

# A 40-year fight against corrosion in kraft recovery boilers: A review

## Low alloy chromium-molybdenum steels have better resistance

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**M**OST OF THE kraft recovery boiler corrosion problems have occurred in the lower furnace. The annual Swedish Recovery Boiler Conference [1] provides a yearly survey of incidents in Swedish black liquor recovery boilers. Among the first corrosion damages reported, there are several occurring in the lower furnace.

### Corrosion studies

From the introduction of the Tomlinson recovery boiler in 1936 and up to around 1960, all kraft recovery boilers in Sweden used Bailey-blocks to protect the tubes on the furnace bottom and lower walls. When in good shape, these blocks offer sufficient protection for the tubes.

The first tube leak damage due to corrosion was reported in 1948. Later on, similar cases were observed during maintenance work on blocked walls. Figure 1 shows the typical appearance of such corrosion between the blocks. At that time, it was still argued whether the corrosion occurred during the weekend shutdowns by galvanic corrosion or if it was caused by the molten smelt.

Since heavy waterside deposits were observed in some cases, elevated tube temperatures were concluded to be a main cause. Corrosion tests showed that the corrosion from molten smelt is very intense, see Fig. 2. As boilers were built

for higher capacities, the use of Bailey-blocks resulted in a construction which was too heavy. Around 1960, boilers with bare carbon steel tubes in tangential tubewalls were introduced (Fig. 3). A few years later the first boiler with studded wall tubes was built in Sweden (Fig. 4).

With time, the working pressure of new boilers increased and around 1960 some boilers with bare carbon steel tubes were designed for a pressure of 7.5 MPa. These boilers were soon found to suffer from extensive tube wall corrosion in the lower furnace. To determine the rate and extent of the corrosion, extensive tube thickness measurements were made on these boilers [3].

Alarming reports about corrosion of the furnace walls caused the Swedish Recovery Boiler Committee to initiate a comprehensive research project to study the corrosion process and to investigate means of preventing tube corrosion [2,4,5,6].

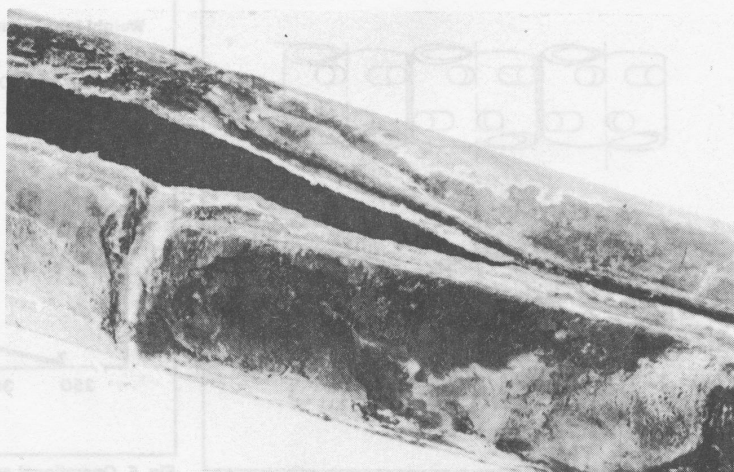
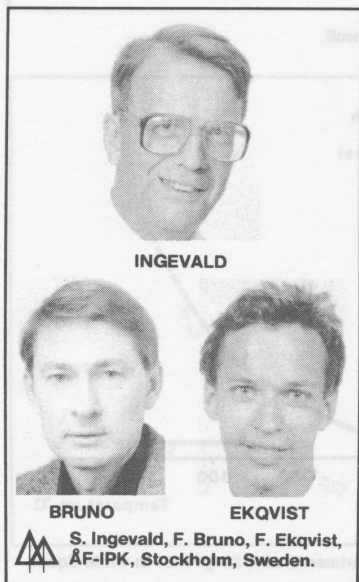


Fig. 1. Corrosion between blocks.

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The results from this fundamental research work on the corrosion of carbon steel can be summarized as follows:

- The highest corrosion rate occurred at a  $O_2:H_2S$  ratio in the flue gas of about 1:1.
- The corrosion rate increased rapidly at temperatures above  $300^\circ C$  (Fig. 5).
- A frozen layer of kraft smelt as well as a magnetite oxide layer, reduced the corrosion rate considerably.
- Molten smelt is extremely corrosive when in direct contact with carbon steel.

Based on these conclusions, the following recommendations were given:

- The boiler pressure should not exceed 6 MPa.
- Internal deposits in the tubes should be avoided.
- The  $O_2:H_2S$  ratio should exceed 2.
- Carbon steel wall tubes in the lower furnace should be protected by studding,

because a frozen smelt layer decreases the corrosion rate considerably.

- Metal spraying with the so-called multicoating system was mentioned as a temporary method to protect the bare tubes in existing boilers.

The author's opinion regarding these methods to protect the furnace tubes is as follows.

**Protection by studs:** To get a good protection with studs (Fig. 6) they must secure a permanent frozen smelt layer on all tube parts. We recommend the following practices:

- The total cross-section of area of the studs should not be less than one fourth of the corresponding tube wall area.
- The stud length should not exceed 20 mm.
- The wall should be studded up to least one metre above the secondary air level.

Studded tubes will probably not be

used in new boilers in the future. Restudding and complementary studding will, however, still be made.

The following precautions should be considered.

- An effective cleaning method must be used, leaving the surface free from smelt and oxides.
- Generally, the old studs have to be "top" ground to provide a good fusion. Lack of fusion causes excessive metal temperatures and shortens stud life considerably.
- A thoroughly-tested weld method should be used along with experienced welders.
- The restudding should be, at least, as closely spaced as the original.
- Stud materials alloyed with Al and as much as up to 25% Cr have shown good results when used in some boilers. (German Werkstoff No. 1.4742, X10CrA113 and 1.4762, X10CrA124.)

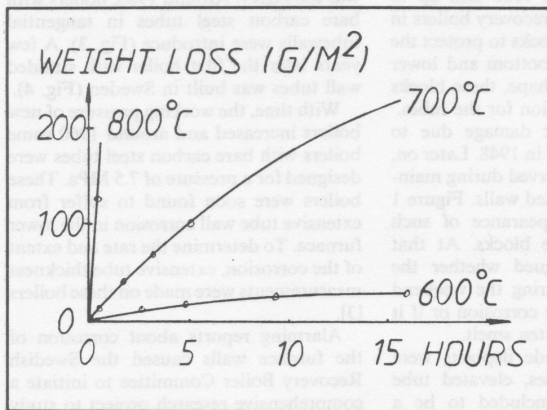


Fig. 2. Carbon steel corrosion by kraft smelt [2].

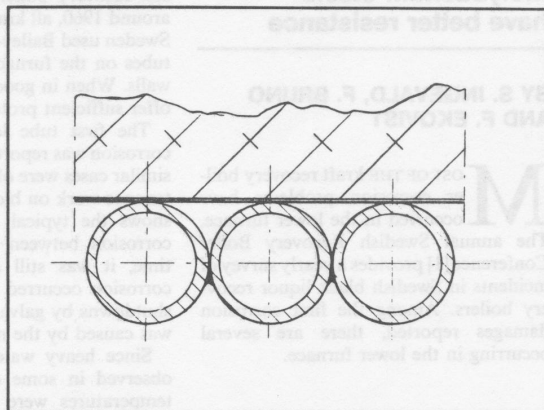


Fig. 3. Tangential tube wall.

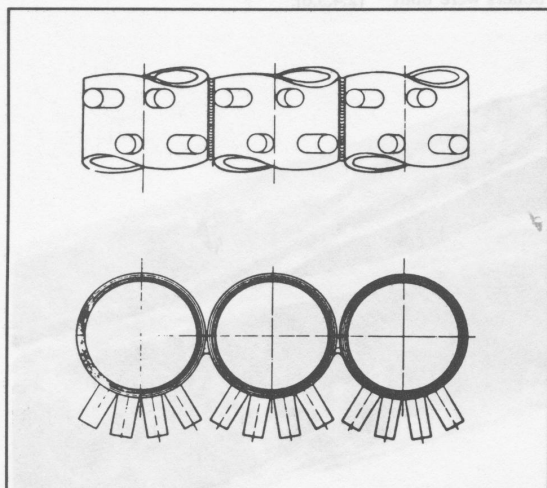


Fig. 4. Studded tube wall.

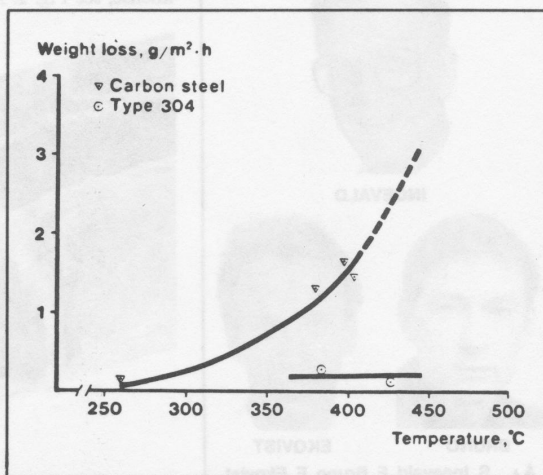


Fig. 5. Operational experiments with 20 g NaCl in white liquor. Exposure 336 hours [2].

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**Protection by metal spraying:** A perfect pre-cleaning is very important for metal spraying. Recent experience from wood-waste boilers indicates that modern metal spray techniques may be useful for protection in areas such as above the studded parts.

**Protection by clad welding:** Clad welding has been used in Sweden only in cases with very local tube thinning. This method is too expensive for big areas, and quality control is difficult.

**Stainless steel: Composite tubes:** *Corrosion studies.* The corrosion studies conducted during the 60s together with the pilot studies performed on boilers in Finland and Sweden, led to the use of stainless steels. At the same time, Sandvik AB introduced its composite tubes. A test panel with clad welded tubes and composite tubes was installed along with

other types and designs in the Kaukopää Mill in Finland in 1967 and in Munksund, Sweden from 1970 to 1973.

At the same time, research studies were performed in Finland and Sweden to investigate whether some of the common alloy steel grades had better resistance than plain carbon steel in the recovery boiler [7,8,9,10].

The results of these studies indicated that stainless steel with a chromium content above 116% had a corrosion rate 10 times lower than carbon steel when tested in the laboratory under the same simulated furnace conditions (Fig. 7).

*Experiences of composite tubes.* Based on the promising results of these laboratory investigations and the test panels with Sandvik composite tubes in kraft boilers, Lövhölmens Bruk decided to use composite tubes in the lower furnace of its new

boiler in 1972. This boiler has now been in service for 15 years and no corrosion at all has been recorded.

The stainless layer on the tubes used at Lövhölmens is of the general AISI 304 type. The same type of stainless steel, nowadays low-carbon, has now been used in almost 100 kraft recovery boilers. The general corrosion of these tubes seems in practice to be even less extensive than that predicted by the laboratory results [11].

*Erosion: Corrosion at smelt spout openings.* Local thinnings due to erosion-corrosion by the smelt flow have been observed in a few cases. The corrosion rate has at most been up to 0.2 mm/y. Local weld repairs and spraying with ceramics have been tried with good results in one boiler.

*Corrosion at primary air ports.* Since 1983, as many as four recovery boilers have suffered damage by corrosion in the

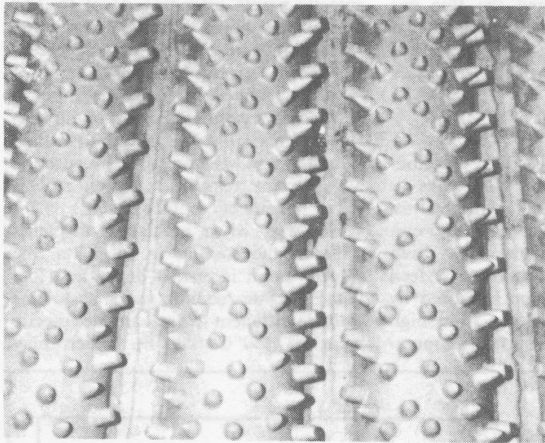


Fig. 6. Membrane wall with studded tubes.

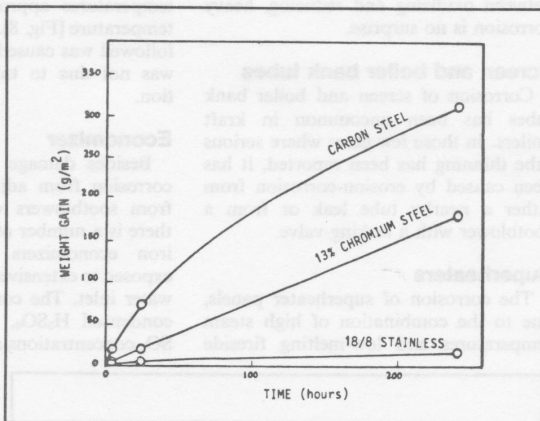


Fig. 7. (0.1% H<sub>2</sub>S, 0.1% O<sub>2</sub>, 10% H<sub>2</sub>, 2% H<sub>2</sub>O, balance N<sub>2</sub>, 400°C) [7].



Fig. 8. Scaling of superheater tube.

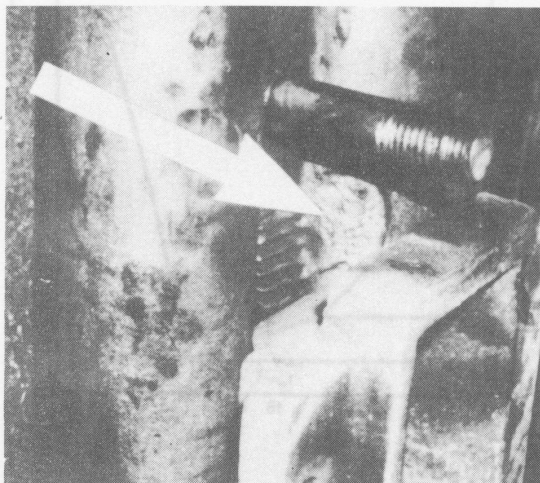


Fig. 9. Corrosion site at air inlet nozzle.

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primary air ports.

**Corrosion in the upper furnace:** This corrosion has been found just above the tertiary air level. In some furnaces the tubes have been very thin. The location of the corrosion pattern suggests that the liquor guns are where the problem originates.

With conventional liquor spraying, liquor drops are sprayed on the opposite walls of the furnace. Due to the liquor gun sway, the sprayed liquor forms a parabolic pattern on the side walls, with the peak somewhere in the middle, slightly above the liquor gun level. The corrosion attack sometimes follows the borders of this pattern. Burning liquor char sticking to the wall causes reducing conditions locally underneath the deposits. When the deposits fall off, oxidation occurs on the wall surface. With conditions fluctuating between oxidizing and reducing, heavy corrosion is no surprise.

## Screen and boiler bank tubes

Corrosion of screen and boiler bank tubes has been uncommon in kraft boilers. In those few cases where serious tube thinning has been reported, it has been caused by erosion-corrosion from either a nearby tube leak or from a sootblower with a leaking valve.

## Superheaters

The corrosion of superheater panels, due to the combination of high steam temperatures and low-melting fireside

deposits is not a common problem in Sweden. One reason for this may be that the typical superheater outlet steam temperature is moderate, 450°C (842°F). Another reason is Swedish still-moderate levels of salt-melting range depressants like chlorides and potassium.

One recovery boiler, however, suffered high temperature corrosion of the secondary superheater, caused by an unstable steam temperature control combined with a leak in one of the two steam attemperators. Due to the steam attemperator leak, boiler water entered the secondary superheater, where the boiler water constituents were left on the tube walls causing overtemperatures.

The high overtemperatures caused the tubes to form a thick oxide layer. This thick layer spalled off and caused blockage of the tube bends, so the tube wall temperatures approached the flue gas temperature [Fig. 8]. The tube burst that followed was caused by rapid creep and was not due to tube thickness reduction.

## Economizer

Besides damage caused by erosion-corrosion from adjacent tube leaks or from sootblowers with leaking valves, there is a number of tube bank and cast iron economizers which have been exposed to extensive corrosion at the feed water inlet. The corrosion is caused by condensed  $H_2SO_4$ , resulting from high  $SO_3$  concentrations and surface tempera-

tures below the acid dew point. These cases can be explained by a too-low feed water temperature.

## Corrosion on the outside

**Primary air register corrosion:** Some older Swedish recovery boilers, have suffered badly from corrosion in the primary air register areas (Fig. 9). The corrosion model is based on the condensation of hydroxide vapors, which form low-melting point deposits in hidden areas in the primary air register.

The vapors are formed while incinerating the liquor. The corrosive deposits contain mainly carbonates and hydroxides. The sulphur content of the deposits is usually low, indicating that the corrosion is not caused by kraft smelt per se.

As a consequence of the high hydroxide content of the deposits, they will have low eutectic points extending down to, and below, the boiler water temperature. Thus, units with a higher steam pressure are more vulnerable to this type of corrosion. The eutectic temperature of pure sodium hydroxide-sodium carbonate mixtures is not low enough to initiate corrosion at 6 MPa pressure, because the tube surface temperature then still is below the eutectic point (Fig. 10).

However, when potassium displaces some of the sodium in the salts, the eutectic point is further depressed (Fig. 11). Potassium/sodium ratios as low as 1:10 are sufficient to decrease the eutectic point to 250°C (480°F), which may

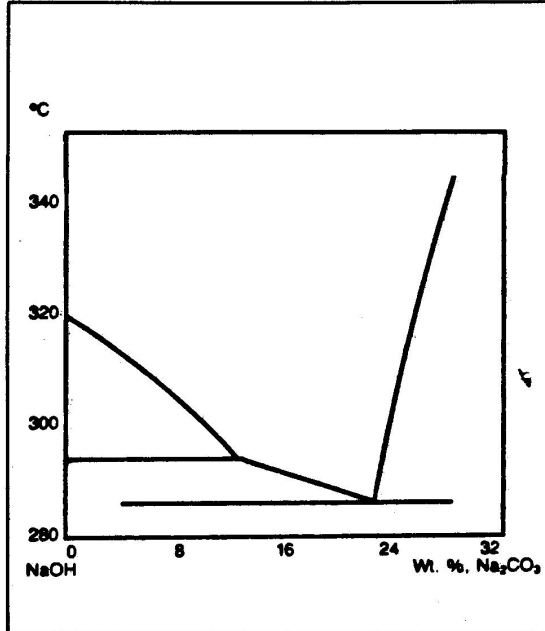


Fig. 10. Phase diagram NaOH- $Na_2CO_3$  [12].

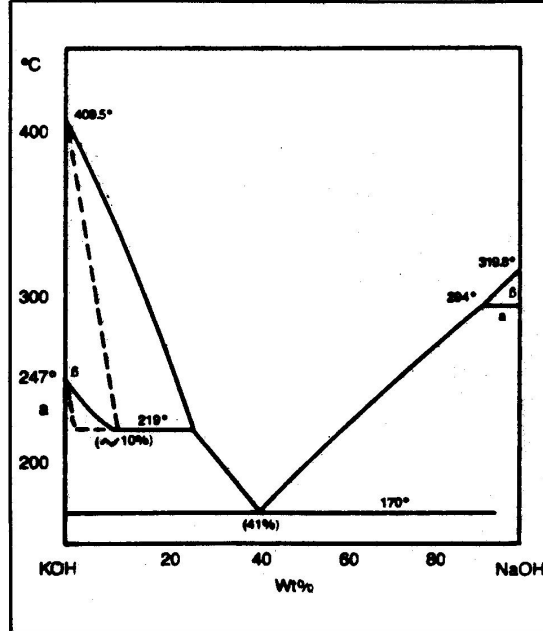


Fig. 11. Phase diagram KOH-NaOH [12].

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explain the composite tube corrosion attack mentioned earlier.

**Corrosion below smelt spouts:** Weak wash liquor used to clean the smelt spouts has been a source of frequent worry in Swedish recovery boilers. Several incidents have occurred over the years when the weak wash has seeped behind the insulation and corroded the front tubes and headers below the smelt openings. One case was initiated by weak wash causing stress corrosion cracking of the stainless plate frame which protected the front wall around the smelt spout openings.

### Water side corrosion

**In furnace tubes:** Localized corrosion in the waterside has been reported in two cases. In one case, the corrosion occurred opposite to the plates of the primary air ports. In the other case, the corrosion appeared opposite to the pin studs (Fig. 12). This type of corrosion is caused by a high local heat flux in combination with unsuitable water treatment. Deposits will form opposite areas with high heat flux, causing wick boiling and local enrichment of boiler water constituents [13].

**In economizers:** Economizer cracking has been a recurring problem in several Swedish recovery boilers. The cracking occurs most often in the colder parts of tube economizers, often at the inlet header but also at the outlet header of the first and second economizer banks. The internal cracks occur circumferentially on the economizer tubes, often about 5 to 10 mm off the weld to the header (Fig. 13).

The bending stresses of the tubes are highest here because the tubes close to the header are supported by a rigid header and weld configuration (Fig. 14). Since the economizer is not steaming, it lacks the temperature stabilization of the boiling process which otherwise would keep the temperature of the tubes close to the water boiling point.

Generally, newer economizers are longer than older ones, although the design has not changed otherwise. The tubes are then more free to absorb internal stresses. Any dissolved oxygen in the water contributes to cracking. Improved deaerating of the feed water has remedied most of this problem.

**Erosion-corrosion of feed water piping:** The tendency to erosion-corrosion is dependent on water velocity, temperature, pH, water-dissolved oxygen content and hydrodynamic design [14]. Simple velocity criteria which are used independent of water chemistry can thus be faulty, especially if the boiler is running outside its scheduled water chemistry during upset conditions. Low alloy

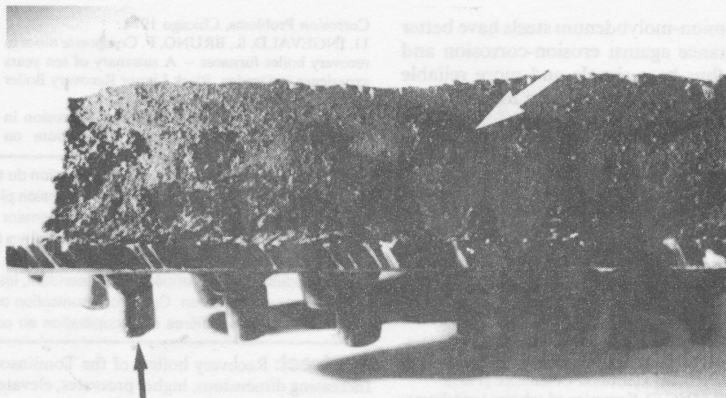


Fig. 12. Corrosion opposite pin studs.

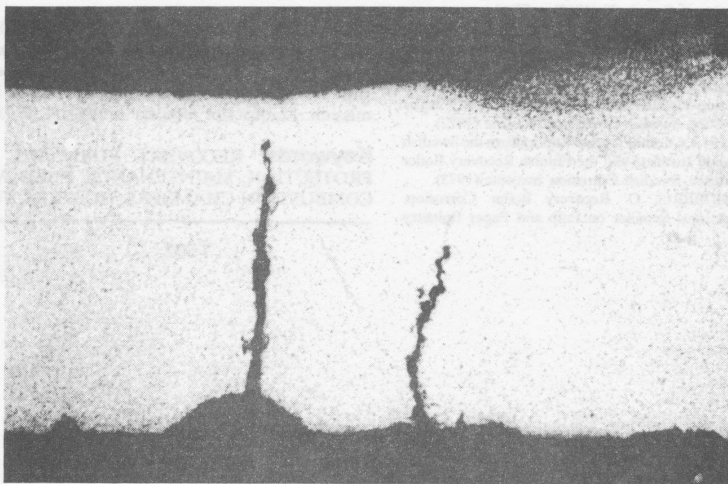


Fig. 13. Corrosion cracks near weld to header. Note corrosion pits.

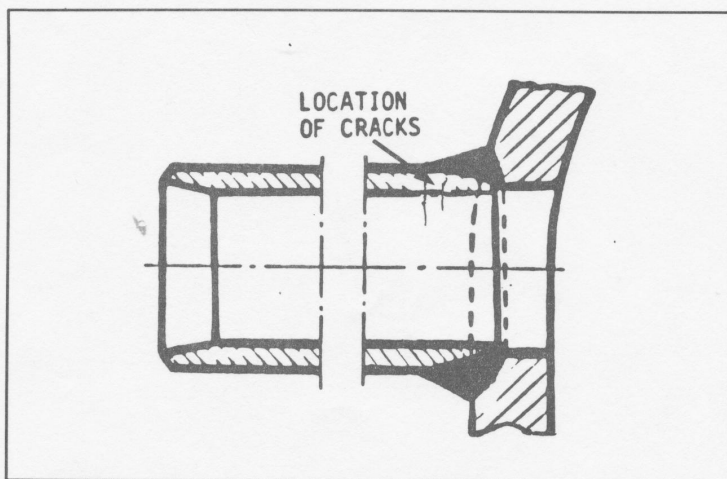


Fig. 14. Location of cracks.

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chromium-molybdenum steels have better resistance against erosion-corrosion and will thus be a simple and more reliable means of reducing damage to feed water piping.

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**Résumé:** Les chaudières de récupération du type Tomlinson sont utilisées en Suède depuis 1936. L'accroissement des dimensions, des pressions plus élevées, des températures plus hautes et de plus fortes capacités ont provoqué un accroissement des problèmes dus à la corrosion. En Scandinavie, on a fait des efforts considérables pour réduire la corrosion des zones exposées à la flamme. Des recherches fondamentales ont été menées dans les années 60. Des tubes en matière composite ont été introduits dans les années 70. Cependant, les chaudières de récupération présentent encore des problèmes de corrosion. Cette communication constitue en résumé de l'expérience suédoise sur la corrosion des chaudières de récupération au cours des quarante dernières années.

**Abstract:** Recovery boilers of the Tomlinson concept have been used in Sweden since 1936. Increasing dimensions, higher pressures, elevated temperatures and higher capacities have caused increasing corrosion problems. Considerable effort has been made in Scandinavia to reduce the fireside corrosion. Fundamental research was conducted in the 60s. Composite tubes were introduced in the 70s. However, recovery boilers still have corrosion problems. This paper reviews Swedish experience on recovery boiler corrosion, during the last four decades.

**Reference:** INGEVALD, S., BRUNO, F., EKQVIST, F. A 40-year fight against corrosion in kraft recovery boilers: A review. *Pulp Paper Can* 88(12): T497-502 (Dec. 1987). Paper presented at the 1985 International Recovery Conference of the Technical Section, CPPA, co-sponsored with TAPPI at New Orleans, LA, April 28 to May 3, 1985. Not to be reproduced without permission. Manuscript received January 4, 1985. Approved by Review Panel, August 20, 1987.

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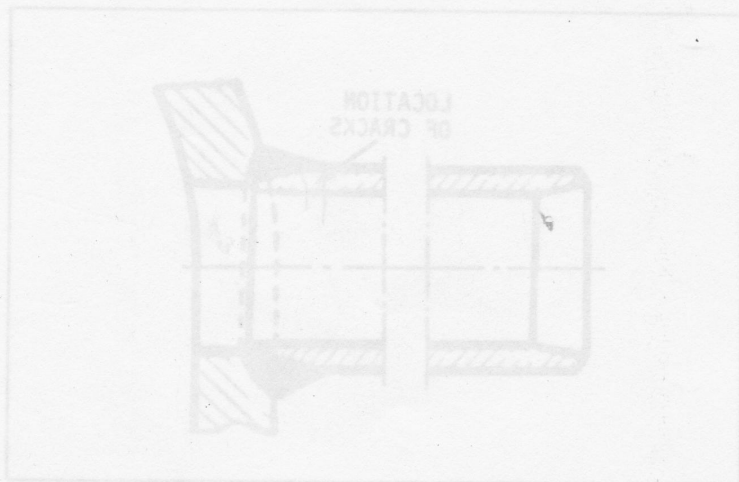


Fig. 14. Location of cracks.

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