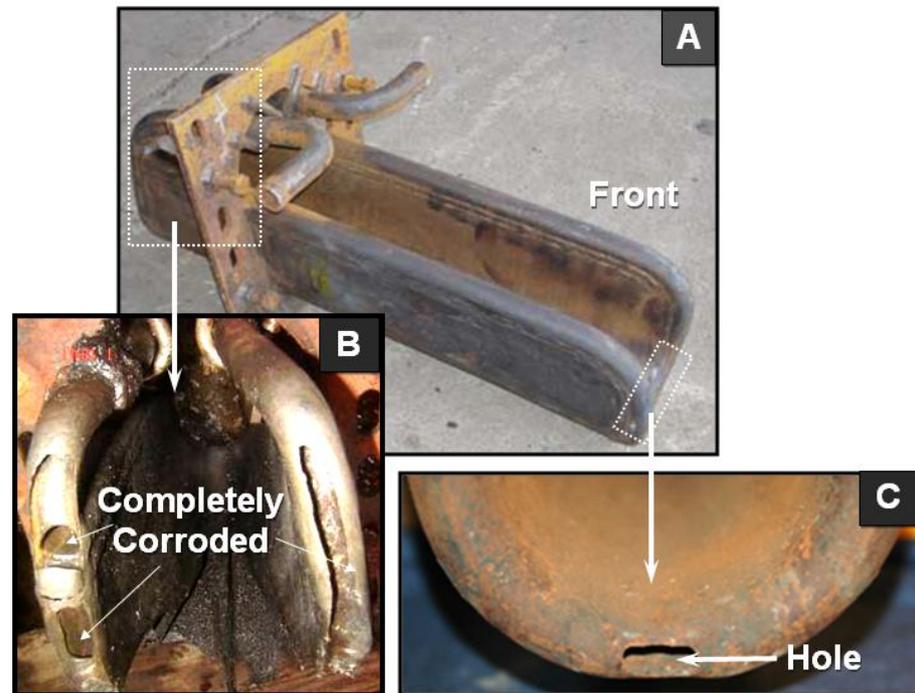


#2 Recovery Boiler Smelt Spouts

Corroded Spout



Corrosion in Spout #5



Methodology

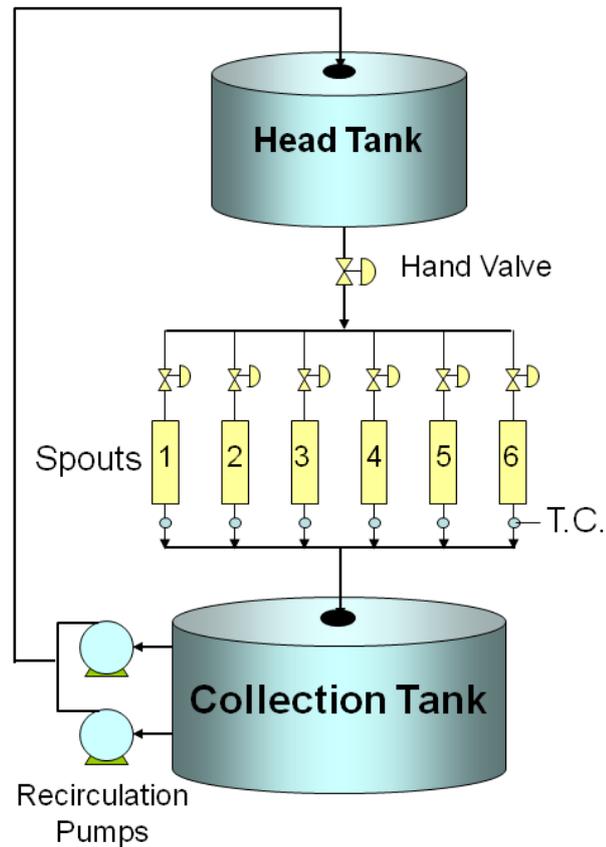
Methodology

- Smelt Spout Information
- Events leading to the problem
- RB behaviour – trends
- Non-destructive tests
- Metallurgical analysis of corroded and non-corroded spouts (by Nalco, USA)

Smelt Spout Information

- All smelt spouts are replaced every year
- Carbon steel, no weld overlay, inserted into the boiler
- Pressurized water cooling system
- Water temperature is controlled at 70 °C
- These specific set of spouts were in service for 10 months and were supplied by the boiler manufacturer

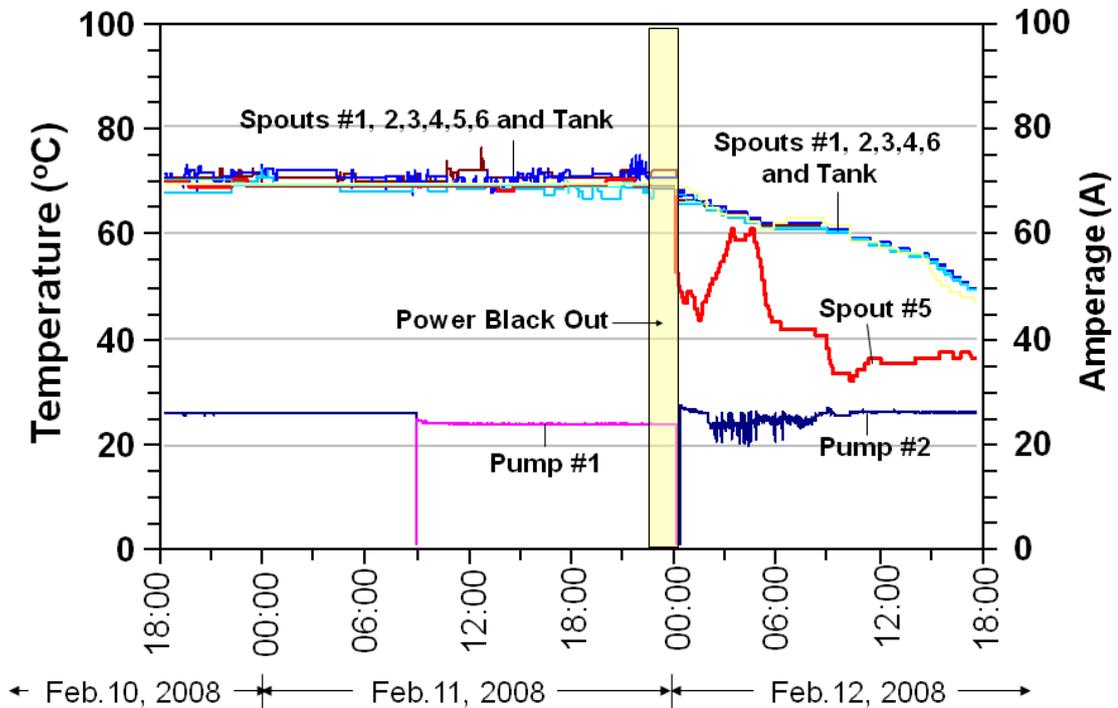
Smelt Spout Cooling System



February 11, 2008 9:02 PM - Black Out

- Short circuit in the TG#1
 - Mill had no power for 71 min.
 - Most emergency systems failed
- #2RB tripped, but smelt continued to flow for some time after the boiler trip
- Both recirculation pumps stopped shutting off the return cooling water flow to the head tank
- The boiler was down for 5 days while TG#1 was repaired

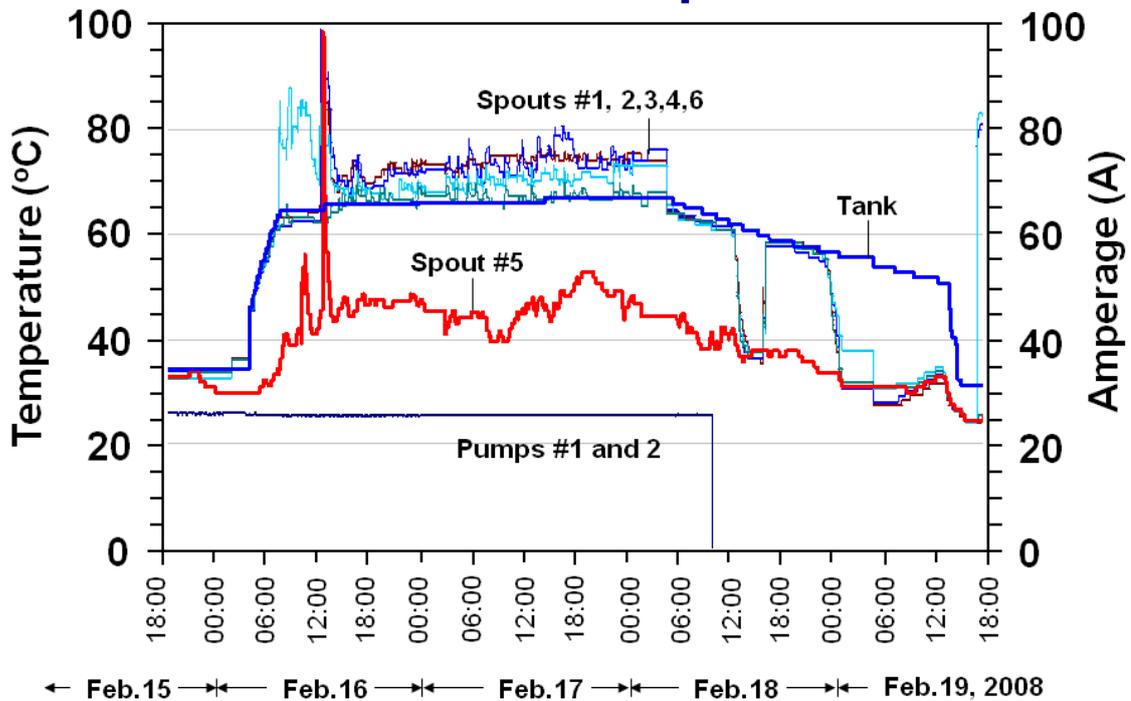
Cooling Water Temperature Profiles Before and After Power Black Out



February 16, 2008 3:10 AM - Startup

- Began burning liquor at 9:40 AM
- Noted unusually low and erratic cooling water temperature on spout #5
 - Faulty thermocouple was suspected
 - Thermocouple was checked after ESP, but found normal; no replacement was made.

Cooling Water Temperature Profiles After Boiler Start up and ESP

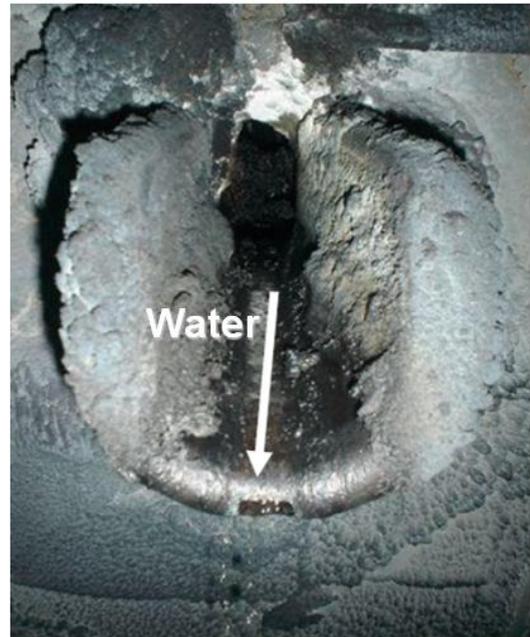


February 18, 2008 3:29 AM - ESP

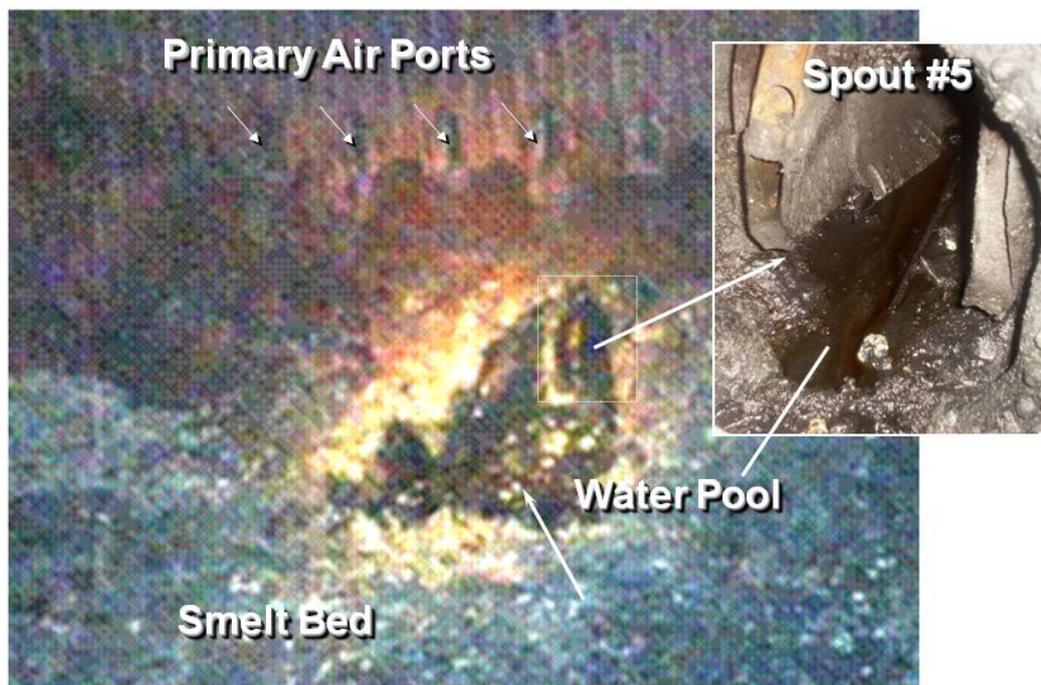
- Small explosions were found inside the furnace, and smelt was dark and stopped flowing.
- Operator started cleaning the spout with a steel lance, he noted suddenly that
 - Water was flowing down the spout trough
 - Bed was dark near the spout area
- Operator shut off the cooling water valve to stop the water flow to that spout
 - Water kept flowing out from the furnace even after the valve had been closed
 - Water was sizzling and rumbling inside the furnace and it appeared to come from a primary air port tube nearby
- Operator immediately called for an ESP

February 19, 2008 - Damage Inspection

- Water was still running down the trough of spout #5 from within the furnace as well as from a hole at the spout lip about 12 hours after the ESP



February 19, 2008 - Damage Inspection

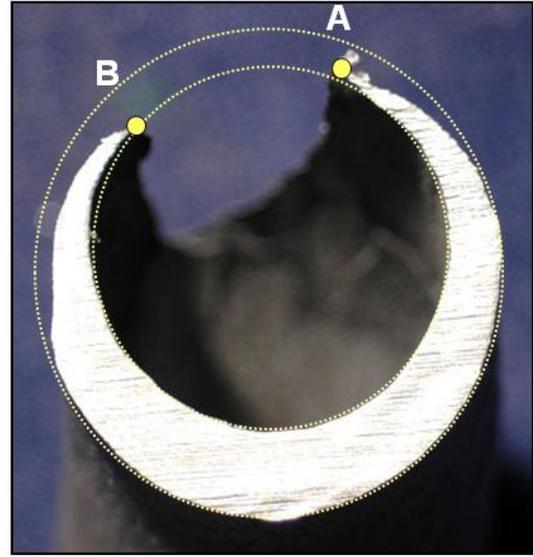
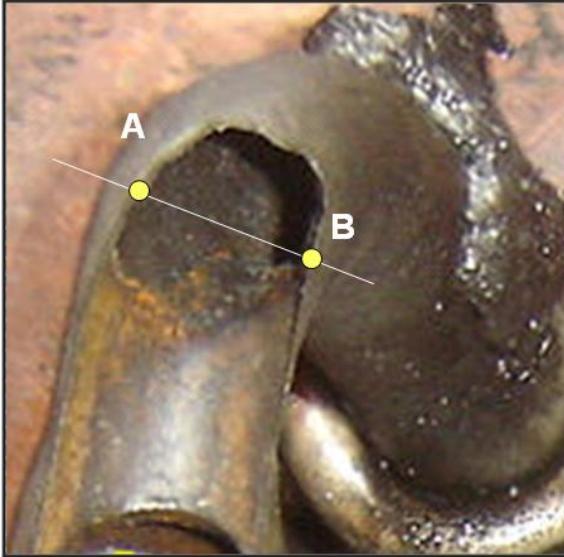




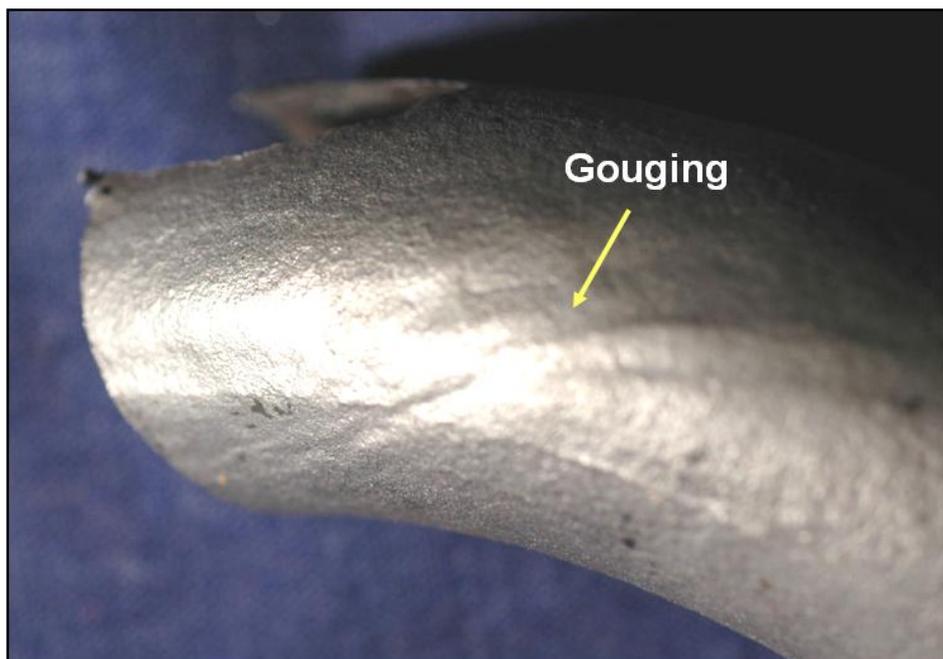
Investigation Results

- Spouts #1, 2, 3, 4 and 6 were in good shape
 - No sign of thinning or cracking
 - No internal deposits
- Only Spout #5 was severely damaged
 - A “defect” was found in the weld joint between the cooling water tube and the spout
- Metallurgical analysis of damaged area suggests overheating
- Some water passages were clogged with smelt

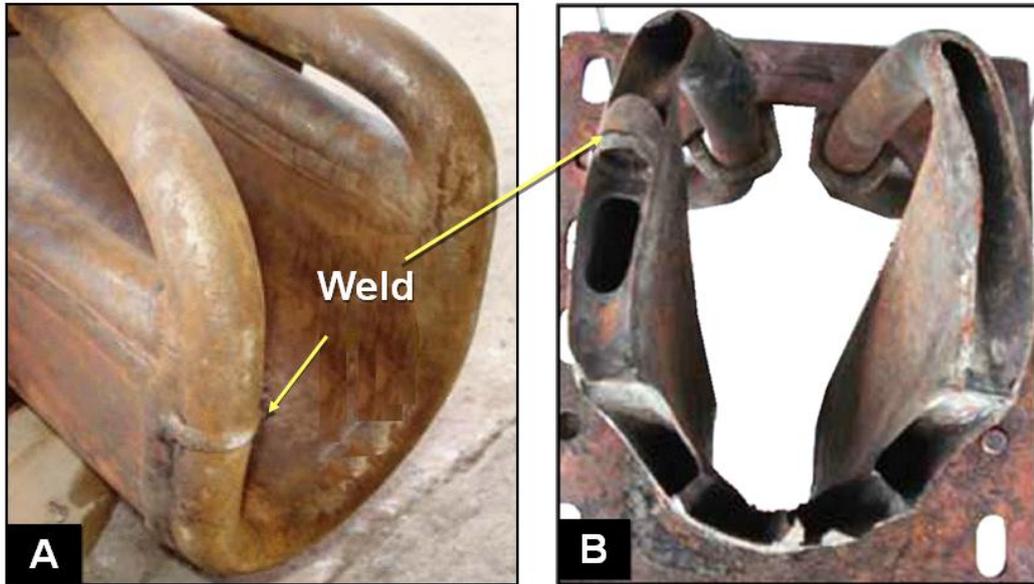
Wall Thickness



Flowing Smelt Gouging

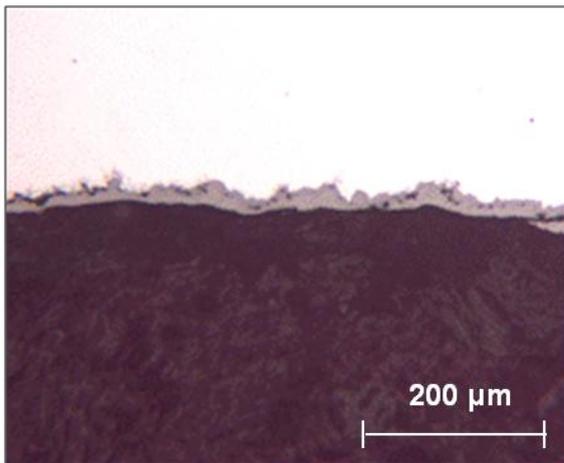


Weld Defect?

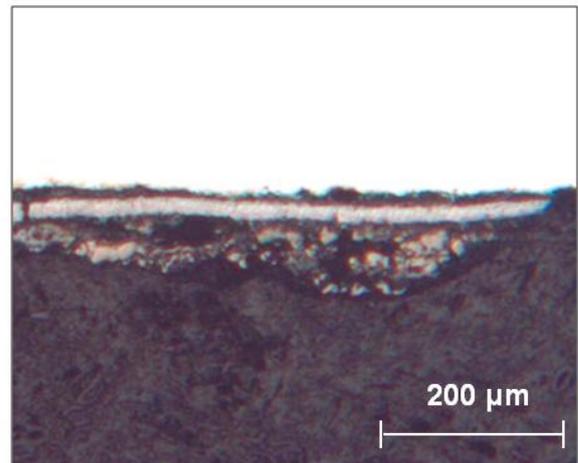


Metallurgical Analysis

Spout #3

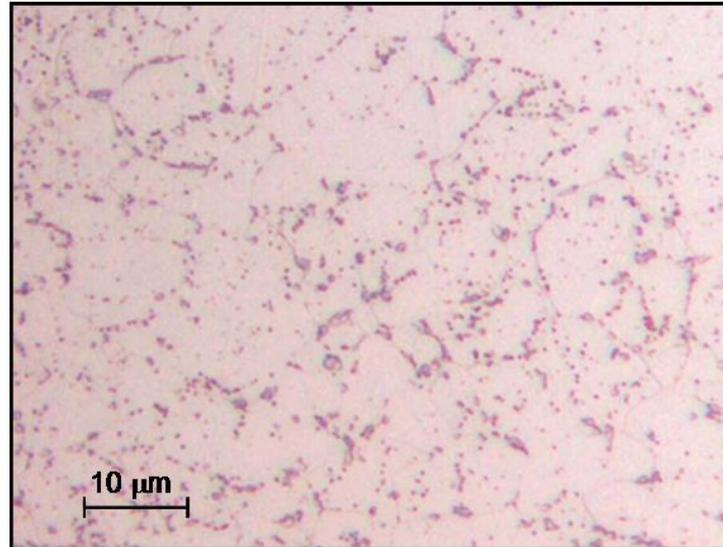


Spout #5



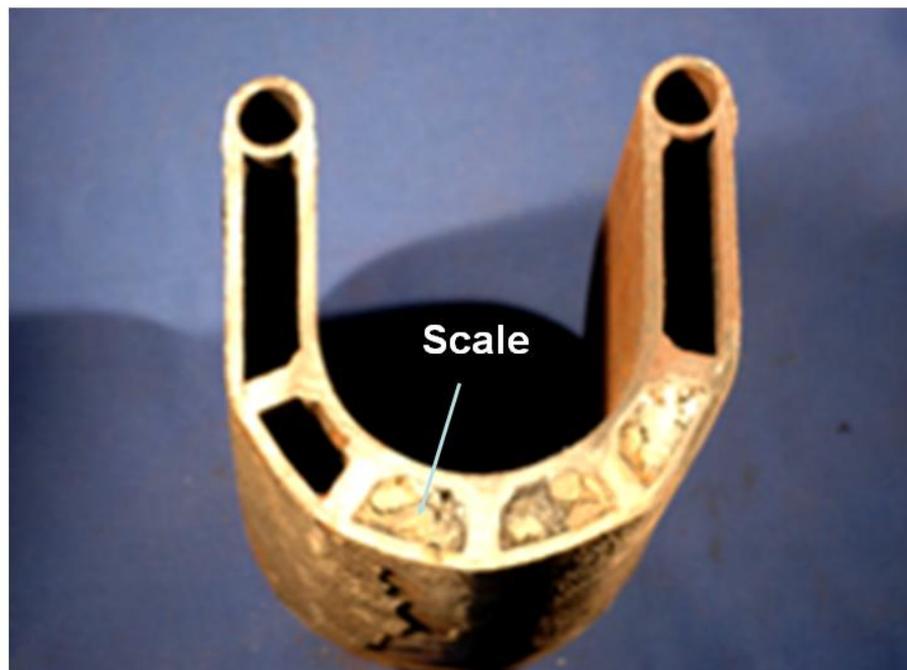
They have ran for the same time at the same condition.

Microstructure of the metal near the corroded area of spout #5



Microstructure consisting of spheroidized carbides in a ferrite matrix → Typical of overheating.

Smelt Deposits in Water Passages



Results

- Identification of the cause(s)
- Devising recommendations and preventive measures

Speculated Causes

- The weld defect in spout #5 may have failed during the power blackout and boiler trip.
- Problem was further worsened by reduced cooling water flow to spouts
- Initial Spout failure resulted in
 - more cooling water leaking to the furnace
 - less water circulating in the spout causing it to overheat and to corrode (high temperature corrosion due molten smelt)
 - larger corroded (damaged) area
 - more cooling water leaking to the furnace

Countermeasures

Actions	Before the Incident	After the Incident
Inspection of new smelt spouts	<ul style="list-style-type: none"> - Keep complete records of each set of spouts (design and fabrication data). - Perform dye-penetrant tests before installation. - Perform a hydrostatic test on each spout after installation to ensure no leakage 	<ul style="list-style-type: none"> - Same as before the incident, with improved testing and commissioning procedures - Pay more attention to spout welds - Check connections between spouts and their cooling water lines to ensure no mislabeling
Cooling water flow measurement	No	A flowmeter installed on each spout line
Head tank level indicator	No	Installed
Emergency power and water supplies to the cooling system	<ul style="list-style-type: none"> - Grid and diesel generators - No emergency water supply 	<ul style="list-style-type: none"> - Grid and diesel generators - Water from firefighting system
Cooling water inspection at the spout floor elevation	<ul style="list-style-type: none"> - Through on-line glass ports (these ports were in an obscure location, not easily accessible) 	<ul style="list-style-type: none"> - An acrylic box was installed. Inspection ports are now easy to access
Operator training	Yes	Retrained
Operating procedures	Yes	Revised

Why no explosion occurred despite smelt-water contact?

- Water leakage started small and grew larger over a long period of time
- Bed temperature was low during start up
- Solidified smelt around the water pool may have served as a barrier, preventing water to be in direct contact with molten smelt

Conclusions

Conclusions

- **Spout #5 failure was caused by insufficient cooling water flow, causing it to overheat and to corrode**
- **Diagnosis was validated by Metallurgical Analysis of corroded and non-corroded spouts**
- **Insufficient cooling water flow was caused by a sequence of events that occurred after a black out of an electrical energy system at the mill**
 - **It was impossible to positively determine the cause of reduced cooling water flow, due to the operating data loss during the black out**

Conclusions

- **The suspected weld defect in spout #5 may have caused it to fail as a result of large temperature change due to blackout/boiler trip**
 - **Not an unreasonable explanation considering the fact that this is the only smelt spout failure that occurred in 32 years of the mill's operation history**

Conclusions

- **The experience has led to the revision of existing emergency procedures and the development and placement of operating and maintenance procedures**
 - **The main focus → Ensure adequate cooling water flow to smelt spouts under any condition to prevent future failures**

