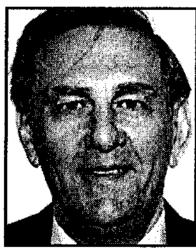
COMPOSITE TUBES IN BLACK LIQUOR RECOVERY BOILERS: AN UPDATE

Newly developed alloys help to resist corrosion

BY J.F. MCGURN



J.F. McGurn, Sandvik Canada Inc., Mississauga, ON. Now with Nickel Alloy Technology Inc.

CORROSION PROTECTION in black liquor recovery boilers (BLRB) has expanded considerably since the first installation of composite tubes in Finland during the 1960s. Sandvik Type 304 stainless steel co-extruded on ASME SA-210 Grade A-1 carbon steel gained widespread use in the pulp and paper industry throughout the 1970s.

Since the early 1980s, Type 304L/ASME SA-210 Gr. A-1 has been employed for waterwalls and floors. Today, there are over 220 recovery boilers around the world with Sandvik composite tubes installed.

Obviously, one of the key benefits in the selection of such a product is to have cost-effective longer life through improved corrosion resistance. The company is now into its 20th year of service with the longest running recovery boiler. Original surveys indicated that useful lifetime in excess of 20 years could be expected. This forecast has proved correct.

There have been cases where service conditions are such that problems have developed. Useful knowledge was obtained by thorough examination of problem areas. Redesign of some sectors within the boiler is very helpful in continuing the long life of composite tubes.

A new composite tube alloy combination, Type 310/T-22, is finding extended use in offsetting corrosion problems in BLRB superheaters.

COMPOSITE TUBES

In the production of composite tubes, an inner component of carbon steel and outer component of stainless steel are carefully machined. The stainless steel is fitted over the carbon steel producing a billet. The billet is prepared, then heated to 1200°C (2190 F) and pushed, or extruded, through a die to form a tube with a sheath of corrosion resisting stainless steel on the outside which is metallurgically bonded to the pressure-containing carbon steel on the inside. Figure 1 shows the technique

TABLE 1. SOME PHYSICAL AND MECHANICAL PROPERTIES OF COMPOSITE TUBES.

	AISI 304L	SA-210 Gr. A1
Yield Strength, N/mm^2 (ksi), min.		
20°C (68°F)	210 (30)	350 (51)
300°C (570°F)	110 (16)	210 (30)
Thermal Conductivity	**W/m, °C**	**Btu, hr ft °F**
20°C (68°F)	15 (8.5)	45 (26)
300°C (570°F)	19 (11)	41 (24)
500°C (930°F)	21 (12)	36 (21)
Thermal Expansion x 10–6	**per °C**	**(F°)**
20 – 100°C (68 – 210°F)	16 (9.3)	12.4 (6.9)
20 – 300°C (68 – 570°F)	17.5 (9.7)	14.1 (7.8)
20 – 500°C (68 – 930°F)	18.2 (10.1)	14.5 (8.0)

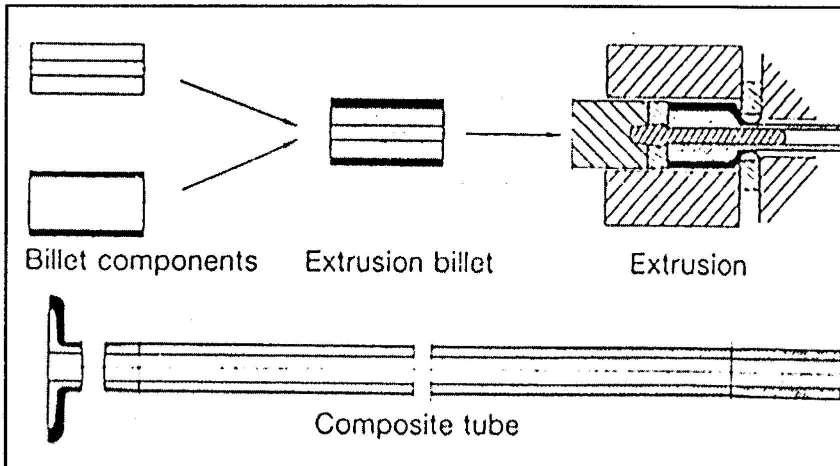


FIG. 1. EXTRUSION OF COMPOSITE TUBES.

employed for this procedure.

Following the high temperature extrusion operation, the composite tube is cooled, cleaned, and cold worked to bring it to the final size. After heat treatment, ultrasonic examination is done to detect any surface defects, assure the correct stainless steel thickness, and check the metallurgical bond between the stainless steel/carbon steel interface.

Metallurgical Bond: A 100% ultrasonic testing operation, Fig. 2, is done by scanning the tube end to end in two directions.

The bond between the stainless steel at the top, and carbon steel at the bottom is critical to permit adequate heat transfer. This is shown in Fig. 3.

Carbon from the steel can migrate into the stainless steel during production of the composite tube. This is not harmful. In boiler service, below 500°C (930°F) there is practically no further carbon migration. However, excess service temperature, over 500°C (930°F), widens the zone where carbon has migrated and thus gives the metallurgist an excellent indication of excessive elevated boiler temperature [1].

Physical and mechanical properties of composite tubes: Yield strength, thermal conductivity and thermal expansion are shown in Table I. Here Type 304L provides the corrosion resistant sheath while the SA-210 material gives the strength to resist boiler water pressures.

At room temperature the difference in thermal conductivity of stainless steel and carbon steel is quite wide. At operating temperatures the range narrows thus reducing stress. Extensive thermal fatigue tests, up to 10 000 cycles, have shown the metallurgical bond remains intact.

Heat treatment: The relief of stress in composite tubes, following close radius cold bending or welding, can be carried out without loss in strength or corrosion resistance at 650°C (1200 °F).

FIELD EXPERIENCE

Before 1960, severe corrosion to carbon steel furnace tubes was infrequent. When problems did occur they were, more often than not, in combination with overheating because of internal deposits on the water side of the tubes.

During the 1960s, the first high pressure black liguor recovery boiler was constructed. Through the years, corrosion and a few explosions have occurred with the use of studded carbon steel tubes and Bailey blocks. Investigations determined that corrosion was due to hydrogen sul-

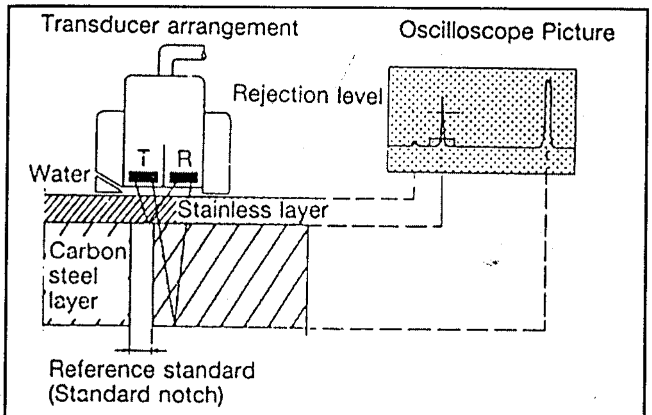


FIG. 2. ULTRASONIC TESTING OF THE METALLURGICAL BOND.

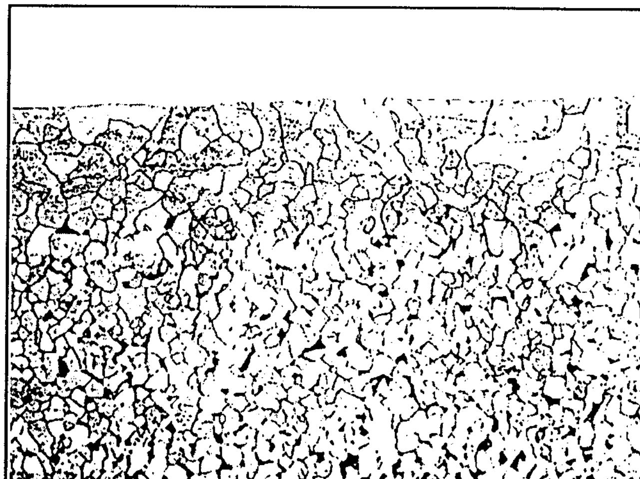


FIG. 3. METALLURGICAL BOND BETWEEN THE STAINLESS STEEL (TOP) AND CARBON STEEL (BOTTOM).

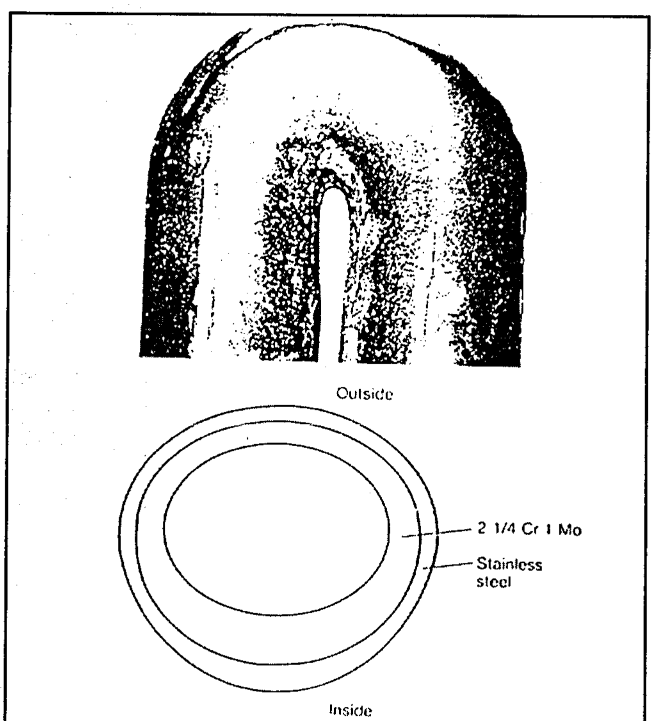


FIG. 4. INDUCTION HEATED, THEN BENT, COMPOSITE TUBE AT THE TOP, WITH A CROSS-SECTION OF THE BEND AT THE BOTTOM.

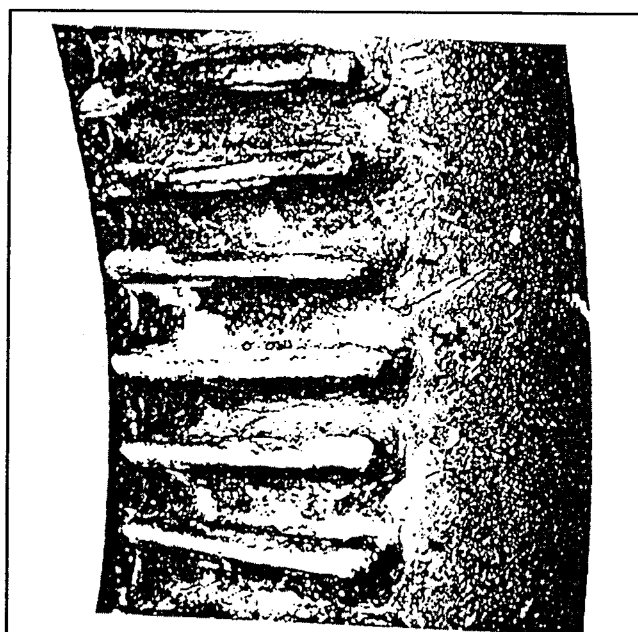


FIG. 5. COMPOSITE TUBE WITH SHORT BARS WELDED TO IT AROUND A SMELT SPOUT OPENING.

phide in flue gases. Research work revealed that stainless steel with 18% chromium and 8% nickel (Type 304) *could resist such an environment.*

Since the early 1960s, there has been a trend toward larger boilers with higher pressures. This accelerated problems with carbon steel tubes and their life was as short as two to five years.

In 1972, composite tubes with Type 304 stainless steel on the outside were introduced into the complete lower portion of a new boiler at ASSI/Lovholmen mill in Sweden. These tubes are now in their 21st year of corrosion-resisting service and continue to provide the protection necessary for this recovery boiler's satisfactory operation.

Many boilers have composite tubes up to the tertiary air port. However, corrosion has been found on carbon steel above the tertiary and some boilers have composite tubes well above this level.

Most installations are sulphate (kraft) recovery boiler although there are some references for sulphite mills where higher sulphidity is encountered.

Composite tubes have assisted greatly in overcoming fireside corrosion challenges, but there are a few which remain.

SUPERHEATERS

Conventional superheater alloy T-22 has been employed for many boilers. However, in BLRB T-22 has corroded due to the deposits which form on the tubes. In one case deposits with 6% sodium chloride led to a lifetime of only two to three years. Further tests with T-22 tubes installed adjacent to Type 310 stainless steel co-extruded on T-22 revealed only superficial corrosion on the composite tube whereas the T-22 tube had pitting attack 20 mils = (0.020 in.) deep.

In bark-fired boilers, superheater tubes of T-22 were replaced after one to two years use. Composite tubes of Type 310/T-22 did not exhibit any corrosion after one year of operation.

Any material selected for superheaters will require bending to tight radii. Figure 4 shows a U-bent superheater composite tube with a cross-section to show that tight bends can be accomplished.

Type 310/T-22 composite tubes have been installed since 1983 and continue to find use in Canadian boilers, and other boilers worldwide, to help offset corrosion in the superheater sector.

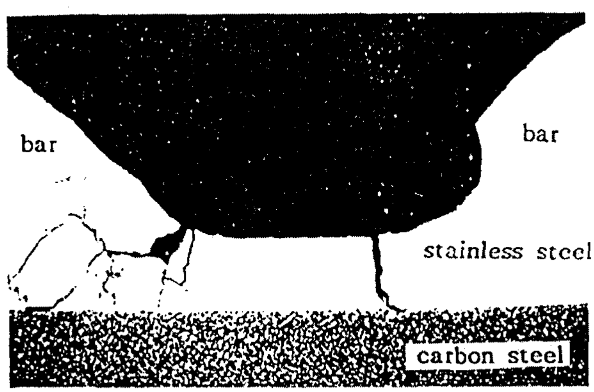


FIG. 6. SECTION THROUGH THE TUBE FROM FIG. 5.

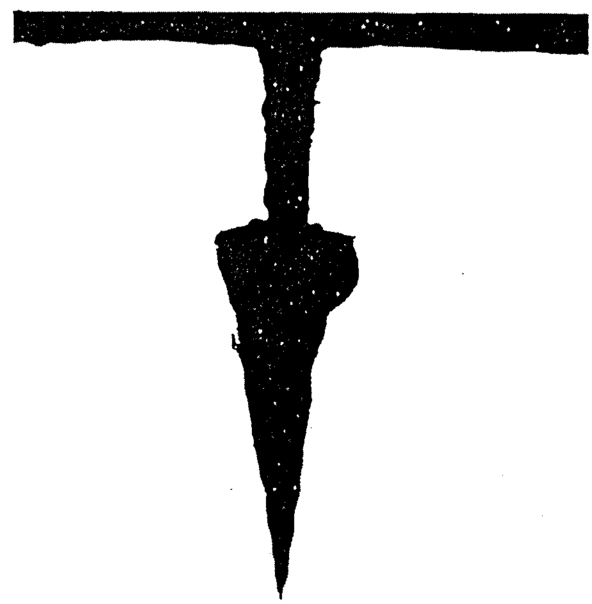


FIG. 8. CRACK PROPAGATING FROM THE OUTER SURFACE OF THE STAINLESS STEEL INTO THE CARBON STEEL.

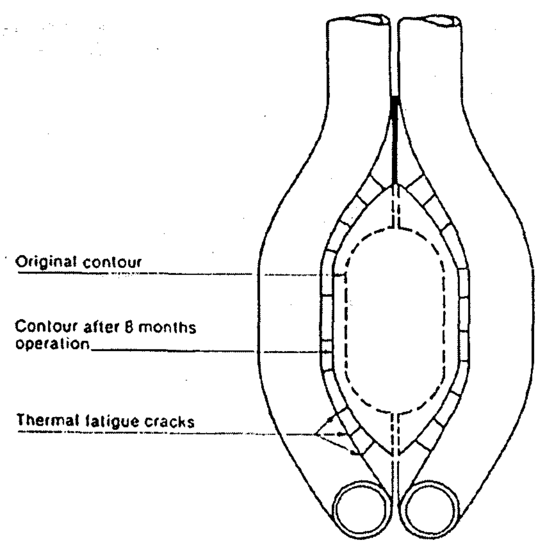


FIG. 7. CRACKING OF LONGITUDINAL FINS ATTACHED TO COMPOSITE TUBES AROUND SMELT SPOUT.

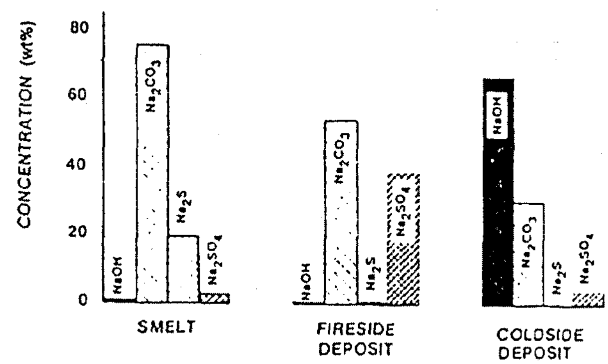


FIG. 9. COMPOSITIONS OF SMELT AND DEPOSITS ON TUBES NEAR A PRIMARY AIR PORT.

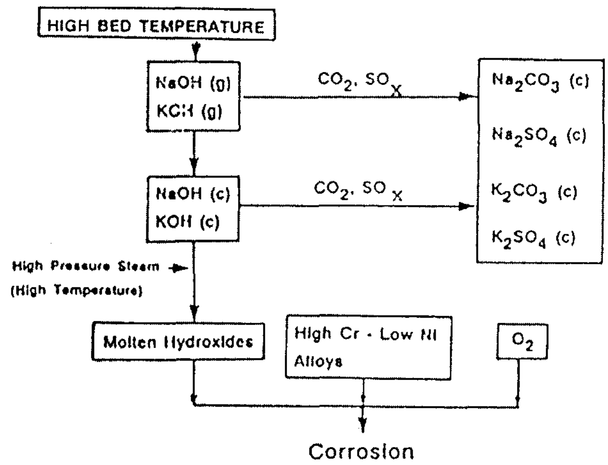


FIG. 10. PROPOSED CAUSES OF AIR PORT CORROSION.

SOME PROBLEMS SOLVED

Smelt spouts: In a Scandinavian boiler, small stainless steel bars were welded to the surface of composite tubes around the smelt spout to offer protection against roding. These corroded badly. In addition, cracks appeared between the bars after two to three years service, Fig. 5.

The cracks did not enter the carbon steel, Fig. 6. Thermal fatigue and stress corrosion cracking were suspected as the cause of the cracks due to stresses from welding and bending of the tubes [2].

In the ASSI/Lovholmen boiler, longitudinal fins of stainless steel had been attached to composite tubes around smelt spouts, Fig. 7. These corroded with some penetration to the carbon steel. Examination revealed overheating and thermal fatigue as the causes of the problem.

New tubes without fins were installed and the spout was allowed to protrude a little into the boiler. This permitted smelt to freeze on the composite tubes and form a protective barrier which has extended the life of the tubes.

Primary air ports: A Canadian boiler, after four years service, formed straight cracks in the composite tube with some of these going into the carbon steel, Fig. 8. One such crack penetrated the carbon steel. Inside the tube, a 1/16 in.-thick iron oxide deposit was found.

Metallurgical examination revealed the tube had experienced a temperature in the region of 500 - 550°C (930 - 1020°F) as determined by a change in the metal microstructure and the growth in the decarburized layer from its original 0.004 in. to 0.014 in.

A Scandinavian boiler exhibited waterside cracking in composite tubes resulting in two through-cracks. This took place in tapered sections in an area 200 mm up from the point where the diameter increased. Thermal fatigue precipitated by over-heating of the tubes and circulation abnormalities of the nearly horizontal tubes were judged to be the cause of this problem. No further corrosion of this type has taken place.[3]

Secondary air-ports: A 3 1/2-year-old Canadian recovery boiler showed wastage in the secondary air port area during 1985. The same problem has also been observed, in the same boiler, at corners in the tertiary and top corners of the primary air ports. Extensive cracking at flat stud notches was observed, as previously, but no cracks reached the tubes. For the above, most wastage was found on the front and right walls [3].

Cold side corrosion [4]: Since 1985, localized cold side wastage of stainless steel behind flat studs and areas shielded by cast iron air port inserts in high pressure Scandinavian and North American boilers has taken place. In some cases this wastage required less than two years to occur. Corrosion appears to slow in most cases when carbon steel is exposed.

Such cold side corrosion is attributed to the presence of molten alkali (NaOH and KOH) in deposits at the tube surface. In a Scandinavian boiler the composition of the smelt and fireside deposit consisted of Na_2CO_3 and Na_2S or Na_2SO_4 with little or no NaOH. The fireside deposit indicated that it was simply an "oxidized" smelt.

Alternatively, the coldside deposit had a large amount of NaOH with small amounts of Na_2SO_4 and no Na_2S which suggests these chemicals were not formed by the same mechanism as the fireside deposit. Compositions of these deposits are revealed in Fig. 9.

Such an effect occurs at elevated temperatures and pressures with the corrosion of Type 304 alloys promoted by alkali hydroxides present at metal surfaces.

Figure 10 proposes the formation mechanism. Here, sodium and phosphorous vaporize from the high temperature smelt bed to form gaseous hydroxides when reacting with H_20. These

Résumé: Des tubes d'assemblage en acier inoxydable de type 304, et plus récemment des tubes en acier inoxydable de type 304L produits par co-extrusion avec un acier de catégorie A-1 selon la norme ASME SA-210, sont utilisés depuis 21 ans pour contrebalancer les effets de la corrosion dans la partie inférieure des chaudières de récupération de la lessive noire. Aux prises aujourd'hui avec des milieux encore plus corrosifs, il est devenu nécessaire de prendre des mesures de prévention encore plus importantes. Notre article décrit certains des problèmes ainsi soulevés et les mesures correctives qui ont été mise en oeuvre pour les résoudre. Nous formulons enfin des commentaires sur une deuxième combinasion d'alliages pour les surchauffeurs, soit un alliage fait d'acier inoxydable de type 310 produit par co-extrusion avec de l'acier T-22.

Abstract: Composite tubes with either Type 304 or presently with Type 304L stainless steel co-extruded on ASME SA-210 Grade A-1 have been used for the past 21 years to help offset the effects of corrosion in the lower portion of black liquor recovery boilers. Now, a more corrosive environment is being experienced which may require greater care in its prevention. This paper will outline some of the problems and corrective measures which have been taken. Comments on a second alloy combination, Type 310 stainless steel co-extruded on T-22 steel, for superheaters, will be offered.

Reference: MCGURN, J.F. Composite tubes in black liquor recovery boilers. *Pulp Paper Can* 94(12): T428-432 (December 1993). Paper presented at the 74th Annual Meeting of the Technical Section, CPPA, at Montreal, Quebec, on January 26 to 29, 1988. Not to be reproduced without permission. Manuscript received November 13, 1987. Revised manuscript approved for publication by the Review Panel, January 20, 1993.

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diffuse with the flue gas going behind the air port and upon cooling a little, condense on the tubes forming hydroxide-rich deposit. The deposits age and react with CO_2 and SO_X in flue gases to form carbonates and sulphates which are solid and harmless.

In the gas atmosphere where CO_2 and SO_3 concentrations are low, close to air ports, alkali hydroxides remain unchanged in deposits. These likely melt in high temperature boilers forming alkali hydroxides which react with the protective Cr_2O_3 on the Type 304L cladding under oxidizing conditions at air ports to form alkali chromates.

Thus for cold side corrosion to occur we require,

- Molten hydroxide;
- High chromium – low nickel, e.g. Type 304L alloy;
- Oxygen.

To help prevent cold side corrosion we want to:

- Seal all areas to prevent the backward flow of gases at air ports;
- Where corrosion has occurred, carry out weld overlay repair with alloy 600 (SANICRO 71 or 72);
- Consider the use of alloy 825 coextruded on SA-210 Gr.A1 where seals cannot be accomplished or where weld overlay cannot be carried out.

Other useful work: Studies are useful for all boiler operators to understand better the forces trying to defeat their long-term operation of a boiler in the most cost-effective manner.

Thermocouples have been attached to known and suspect areas in some boilers to better understand thermal differences [5].

Temperature profiles have been done on membranes which are 1-in.-wide. In the centre of these, temperatures of 400°C (750°F) have been observed. For membranes 1/2-in.-wide, readings were 370°C (700°F) [6].

Work continues in various sectors to better understand the more corrosive environment and recovery boiler operating parameters which are being used today in an increasing number of units.

CONCLUSION

Local areas in a recovery boiler have exhibited corrosion. However, it is also true that the conditions in today's boilers are more severe than was previously experienced by carbon steel tubes.

Newer designs and a better understanding of the more corrosive environments are well advanced and leading to problem solving.

Should it be found that hydroxides are a serious problem, and redesigns cannot be made, there are other alloy combinations available today such as Alloy 825 coextruded on SA-210 Gr.A1 that can help resist such an environment. This offers a strong measure of confidence for the future.

We continue to see further increase in today's 220 furnaces with composite tube and a useful lifetime anticipated in excess of 20 years.

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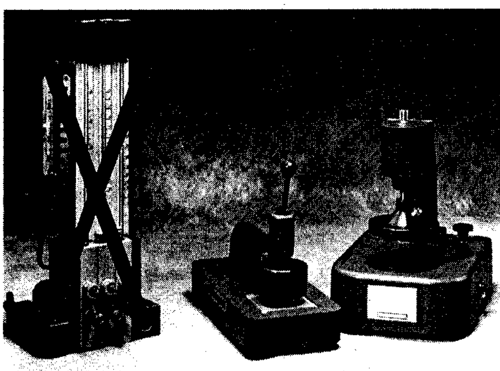

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