**Executive Summary**

Many mills cover bare floor tubes in recovery boilers with decanting floors with some material before start-up. There are, however, significant differences in materials used. In North America, the most commonly used material is lime, while in South America tubes are covered usually with sodium sulphate. Some mills have abandoned the usage of any protective material.

In case the floor needs to be cleaned totally for inspections, the selection of protective material can have a major impact on the time needed for floor cleaning. These implications are discussed and recommendations concerning most suitable materials are made.

With "process-like material" for floor protection, the time needed for cooling, washing and cleaning can be minimized by smelt extraction and enhanced floor washing. Optimizing both the floor protection methods and materials and the cooling, washing and cleaning practices can yield:

- significant savings in mill outage time and corresponding increases in mill production and
- reduced risk of mechanical damage due to mechanical cleaning or hydro blasting during floor cleaning.
Introduction

In some early recovery boiler designs, with flat floors and start-up burners located close to the floor, overheating the floor tubes with start-up burners may have been an issue.

In modern recovery boilers with decanting floors and start-up burners located several meters above the floor, there is no risk that the floor tubes would be overheated. However, floor tubes may be exposed to chemical stresses, and if the stresses are large enough, general corrosion or cracking may result.

Corrosion in floor tubes

Recovery boiler furnaces were initially made of carbon steel tubes, but corrosion problems in the lower furnace walls encountered in the 1960s led to the replacement of carbon steel tubes by compound tubes with 304L cladding in furnace walls, floors and bends connected to floor tubes.

As far as floor tubes made of carbon steel are concerned, there are no major corrosion issues demanding extra protection. Some corrosion can occur due to sulphidation, and also some galvanic corrosion is known to take place near the welds with the compound tubes, but usually the corrosion rates are relatively low, 0.1 – 0.2 mm/a.

However, cracking in 304L floor tubes and bends has been a serious issue. The causes for cracking have been studied thoroughly, and the main conclusions from these studies are the following [1]:

- It appears that cracking (of 304L composite tubes) is most likely to occur during water washes, dry-out fires, or other operating procedures which allow hydrated smelt to come in contact with the surface of the composite tubes at temperatures in the range of about 150-200°C (300-400°F)
- Cracking of 304L composite tubes would therefore be minimized by following an operating procedure during shutdowns in which the bed is burned out completely and water is not allowed to reach the floor until the floor tube surface temperature is below 150°C (300°F). The risk of cracking is greatly increased during a dry-out fire or a start-up if the floor is heated above 150°C (300°F) while in contact with hydrated smelt or concentrated wash water.

When the first cases of severe cracking were discovered in the late 1980s and the early 1990s, some immediate actions were needed. An obvious step was laying some protective material on the floor tubes prior to start-ups. Lime milk and lime mud were readily available, so they were the materials used first. However, boiler manufacturers kept looking for alternative materials. Sodium sulphate was a natural choice, as it was already used routinely in recovery boilers as a make-up chemical. Covering floor tubes with sodium sulphate soon became a standard practice used during first start-ups. Sodium sulphate can be placed on floor in bags (Figure 1) or as a solution, (Figure 2).
This was the case even when 304L was replaced by alternative cladding material, such as Sanicro 38, which proved to be less susceptible to cracking in tests simulating start-up after water washing [2].

Valmet has delivered nine recovery boilers to Brazil and Chile since 2001 with Sanicro 38 floor tube bends in front and rear walls. In all these boilers, floor tubes have been covered with sodium sulphate in the first start-ups, and the same practice has been continued during later outages, when floor tubes have been cleaned for inspections.

Covering floor tubes with some material, such as sodium sulphate, is also believed to protect the floor tubes from direct exposure to black liquor, in case black liquor firing begins in conditions in which unburned black liquor reaches the floor. There is some anecdotal evidence suggesting that if unburned black liquor falls on bare tubes, it may form strongly alkaline solution, which is aggressive enough to cause severe corrosion. This can be prevented by following a proper start-up procedure, i.e. by heating up the furnace with start-up burners first and beginning black liquor firing then, so that liquor burns at first in suspension. If some unexpected problems in start-up are encountered, floor tubes are still protected from direct exposure to black liquor.

**The impact of floor protection materials on outage scheduling**

Most pulp mills currently operate under a constant pressure to maximize annual production, which means, among other things, that outages should be carried out as seldom as possible and kept as short as possible. Since the recovery boiler often sets the total length of the outage for the entire mill, the time needed for boiler cooling and cleaning has a direct impact on the mill outage.

The time needed for recovery boiler cooling can be minimized by extracting smelt from the furnace while the boiler is still operating. Thanks to smelt extraction, the bed remaining on the floor after boiler shut down cools down quickly, typically in 4 – 6 hours, i.e. during depressurization. Consequently, washing with soot blowers spraying water into the furnace can begin without any delays. Compared to a situation in which no smelt extraction is carried out and the cooling period is at least 15 – 24 hours long, smelt extraction saves 10 – 20 hours in outage time.

Experience from numerous smelt extractions shows that the bed remaining on the floor after smelt extraction cools down the same way whether the floor was protected with lime or with sodium sulphate, or if no material was used for floor protection at all.

However, the material selection does have an impact on the amount of material remaining on the floor after smelt extraction.

Ideally, the entire bed is melted and removed by extraction so that at most thin solid crust remains covering the floor tubes. This is achieved when the material covering the floor tubes has a relatively low melting point. Typical smelt with sulfidity in the range of 30 – 40 % has a melting point between 730°C and 770°C. Covering the floor with sodium sulphate, with a melting point of 884°C, can make the bed more difficult to melt. The task of melting the bed completely becomes even harder when lime is used as
the floor protection material, as impurities such Ca, Mg, Al and Si, are mixed with the smelt increasing the melting temperature even higher.

Typically, when no floor protection is used, floor tubes are visible in at least some part of the floor, as shown in Figure 3. However, when the floor has been protected with lime, floor tubes are seldom visible, and a relatively thick crust can be seen covering some part of the floor, as in Figure 4.

Floor protection methods and materials have an even larger impact on floor cleaning.

When lime is used as a floor protection material, it tends to remain as a thin layer next to the floor tubes, but otherwise mixes with smelt. On the top layer, however, smelt flows constantly during operation, so this layer remains free from lime. These three layers can be seen in a cross section of bed shown in Figure 5.

The material in the layer next to the floor tubes remains loose and forms sludge during water washing. Consequently, the solid material covering floor tubes can be easily lifted, once it has been cut into pieces, and the tube surface can be cleaned free of the sludge with ease. For this reason, lime is used commonly as a protective material in boilers with studded floor tubes.
When lime is used as a floor protection material, the material remaining on the floor after smelt extraction tends to contain impurities such as Ca, Mg, Si and Al, which make the smelt insoluble. Consequently, most of the material remaining on the floor after smelt extraction also remains there after washing. For example, Figure 6 shows a floor after washing when the areas in front of the spouts were cleaned during washing using high-pressure nozzles installed through smelt spout openings. The areas in the vicinity of the high-pressure nozzles are clean, but most of the floor is still covered with the same amount of material than remained on the floor after smelt extraction.

The remaining material needs to be removed mechanically, and it may take 20 to 60 hours, depending on the amount of the material remaining, the size of the area to be cleaned and the tools used. Another downside is that since the material needs to be removed using high-pressure washing equipment and/or mechanically, there is a risk that floor tubes will be damaged in the process.

Typical smelt is, on the other hand, soluble in water and can be removed by washing. The washing efficiency can be enhanced by the following actions:

1. Washing with soot blowers is begun in superheaters.
2. Clean water is continuously fed into the furnace so that wash water does not become saturated with salt.
3. Stratification of the water pool on the furnace floor is prevented by mixing and circulating the water pool on the furnace floor continuously by mixing devices installed into the pool.

Experience from several cases involving both smelt extraction and floor washing with the methods described above indicates that floor washing can be carried out effectively while the other parts of the boiler are being washed with soot blowers.

For example, when both smelt extraction and enhanced floor washing were carried out in a recovery boiler with design capacity of 2000 tDS/day, floor area of 120 m² and smelt bed volume of 28 m³ during a 2017 outage, the amount of material remaining on the floor after washing was only 3 m³ and it was removed in 6 hours (Figure 7).
However, when only smelt extraction was done, but the boiler was washed using only soot blowers, as much as 14 m³ of material remained on the floor (Figure 8).

The results gained so far from boilers using sodium sulphate as floor protection material indicate that significant time savings in final cleaning can be obtained as well, although more material may remain. The reason may be that some sodium sulphate is converted to sodium sulphide and sulphite during normal operation. Both sodium sulphide and sulphite have relatively low solubilities at low and moderate temperatures, so they are not as easily dissolved as smelt.

It is possible that the washing results in boilers using sodium sulphate for floor protection can be improved by reducing the amount of sodium sulphate used for floor protection (a moderately thin layer should be enough for floor protection) or by replacing sodium sulphate by sodium carbonate, which has a relatively low melting point (851°C) and high solubility over a wide temperature range.

The impact of floor protection materials on floor cleaning

Lime and refractory are not soluble so they need to be removed by hydro blasting. Salt deposits from superheaters, smelt, sodium sulphate and sodium carbonate are all soluble, so they can be removed by dissolving. Dissolving can be enhanced by:

- Spraying clean water to the furnace.
- Mixing the water pool continuously so that it does not become stratified with salty water on the bottom of the pool.
- Carrying out floor washing at the same time as other parts of the boiler are being washed with soot blowers.

Valmet has developed a floor washing service, Valmet Recovery Boiler Cleaning (previously known as Wash-X), based on the above simple principles.

Summary and conclusions

Floor tubes with 304L cladding have been found to be susceptible to cracking. It is believed that the main cause for cracking has been stress corrosion experienced during and after water washing, when tube materials have been in contact with hydrated salt containing a high level of sulphide and caustic at temperatures between 150 and 220°C. It has been suggested that cracking may occur when water washing is begun while the floor tubes are still hot, or when start-up burners are used for drying the boiler after washing, or during boiler start-up when the floor is covered with hydrated salt [3].
While alternative cladding materials, such as San38, are far less sensitive to such cracking than 304L, they are not completely corrosion resistant. Consequently, the operating guidelines issued by Valmet state the following:

- Water may be introduced into furnace only after the boiler is depressurized, as this guarantees that floor tube temperatures are so low that stress corrosion cracking is not a concern and the maximum core temperature in the remaining bed is below 500°C.
- If some drying is needed, drying is done using primary air or by heating the boiler using start-up burners while keeping floor tube temperatures below the temperatures at which stress corrosion cracking may occur.
- Bare floor tubes are covered with "process-like material" before start-up.

The most suitable materials for floor protection in boilers with decanting floors without studded floor tubes are sodium sulphate and sodium carbonate. Both are more easily removed during smelt extraction and washing than lime. From the two salts used, sodium carbonate appears to be the better option due to its lower melting point and high solubility over a wide temperature range.

Valmet is not recommending that all salt remaining on the floor after water washing be removed and replaced by "process-like material" in every shut down.

Instead, the risk of stress corrosion cracking can be reduced using smelt extraction and floor washing services. When these services are used, sodium sulphide and caustic are removed from the furnace already during smelt extraction. In addition, sodium sulphide and caustic still remaining on the floor after washing are diluted into a relatively large volume of water. It is therefore less likely that the strong solutions needed for stress corrosion cracking would form during start-up.

References


This white paper combines technical information obtained from Valmet personnel and published Valmet articles and papers.

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We are committed to moving our customers' performance forward.