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U.S. Program on Materials Technology for Ultra-Supercritical Coal Power Plants

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The efficiency of conventional fossil power plants is a strong function of the steam temperature and pressure. Research to increase both has been pursued worldwide, since the energy crisis in the 1970s. The need to reduce CO_2 emissions has recently provided an additional incentive to increase efficiency. More recently, interest has also been evinced in advanced combustion technologies utilizing oxygen instead of air for combustion. The main enabling technology in achieving the above goals is the development of stronger high temperature materials. Extensive research-and-development programs have resulted in numerous high-strength alloys for heavy section piping and for tubing needed to build boilers. The study reported on here is aimed at identifying, evaluating, and qualifying the materials needed for the construction of the critical components of coal-fired boilers that are capable of operating with steam at temperatures of 760 °C (1400 °F) and pressures of 35 MPa (5000 psi). The economic viability of such a plant has been explored. Candidate alloys applicable to various ranges of temperatures have been identified. Stress rupture tests have been completed on the base metal and on welds to a number of alloys. Steamside oxidation tests in an autoclave at 650 °C (1200 °F) and 800 °C (1475 °F) have been completed. Fireside corrosion tests have been conducted under conditions simulating those of waterwalls and superheater/reheater tubes. The weldability and fabricability of the alloys have been investigated. The capabilities of various overlay coatings and diffusion coatings have been examined. This article provides a status report on the progress achieved to date on this project.

Keywords corrosion, creep, efficiency, emissions, fabrication, power plants, stress, welding

1. Background

1.1 Need for Ultra-Supercritical Plants

In the 21st century, the world faces the critical challenge of providing abundant, cheap electricity to meet the needs of a growing global population while at the same time preserving environmental values. Most studies of this issue have concluded that a robust portfolio of generation technologies and fuels should be developed to assure that the United States will have adequate electricity supplies in a variety of possible future scenarios.

The use of coal for electricity generation poses a unique set of challenges. On the one hand, coal is plentiful and available at low cost in much the world, notably in the United States, China, and India. Countries with large coal reserves will want to develop them to foster economic growth and energy security. On the other hand, traditional methods of coal combustion emit pollutants and CO_2 at high levels relative to other energy-generation options. Maintaining coal as a generation option will require methods for addressing these environmental issues. One of the options that has received attention worldwide is the development of ultra-supercritical (USC) high-efficiency, coal-fired power plants. The high efficiency of these plants results in fuel cost savings, as well as in considerably reduced levels of emissions and waste products.

The efficiency of conventional fossil power plants is a strong function of the steam temperature and pressure. Research to increase both has been pursued worldwide since the energy crisis in the 1970s. The need to reduce CO_2 emissions has recently provided an additional incentive to increase efficiency. The evolution of steam conditions and the corresponding increases in efficiency are illustrated in Fig. 1 (Ref 1). The plants built in the fifties, and earlier, were *subcritical* (i.e., less than ~3200 psi [or 22 MPa] pressure) and had efficiencies in the range of a 35 to 37% high heating value (HHV), which related to the assumption regarding the recovery of the heat of the vaporization of moisture. (Plants operating at >3208 psi at 538 to 565 °C [1000 to 1050 °F] are generally termed *supercritical*, and those operating at >565 °C (1050 °F) are termed *ultra-supercritical*.)

In the 1960s, supercritical technology was introduced, and steam conditions reached as high as temperatures of 563 °C (1050 °F) and pressures of 25 MPa (3600 psi). Thus, the steam temperatures of the most efficient fossil power plants are now in the 600 °C (1112 °F) range, which represents an increase of about 70 °C (108 °F) in 30 years. Nearly two dozen plants have been commissioned worldwide with main steam temperatures of 580 to 600 °C (1080 to 1112 °F) and pressures of 24 to 35 MPa (3400 to 4200 psi). It is expected that steam temperatures will rise another 50 to 100 °C (90 to 180 °F) in the next 20 to 30 years.

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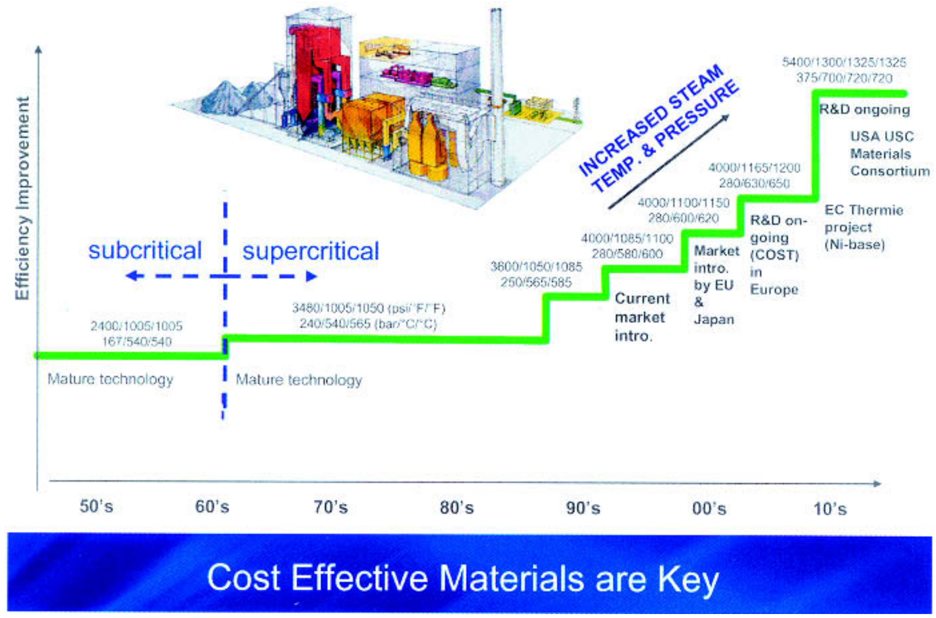


Fig. 1 Historical evolution of steam conditions for coal power plants. Source: (Ref 1)

The main enabling technology in achieving the above goals has been the development of stronger high-temperature materials. Worldwide research has resulted in numerous high-strength alloys for heavy section piping, for the tubing needed to build boilers and rotors, and for the casings, bolting, and blading required to build the steam turbines. The materials community can rightfully take credit for major advances in alloy development during the last decade.

A detailed review of material developments with respect to boilers and turbines was published a few years ago (Ref 2). Since that review, several new alloys have been introduced in the market. Additionally, a major collaborative project has been undertaken in the United States with the goal of achieving steam conditions with temperatures of 760 °C (1400 °F) and pressures of 35 MPa (5000 psi). This article will provide some background and will review the results achieved to date in this study.

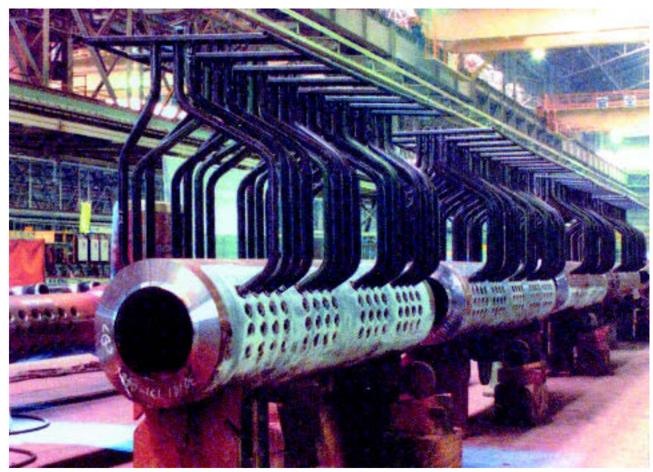


Fig. 2 Illustration of a header

1.2 Boiler Materials Requirements

The key components for which performance is critical for USC plants are high-pressure steam piping and headers, superheater tubing, and waterwall tubing. Steam pipes carry high-pressure, high-temperature steam from the boiler to the turbine. Main steam pipes may be about 50 cm (20 in.) in outer diameter (OD) and 10 cm (4 in.) in wall thickness. Headers are also pipes, but they contain numerous tube penetrations that either bring in or take out steam to or away from the header. An illustration of a header is provided in Fig. 2. Superheater tubes are similar in size to those shown in Fig. 2 and carry superheated steam to the headers. The waterwalls constitute the furnace walls where water is first converted to steam. All of these components have to meet creep-strength requirements. In addition, pipes and headers, which are heavy-section components, are subject to fatigue induced by thermal stresses. Ferritin and martensitic steels are preferred due to their lower coefficient of thermal expansion and higher thermal conductivity compared with austenitic steels. Many of the early problems in the USC plants were traceable to the use of austenitic steels, which were very prone to thermal fatigue. Research during the last decade has, therefore, focused on developing cost-effective, high-strength ferritic steels that could be used in place of austenitic steels. This has resulted in ferritic steels that are capable of operating at metal temperatures up to 620 °C (1150 °F) with good weldability and fracture toughness. At higher temperatures, however, more creep-resistant Ni-base alloys are needed.

Superheater and reheater (SH/RH) tubing applications call for high creep strength, thermal fatigue strength, weldability, resistance to fireside corrosion/erosion, and resistance to steamside oxidation and spallation. Thermal fatigue resistance as well as cost considerations would dictate the use of ferritic or martensitic steels. Unfortunately, the strongest of these steels can be used up to metal temperatures of 620 °C (1150 °F) from a purely creep strength point of view and are still limited by a fireside corrosion metal temperature of 593 °C (1100 °F). (All temperatures cited in this article are steam temperatures

Table 1 Chemical compositions of materials applicable to the temperature above 700 °C (1300 °F)

Materials	C	Si	Mn	Ni	Cr	Mo	W	V	Nb	Ti	B	Others
Super304H	0.10	0.2	0.8	9.0	18.0	…	…	…	0.40	…	…	Cu 3.0, N 0.1
XA704	0.03	0.3	1.5	9.0	18.0	…	2.0	0.3	0.35	…	…	N 0.2
TP310S	0.08	0.6	1.6	20.0	25.0	…	…	…	…	…	…	…
SAVE25	0.10	0.1	1.0	18.5	23.0	…	1.5	…	0.45	…	…	Cu 3.0, N 0.2
Sanicro25	0.08	0.1	1.0	25.0	22.0	…	3.5	…	0.50	…	…	Cu 3.0, Co 1.5, N 0.2
HR3C	0.06	0.4	1.2	20.0	25.0	…	…	…	0.45	…	…	N 0.2
NF709	0.15	0.5	1.0	25.0	20.0	1.5	…	…	0.20	0.10	…	…
Tempaloy A-3	0.05	0.4	1.5	15.0	22.0	…	…	…	0.70	…	0.002	N 0.15
CR30A	0.06	0.3	0.2	50.0	30.0	2.0	…	…	…	0.20	…	Zr 0.03
HR6W	0.08	0.4	1.2	40.0	23.0	…	6.0	…	0.18	0.08	0.003	…
Alloy 800H	0.08	0.5	1.2	32.0	21.0	…	…	…	…	0.50	…	Al 0.4
Hestelloy X	0.08	0.4	0.8	Bal.	22.0	9.0	0.5	…	…	…	…	Fe 18.0, Co 2.0
Hestelloy XR	0.08	0.4	0.8	Bal.	22.0	9.0	0.5	…	…	…	…	Fe 18.0
Inco 617	0.06	0.3	0.3	Bal.	22.0	9.0	…	…	…	0.50	…	Fe 0.6, Co 12.0, Al 1.0, Cu 0.02
Incon 740	0.03	0.5	0.3	Bal.	25.0	0.5	…	…	2.00	1.80	…	Fe 0.7, Co 20.0, Al 0.9
Nimonic 263	0.06	0.1	0.3	Bal.	20.0	5.8	…	…	…	2.20	…	Fe 0.3, Co 20.0, Al 0.4
Hynes 230	0.01	0.4	…	Bal.	22.5	1.3	14.0	…	0.05	…	…	Fe 1.3, Co 0.2, Al 0.3

Source: (Ref 3)

unless otherwise specified. For headers and piping, the metal temperature is nearly equal to the steam temperature. For tubing, the metal temperature is generally higher than the steam temperature by up to 28 °C [50 °F].) This corresponds to a steam temperature of about 565 °C because the SH/RH metal temperature can exceed the steam temperature by as much as 28 °C (50 °F). Poor resistance to steamside oxidation and exfoliation of the oxide scales causes multiple problems. Loss of the cross section and the temperature increase, resulting from decreasing heat transfer, lead to premature creep failures. Exfoliated oxides can cause tube blockages that lead to associated creep failures and erosion damage in the turbine. The excessive corrosion of ferritic steels caused by liquid iron-alkali sulfates in the tube deposits is an acute concern in the United States, where high-sulfur corrosive coals are used more frequently. Therefore, high-strength ferritic stainless steels such as T-91 are infrequently used in the United States. The standard current practice is to use T-22 steel for the lower temperatures and SS304H or SS347 steel for the highest temperatures. At higher temperatures, however, stronger austenitic steels or Ni-base alloys would be needed. Table 1 lists the compositions of typical austenitic steels and Ni-base alloys that are capable of operating at temperatures of >700 °C (1300 °F) (Ref 3). For the composition of other alloys, see Ref. 2.

With respect to waterwall tubing, the concern is twofold. High supercritical pressures and the use of high-heat-release furnaces will increase the waterwall temperatures to the point that easily weldable low-alloy steels such as T-11 (an ASME boiler code steel designation; equivalent pipe steels would be designated as, e.g., P-11 or P-92, while forgings would be designated, e.g., F-11 or F-91) (1.25Cr-0.5Mo) have insufficient creep strength. Higher-strength steels such as T-91 are available but require postweld heat treatments. The second concern is corrosion. Recent results in the United States concerning boilers that were retrofitted with low-NOx burner systems using overfire air have indicated that the present low-alloy steels can suffer from excessive corrosion, as high as 2 mm/year. Weldable high-strength alloys clad or overlaid with high-Cr alloys have to be used to reduce or eliminate excessive corrosion.

1.3 Historical Evolution of Alloys

Masuyama (Ref 3) has presented an excellent historical perspective on the development of steels for power plants. An example of the evolution of materials for boiler application is the evolution of ferritic steels, as shown in Fig. 3. Figure 3 shows 10^5 h creep rupture strength at 600 °C (1112 °F) by year of development. Four generations of evolution have taken place increasing the creep rupture strength at 600 °C for 100,000 h from a mere 60 MPa (8.5 ksi) to nearly 180 MPa (26 ksi). The evolution of ferritic steels has consisted of adding Mo, V, and Nb to simple 9 to 12 Cr steels in the 1960s and 1970s, with optimization of C, Nb, and V content occurring during the late 1970s and early 1980s, Partial substitution of W for Mo in the late 1980s and early 1990s was followed by the additions of more W and Co in the current generation of steels.

The role of alloying elements in the development of the ferritic steels has been extensively investigated. Tungsten, Mo, and Co are primarily solid-solution strengtheners. Vanadium and Nb contribute to precipitation strengthening by forming fine and coherent precipitates of the M(CN)X-type carbonitrides in the ferritic matrix. Vanadium also precipitates as VN during tempering or during long-term creep. The two elements are more effective in combination at levels of about 0.25% V and 0.05% Nb. Chromium contributes to solid solution strength, as well as to oxidation and corrosion resistance. Nickel improves the toughness but at the expense of creep strength. The partial replacement of Ni by Cu helps to stabilize the creep strength. Carbon is required to form fine carbide precipitates, but the amount needs to be optimized for good weldability. Atom probe results have shown that B enters the structure of $M_{23}C_6$ and segregates to the $M_{23}C_6$-matrix interface. It has also been suggested that B helps to reduce the coarsening of $M_{23}C_6$ and assists in the nucleation of VN, enhancing the "latent creep resistance." Cobalt is an austenite stabilizer and is known to delay recovery on tempering of martensitic steels. Cobalt also promotes the nucleation of finer secondary carbides on tempering. This is attributed both to its effect on recovery and its effect on the activity of C. Cobalt also slows coarsening of alloy carbides in secondary hardening steels. This may be the result of Co increasing the activity of C

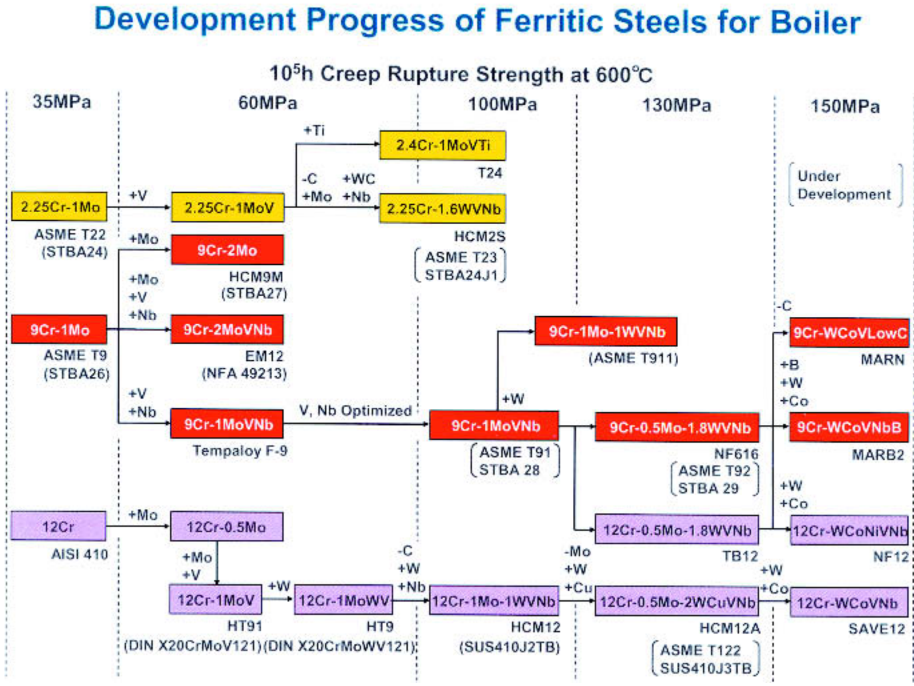


Fig. 3 Evolution of ferritic steels for boilers. Source: (Ref 3)

because Co is not soluble in alloy carbides. Hidaka et al. (Ref 4) have reported extensively on the role of Co in ferritic steels.

Ferritic steel developments are mostly aimed at their use for thick section pipes and headers. Among the 9% Cr steels fully commercialized, the P91 steel has the highest allowable stress, and has been extensively used all over the world as a material for headers and steam pipes in USC plants operating at steam temperatures up to 593 °C (1100 °F). Alloy NF616 (P-92), which was developed by substituting part of the Mo in P91 steel with W, has an even higher allowable stress and can be operated at steam temperatures up to 620 °C (1150 °F). E911 is a European alloy that is similar in composition to NF616 and has similar high-temperature strength capabilities. Beyond 620 °C (1150 °F), the 9% Cr steels are limited by their oxidation resistance, and 12% Cr steel and austenitic steels have to be used.

Among the 12% Cr steels, HT91 has been widely used for tubing, headers, and piping in Europe. The use of the steel in Japan and the United States has been limited due to its poor weldability. HCM12 is an improved version of HT91 with 1% W and 1% Mo, and has a duplex structure of δ-ferrite and tempered martensite, leading to improved weldability and creep strength. Further increases in creep strength are achieved by substituting more W for Mo, and adding Cu. This has resulted in alloy HCM12A (P-122), which can be used for header and piping up to 620 °C (1150 °F). Two alloys, NF12 and SAVE12, have even higher creep strengths than HCM12A and are in the developmental stage. NF12 contains 2.5% Co, 2.6% W, and a slightly higher quantity of B compared with HCM12A. SAVE12 contains 2% Co, 3% W, and minor amounts of Ta and Nb. These latter elements contribute to strength by producing fine and stable nitride precipitates. HCM2S (T-23) is a low-C 2.25Cr-1.6W steel with V and Nb. It is a cost-effective steel with a higher creep strength than T-22. Due to its excellent weldability without preweld or postweld heat treatment, it is a good candidate for waterwall tubing.

In the field of austenitic steels, efforts were made from the 1970s to the early 1980s to improve conventional 18Cr-8Ni series steels that were originally developed as corrosion-resistant materials for chemical use, mainly with respect to their creep strength. Another goal pursued from the 1980s to the early 1990s was to improve the creep strength of conventional 20 to 25Cr steels that have superior oxidation and corrosion resistance.

Austenitic steels are candidates primarily in the finishing stages of SH/RH tubing, where oxidation resistance and fireside corrosion, in addition to creep strength, become important. From a creep strength point of view, T-91 is limited to 565 °C steam (593 °C metal), while NF616, HCM12A, and E911 are limited to 593 °C steam (620 °C metal). Even the strongest ferritic steel today is limited to a metal temperature of 593 °C (1150 °F) from an oxidation point of view. At temperatures above these, austenitic steels are required. Hence, there has been considerable development with respect to austenitic stainless steels. In actual practice in the United States, SS304M and SS347 are widely used instead of T-91 in superheater applications, mainly because they are easier to weld and the cost difference is relatively small.

An evolution tree for austenitic steels, similar to that in Fig. 3, may be found in the article by Masuyama (Ref 3). The austenitic steels fall into four categories: 15% Cr; 18% Cr; 20 to 25% Cr, and >25% Cr stainless steels. The various stages in the evolution of these steels have consisted of initially adding Ti and Nb, or Mo, to stabilize the steels from a corrosion point of view, then reducing the Ti, Nb, and Mo content while increasing the C content (i.e., understabilizing) to promote creep strength rather than corrosion resistance. This is followed by Cu additions to increase precipitation strengthening through a fine dispersion of a Cu-rich phase (Super 304H) or through heat treatment to obtain a fine grain size with low oxide exfoliation tendencies (347HFG). Further trends have included austenitic stabilization using 0.2% N with W addition for solid solution strengthening (347W). Thus,

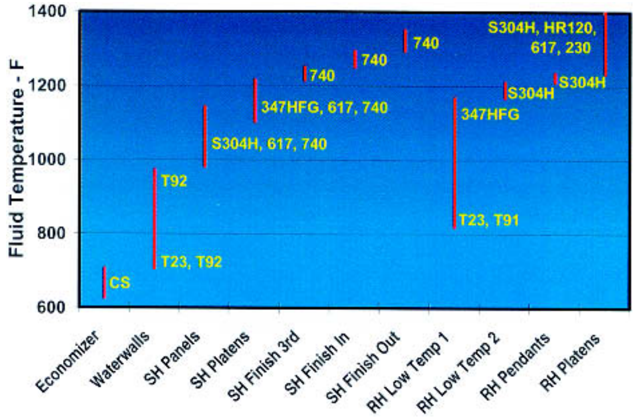


Fig. 4 Possible alloy choices for various components of a USC boiler. Source: (Ref 8)

Table 2 Candidate alloys for USC boiler in the US program

Alloy	Nominal composition	Developer	Application
Haynes 230	57Ni-22Cr-14W-2Mo-La	Haynes	P, SH/RH tubes
Inco 740	50Ni-25r-20Co-2Ti-2Nb-V-Al	Special Metals	P, SH/RH tubes
CCA 617	55Ni-22Cr-.3W-8Mo-11Co-Al	VDM	P, SH/RH tubes
HR6W	43Ni-23Cr-6W-Nb-Ti-B	Sumitomo	SH/RH tubes
Super 304H	18Cr-8Ni-W-Nb-N	Sumitomo	SH/RH tubes
Save12	12Cr-W-Co-V-Nb-N	Sumitomo	P
T-92	9Cr-2W-Mo-V-Nb-N	Nippon Steel	WW tubes
T-23	2-1/4Cr-1.5W-V	Sumitomo	WW tubes
HCM12	12Cr-1Mo-1W-V-Nb	…	WW tubes

Note: P, pipe; WW, waterwall

the most creep-resistant steel contains Cr, Ni, W, Co, Cu, and N.

2. Objectives and Task Description

This study, through a government/industry consortium, has undertaken a five-year effort to develop materials that allow the use of advanced steam cycles in coal-fired power plants. The specific objective of the study is to identify, develop, and evaluate materials for application in critical components in fossil boilers that are capable of operating at a temperature of 760 °C and a pressure of 35 MPa (1400 °F/5000 psi). This objective is expected to be achieved through the eight tasks listed below:

Task 1. Conceptual design and economic analysis;
Task 2. Mechanical properties of advanced alloys;
Task 3. Steamside oxidation and resistance;
Task 4. Fireside corrosion resistance;
Task 5. Weldability;
Task 6. Fabricability;
Task 7. Coatings; and
Task 8. Design data and rules

The progress made to date on each of these tasks is described below.

3. Results

3.1 Preliminary Design and Economic Studies

Conceptual design and economic studies have been completed. Alloy selection, component sizing, and the delineation of temperature/stress profiles have been performed. Economic viability has been shown. Material procurement has been completed. Based on metal temperature calculations performed for various sections of a conceptual boiler (Ref 5-7), possible material selections for various sections of the boiler were performed and are summarized in Fig. 4 (Ref 8). Based on creep strength and allowable stress considerations, and on data availability considerations, Haynes 230, Inconel 740, and CCA 617 (a designation for composition alloy modified alloy 617) were selected for heavy-section, high-temperature headers and pipes, and SH/RH tubing. The austenitic HR 6W and Super 304H steels were selected primarily for use in high-temperature SH/RH sections, while ferritic alloy SAVE12 was selected for use in heavy sections at lower temperatures. Alloys T-92, T-23, and HCM12 were considered for applications in waterwall tubing. The compositions and intended applications of the various alloys are shown in Table 2.

The feasibility of designing a USC 750 MW boiler operating under throttle steam conditions of 760 °C (1400 °F) and 35 MPa (5000 psi) with existing material technology is encouraging. It was estimated that this design will increase the plant efficiency from an average of 37% HHV (current domestic subcritical fleet) to approximately 45% (HHV) (Ref 5, 6). For a double-reheat configuration, the efficiency will reach 47%. The efficiency increase from 37 to 47% HHV is expected to save nearly $16.5 million annually in fuel costs, or $330 million over a 20-year plant life for a 750 MW plant operating at 80% capacity at a coal cost of $1.5 per MBtu. The CO_2 and other fuel-related emissions will be reduced from 0.85 to 0.67 tonnes/MWh, a reduction equal to nearly 22%. This reduction in emissions amounts to an annual reduction of nearly 700,000 tons of CO_2 (Ref 7). The economic viability of a USC plant is encouraging. As a result of the reductions in fuel and balance-of-plant (BOP) costs, boiler and steam turbine capital costs can be permitted to climb by 40 to 50% compared with a conventional subcritical plant. The actual estimated cost increase due to material costs was estimated to be only 28%, indicating that a USC plant would be economically viable despite higher material costs.

3.2 Mechanical Properties

Figure 5 is a plot of the allowable stresses versus temperature for comparing the temperature capabilities of various classes of alloys (Ref 9). The figure also shows the actual stresses at several steam pressures (Ref 9). The Ni-base alloys are superior to the austenitic steels, which, in turn, are better than the ferritic steels. The Ni-base alloys Inconel 740, Haynes 230, Inconel 625, Inconel 617, HR6W, and HR 120 have a much higher temperature capability (in decreasing order as listed) compared with austenitic steels. The ferritic steels follow the austenitic steels. Purely from the creep strength point of view, at a pressure of 35 MPa (5000 psi) for a 5 cm (2 in.) outside diameter tube with a 1.25 cm (0.5 in.) wall thickness

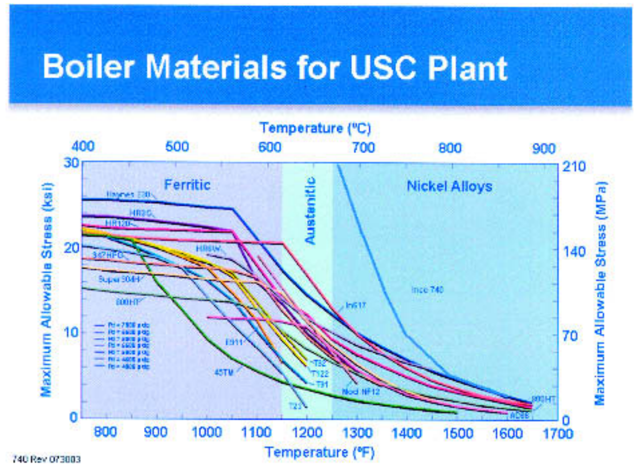


Fig. 5 Allowable stress for various classes of alloys. Source: (Ref 9)

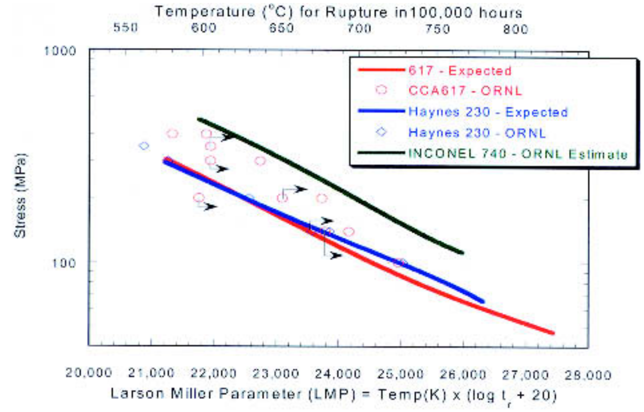


Fig. 6 Example of creep rupture data obtained. Source: (Ref 10)

(stress equal to 60 MPa or 8.6 ksi), ferritic steels are useful up to a metal temperature of ~620 °C (1150 °F), and austenitic steels are useful up to ~675 °C (1250 °F). At metal temperatures higher than this, Ni-base alloys need to be used.

Creep rupture tests were completed on several alloys for times exceeding 14,000 h (Ref 10). Figure 6 illustrates the type of data that was generated (Ref 11). Several preliminary conclusions have so far been reached.

The creep-rupture properties of Super 304H superheater tubing are as expected. The creep-rupture strength of HR6W superheater tubing is lower than expected and does not show strength improvement compared with current commercial materials. A modified chemistry 617 alloy, named CCA617, shows much improved creep rupture strength compared with 617 at temperatures between 600 °C (1112 °F) and 700 °C (1292 °F). However, the strengths appear to converge at between 750 °C (1382 °F) and 800 °C (1475 °F). The creep-rupture properties of Haynes 230 are as expected, with the weld metal being weaker than the base metal. Inconel 740 has sufficient strength to reach the target steam conditions of the program for the hottest section of the boiler. The rupture properties obtained in this program for Iconel 740 exceed those reported in the literature, presumably due to the use of an optimized heat treatment.

Future mechanical property work that will be pursued includes: long-term creep tests on all the materials; notched bar creep tests; creep-fatigue testing; the testing of weldments and dissimilar metal welds; the mechanical characterization of thick section materials (including 7.5 cm [3 in.] thick welded plates); cold work limits (U-bend tubes under pressure); and model validation tests (i.e., creep testing on deeply notched thick sections). A new 9% Cr alloy developed by the National Institute of Materials Science (NIMS) of Japan has been advertised to have a rupture life that is two orders of magnitude higher than that of the strongest known 9% Cr alloy (T-92).

3.3 Steamside Oxidation Tests

These studies are designed to determine the steam-side oxidation behavior and temperature limits of commercially available ferritic materials, austenitic stainless steels, and Ni-base alloys, to collect the available literature on the steam-side oxidation of these materials, and to increase our understanding of the mechanism of steam-side oxidation and the effects of variables such as alloying content and environmental conditions (Ref 11).

The test environment used is high-purity water with 100 to 300 ppb of dissolved oxygen and 20 to 70 ppb ammonia, resulting in a pH of 8.0 to 8.5. Inside a furnace, the test solution flashes to steam and passes into the retort that contains the test specimens. The specimens are coupons that are hung from a test frame and oriented parallel to the flow stream. The test setup has been explained in greater detail elsewhere (Ref 11).

In general, six coupons are tested from each material at each temperature. The coupons are measured and weighed prior to testing. At each shutdown, the coupons from each material are removed and weighed to determine the mass change. One coupon from each material is cross-sectioned and metallographically examined in the scanning electron microscope, which is equipped with an energy-dispersive x-ray spectrometer, to determine oxide morphology and composition. The other coupon from each material is descaled and reweighed to determine the descaled mass loss experienced by each material.

Steamside oxidation testing has been completed at 650 °C (1200 °F) up to durations of 4000 h (Ref 11). Test results show that among the ferritic steels, two new steels, MARB2 (developed by NIMS) and VM12 (Vallourec & Mannesman Tubes, Boulogna Cedex, France) display the best oxidation behavior, and all other 2 to 9% Cr steels are subject to severe oxidation (Fig. 7). The mass loss exhibited by ferritic steels appears to correlate with the factor (0.9Cr-63C-240B). The chromized P-92 steel appeared to perform better than the uncoated ferritic steels, but not as well as the austenitic steels. Ferritic steels that exhibit the lowest mass loss also exhibited the lowest tendency to spall. Clear evidence of spallation is observed in T-23, T-91, and T-92. Other ferritic steels had much better resistance to spallation. No spallation is observed in the austenitic steels or Ni-base alloys in the tests conducted at 650 °C (1200 °F). Of the austenitic and Ni-base alloys, the cocontaining ones (i.e., Nimonic 263, and CCA 617 and 740) exhibited the best oxidation behavior. The results also indicate that at 650 °C (1200 °F), all of the austenitic and Ni-base alloys formed a dense Cr oxide that resulted in low oxidation rates. The oxidation of the alloys primarily followed parabolic kinetics, and the rate constants calculated from the tests were in agreement with literature data for alloys where this information was available.

Steamside oxidation testing has been performed at 800 °C (1475 °F) for up to 1000 h on 20 different ferritic, austenitic,

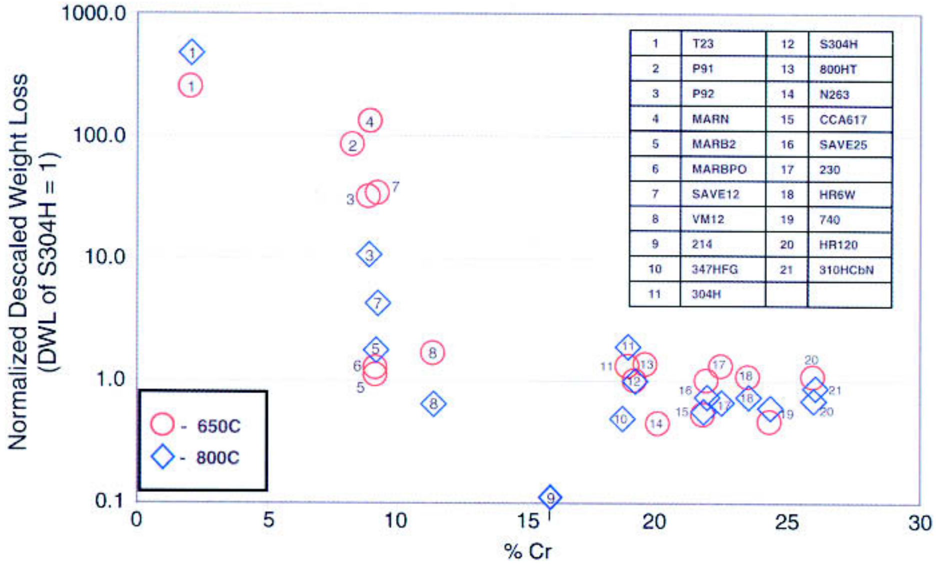


Fig. 7 Normalized mass loss of sample after steamside oxidation for 1000 h at 800 °C. Source: (Ref 11)

and Ni-base alloys and coated materials. The results from this test shown in Fig. 7 indicate that the oxidation susceptibility is independent of Cr level, once a threshold level of about 10% is reached. The ferritic steel VM12 performed as well as some austenitic steels and Ni-base alloys. As expected, all alloys experienced greater oxidation at 800 °C (1475 °F) than at 650 °C (1200 °F). The austenitic alloy 214 (which contains ~4.5% Al) exhibited the lowest amount of oxidation and was found to have formed a dense Al oxide scale during exposure. Nickel-base alloys containing between 0.5 and 1.3% Al displayed near-surface intergranular Al oxide penetrations. Ferritic steel MARB2 and austenitic steel 304H formed oxide islands, which is indicative of the development of a nonprotective oxide. The predominant tendency among the austenitic steels for scale exfoliation was found in 347HFG. Among the diffusion coatings applied in this research, SiCr and FeCr coatings performed much better than AlCr coatings.

3.4 Fireside Corrosion

The objective of these studies was to evaluate the relative resistance of various advanced alloys to fireside corrosion over the full temperature range expected for the USC plant (Ref 12). The corrosive environment, promoted by three different coals, represented by an eastern coal, a Midwestern coal, and a western coal, were evaluated. Eastern and midwestern coals generally tend to be higher in S, and hence, more corrosive compared with the western coal.

Three types of testing were undertaken: laboratory testing, wherein, specimens coated with the appropriate deposit composition were exposed to a gas mixture simulating the fireside corrosion/superheater corrosion environment; steam loops formed by welding together spool pieces of the various materials, which were inserted into the superheater circuit for exposure to the actual boiler conditions (by controlling flow rates to various locations, temperatures could be controlled); insertion of retractable air-cooled probes inside the boiler; and evaluation of the samples after various exposures. Of these, only the laboratory corrosion tests have been completed. The field testing using steam loops has been started, but results have not yet been obtained and analyzed.

Laboratory tests have been completed under waterwall conditions at 454 °C (850 °F), 525 °C (975 °F), and 593 °C (1100 °F) for 1000 h. Similarly, fireside corrosion tests under superheater conditions have been completed at 650 °C (1200 °F) and 816 °C (1500 °F) for 1000 h. The waterwall experiments consisted of coating the specimens with a deposit of FeS, $CaSO_4$, Fe_3O_4, and C of variable compositions and exposing them to flue gas containing CO, CO_2, H_2O, and N with varying levels of SO_2. The SH/RH conditions called for deposits containing alkali sulfates, $CaSO_4$, and C, and a flue gas composition of O_2, H_2O, CO_2, and variable levels of SO_2 and Cl. In other words, the waterwall conditions are more reducing than the SH/RH conditions.

Figure 8 illustrates the data obtained under SH/RH simulation at 650 °C (1200 °F) (Ref 12). As expected, specimens tested using midwestern and eastern coals exhibited more wastage than those tested using western coals. For wrought alloys, the wastage decreased as the Cr level increased. In the absence of the Mo effect (i.e., in the 816 °C [1500 °F] specimens), the wastage tended to level off for alloys in the 22 to 27% Cr range. Specimens tested at 650 °C (1200 °F) and 704 °C (1300 °F) displayed more surface attack, whereas specimens tested at 816 °C (1500 °F) exhibited more subsurface penetration. At 816 °C (1500 °F) using midwestern coal specimens, the Mo-containing alloys experienced more attack than the alloys without Mo. In other words, the higher the Mo content, the greater the wastage.

Of the weld overlays, 72 (typically 42% Cr) and 52 (typically 28% Cr) performed better than 622 (typically 21% Cr) at all temperatures, with 72 performing better than the 52. At 650 °C (1200 °F) and 704 °C (1300 °F), the 72 and 52 were better than the wrought alloys in the 22 to 27% Cr range. With regard to the diffusion coating (on Super 304H), the FeCr and SiCr performed better than the AlCr, which exhibited the most extensive subsurface penetration. The FeCr and SiCr were comparable to the weld overlays, but because they are thinner they will be breached more quickly.

In the case of the waterwall corrosion, testing performed using midwestern and eastern coals exhibited more wastage than that using western coal (Fig. 9) (Ref 12). The difference in

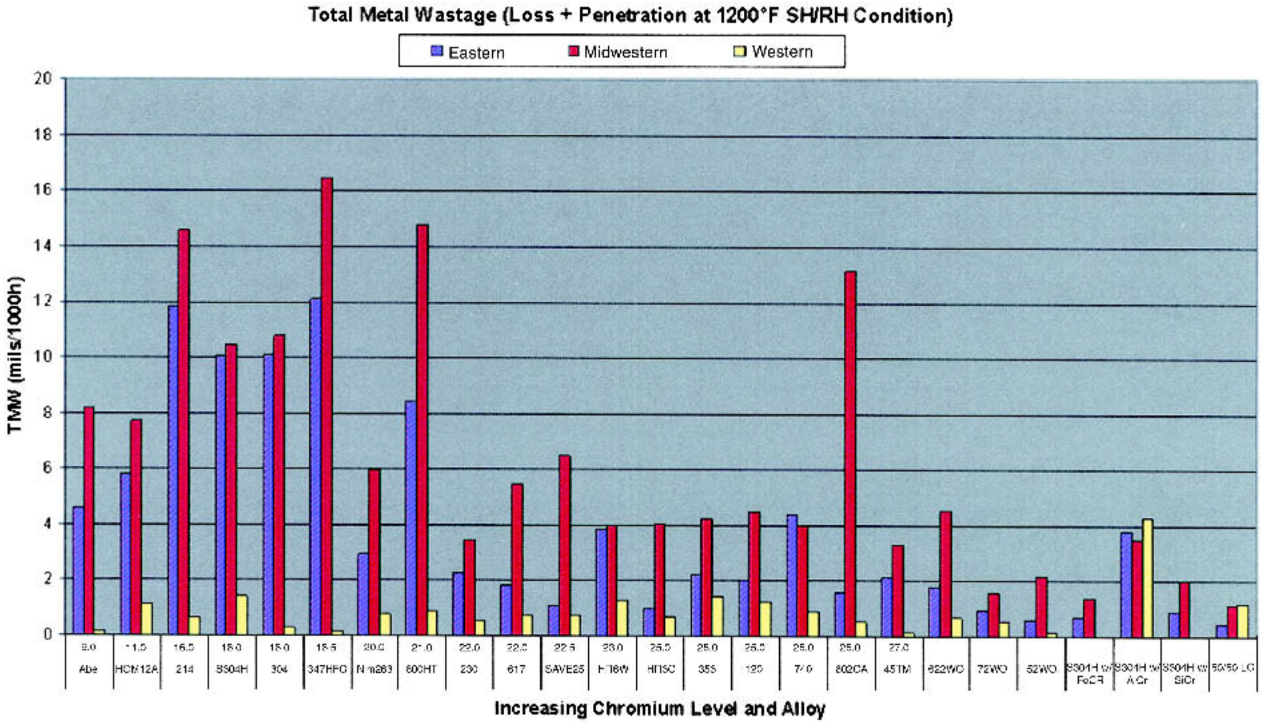
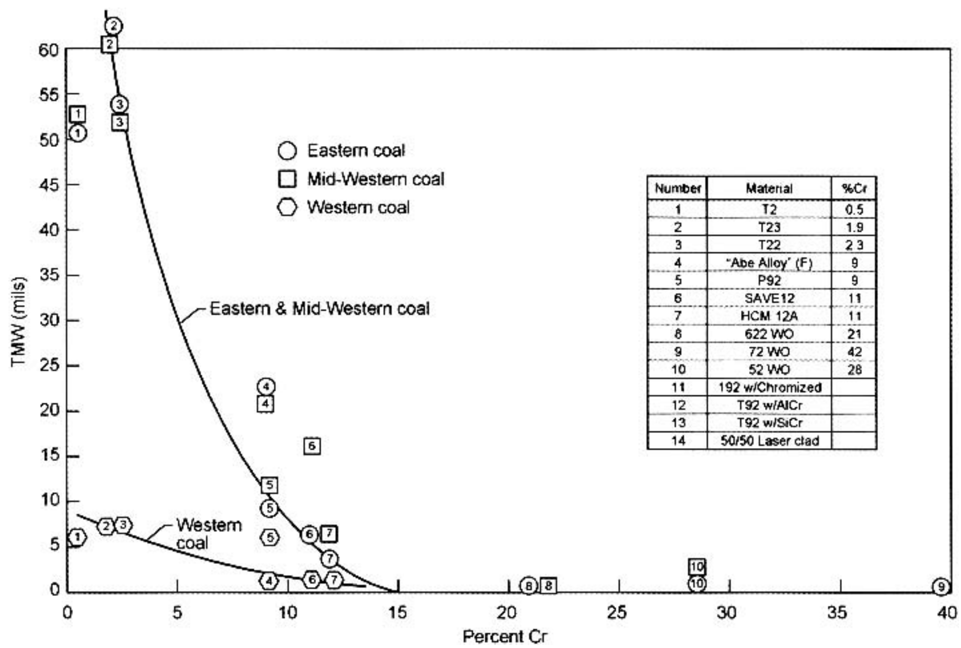


Fig. 8 Illustration of fireside corrosion under superheater conditions for 1000 h at 650 °C (1200 °F). Source: (Ref 12)



Number	Material	%Cr
1	T2	0.5
2	T23	1.9
3	T22	2 3
4	"Abe Alloy" (F)	9
5	P92	9
6	SAVE12	11
7	HCM 12A	11
8	622 WO	21
9	72 WO	42
10	52 WO	28
11	192 w/Chromized	
12	T92 w/AlCr	
13	T92 w/SiCr	
14	50/50 Laser clad	

Fig. 9 Total metal wastage for alloys under waterwall conditions at 525 °C (975 °F) for 1000 h. Source: (Ref 12)

the amount of wastage between the midwestern/eastern and western coal conditions was greater at 454 °C (850 °F) and 525 °C (975 °F) than at 593 °C (1100 °F). The Abe and SAVE12 alloys displayed higher wastage than the P-92 and HCM12A alloys, respectively, at all three temperatures. The Abe and SAVE12 alloys contained Co.

The 622, 52, and 72 weld overlays, and the 50/50 laser clad overlay material, display significant improvement in corrosion resistance compared with the wrought alloys at all temperatures. The 622 overlay started to show more attack at 593 °C (1100 °F) compared with 52 and 72. With regard to the diffusion coatings (on T-92), they also exhibited significantly improved corrosion resistance compared with the wrought alloys. The chromized coating displayed the best performance followed by the SiCr and the AlCr. As in the SH/RH tests, the AlCr coating exhibited the most significant subsurface attack.

Two steam loops were fabricated, hydrotested for leaks, and installed at a utility power station during a scheduled outage

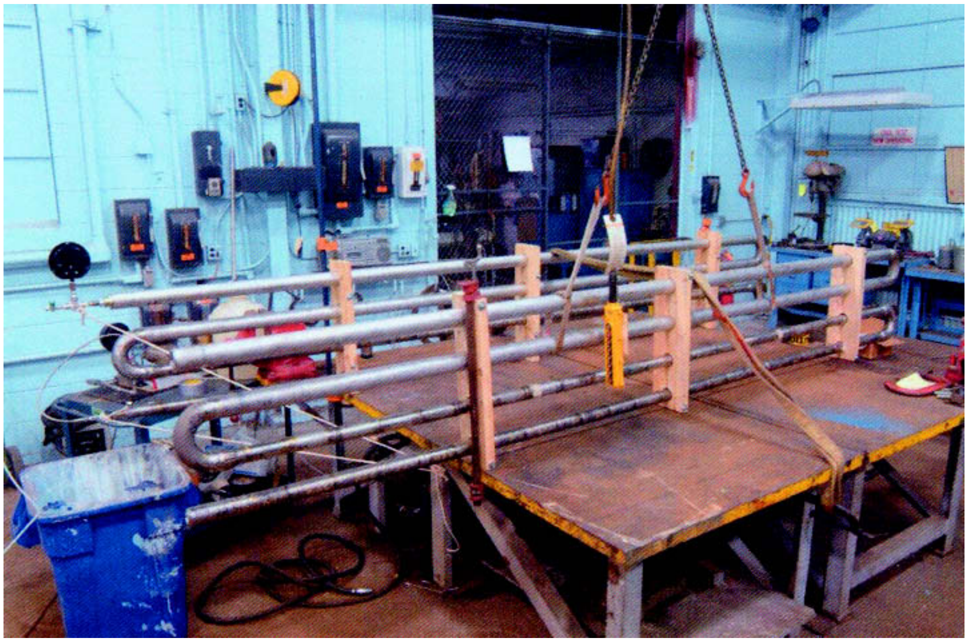


Fig. 10 Steam loop assembly being hydrotested prior to the attack in a boiler at the Niles power station. Source: (Ref 13 and 14)

(Ref 13, 14). Figure 10 shows one of the loops being hydrotested prior to installation in a boiler. The testing of loops at a plant that burns high-sulfur coal has been initiated. Throughout the planned 18 month testing of the loops, steam flow will be throttled to simulate the operating conditions of a USC boiler design, in which metal temperatures up to 760 °C (1400 °F) will be maintained. Operating parameters during the test will be monitored using an online remote-access computer system. During outages at the plant, the test loops will be physically examined within the boiler, diametrically measured for hot corrosion wastage, photographed, and assessed for performance.

3.5 Weldability Studies

The scope of this task included the study of six different alloys (SAVE12, Super 304H, HR6W, Haynes 230, Inconel 740, and CCA 617) utilizing two product forms (i.e., tubing and pipe, or plate). Welding procedures for 15 alloys/product forms/welding process combinations were developed, and weldments for the evaluation of each of the 15 combinations were produced. It was also desired that a welding procedure be developed for three dissimilar metal weld configurations (Ref 15).

Preliminary results indicate that submerged arc welding (SAW), a high-deposition rate process favored by boilermakers for thick sections, might not be feasible for Ni-base materials. Tests on Haynes 230 and Inconel 740 have been unsuccessful, and the process has been temporarily suspended, at least on these alloys. A 7.5 cm (3 in.) thick plate of Haynes 230 was successfully welded using the pulsed gas metal arc welding (GMAW) technique, as shown in Fig. 11 (Ref 16).

An orbital gas-tungsten arc-welding (GTAW) process has been qualified for Super 304H, and test specimens are being fabricated. Attempts to weld tubing using an automatic GMAW process were unsuccessful. Switching to type 347 weld filler produced acceptable welds. An orbital GTAW process was qualified for CCA 617 tubing. The SAW process was qualified for use with plate, and test specimens are being fabricated. Attempts to perform shielded metal arc welding (SMAW) using matching filler were unsuccessful due to slag control problems with the CCA 617 electrodes. On the other hand, successful SMAW welds were achieved using conventional 617 electrodes. Collaboration is being pursued with the alloy vendor (Special Metals, Huntington, WV) in view of their experience in welding 2.5 cm (1 in.) thick plates of Inconel 740 using GMAW. Summary results of welding trials to date are presented in Table 3 (Ref 15) for SAVE12. Similarly, results have been recorded for the other alloys.

Fig. 11 End view of a completed 7.5 cm (3 in.) thick Haynes 230 alloy weld. Source: (Ref 16)

3.6 Fabricability Studies

The primary objective of this task was to conduct fabrication studies on USC materials and to assess the effect of fab-

Table 3 Illustration of weldability data for SAVE12

Product form	Weld type	Process	Filler	Comments
2-in OD tube	Butt	Manual GTAW	Grade 92	Qualified
		Manual GTAW	Save 12	First sample failed bend testing; second sample completed using modified PWHT, awaiting results of qualification tests
		SMAW	SAVE 12	First sample failed bend testing; second sample completed using modified PWHT, awaiting results of qualification tests
13.78-in. OD pipe	Butt	Manual GTAW	SAVE 12	Sample welded, PWHT pending results of tube qualification tests
		SMAW	SAVE 12	Sample welded, PWHT pending results of tube qualification tests
		SAW	SAVE 12	Sample welded, PWHT pending results of tube qualification tests

Source: (Ref 15)

rication on material properties, so that potential fabrication problems may be identified (Ref 16). Experience in welding, machining, cutting, boring, and grinding USC alloys Haynes 230, Inconel 740, HR6W, CCA 617, and Super 304 H stainless steel has been gained during the development and construction of the two USC test loops. Protective weld overlay claddings with alloys Inconel 52, Inconel 72, and Inconel 622 were also successfully applied to tube sections that form the loops. Field welding of the USC materials was additionally demonstrated during the installation of the test loops at the Niles, OH, plant. Controlled straining (range 0 to 50%) of special tapered tube specimens was conducted to produce deformed materials needed to conduct studies in characterizing the recrystallization/precipitation behavior of USC alloys. The fabrication of multiple U-bends produced from Haynes 230 and HR6 W tubing (5.1 cm [2 in.] outside diameter × 1 cm [0.4 in.] MW) was successfully demonstrated using production equipment. Tube U-bends with strains of 15, 20, and 35% were produced. These examples are shown at the bottom of Table 4. Swaging trials of two of the USC alloys were also completed. Technical data on recrystallization behavior, phase precipitation, and dissolution in USC alloys are being compiled to assist in the understanding and development of USC boiler fabrication procedures. The fabricability evaluation of most of the alloys is nearly complete. A sample table illustrating the results summary for one of the alloys is shown in Table 4 (Ref 17). Similarly, results have been recorded for the other materials.

To demonstrate the fabrication capabilities achieved in the course of this project, a mock-up section of a header was fabricated using plate to form the header by bending (Fig. 12). The mock-up illustrates the capabilities for the fabrication of the CCA 617 alloy into a header shape. Girth welding, seam welding, socket welding, machining, swaging, hole drilling, and bending of the CCA 617, as well as dissimilar welding between CCA 617 and 304H and T-91 tubing, have been successfully accomplished.

3.7 Coatings

Several specimens with claddings, spray coatings (cold spray, high-velocity oxyfuel (HVOF)) and diffusion Cr, Cr-Si, and Cr-Al coatings have been prepared and subjected to steam oxidation tests in the laboratory (Ref 8). The results show that ferritic steels benefit most from coating, while austenitic steels may benefit. Ni-base alloys are not likely to need coatings at these temperatures. Process scale-up activities are being pursued. The scale-up tests for the chromizing process have been completed, and the evaluation of the results revealed excellent reproducibility for both Super 304H and T-92. The development of parameters for depositing HVOF and cold-spray techniques for 50Ni-50Cr coatings is complete. Based on these results, optimal parameters have been selected and used to coat Haynes 230 tubes. Developing plasma-transferred arc parameters for the deposition of 50Ni-50Cr has begun. Laser-cladding parameters for depositing the 50Ni-50Cr alloy are in the process of being developed.

3.8 Design Approaches

Within the current design codes for boilers, piping, and pressure vessels, there are a number of different equations for the thickness of a cylindrical section under internal pressure. Some of the design codes have more than one formulation, and, in the most extreme case, ASME section I contains three. This "design-by-rule" approach is empirical and suffers from numerous shortcomings, such as the inability to deal with different configurations, discrepancies between international codes, variability in factors of safety, the inability to address non-steady loads, inadequacy in treating welds, the lack of a practical methodology for use with advanced finite-element techniques, and the empiricism of the safety margins applied. At the present state of the art, a single formula that can retain the same safety margins in both the time-dependent and time-independent regimes could replace all of these various formulations. Fishburn and Perrin (Ref 18) have proposed a reference stress approach that permits a "design by analysis," overcoming many of the limitations of the current practice. The new set of equations proposed under this approach applies to all cylindrical components using analytical methods. The impact of the new design equations will be that a consistent failure criterion will be applied to all sizes and types of cylindrical sections. This criterion incorporates a limit-load approach in the time-independent regimen and a reference stress approach in the time-dependent regimen. The significance of these equations is that in high-pressure designs the equations are less conservative than those currently in use. Specifically, the following benefits will be derived from the proposed rules: they will permit the use of thinner wall components than would be permitted under the current ASME and European rules without compromising component reliability and safety. It is estimated that in USC boilers, where expensive materials are required, a 12% reduction in the cost of boiler pressure parts can be achieved. Thinner wall components are also less prone to thermal fatigue, and therefore, the plant would be able to be cycled. The less conservative approach would be to permit the use of lower-creep-strength materials under a given set of conditions, thus offering a wider selection of materials for use at high temperatures. The proposed revisions to section I of the ASME code to permit the use of simplified, and more technically defensible, design equations were submitted to Subcommittee I and were accepted by them on September 2, 2004. Subsequent

Table 4 Current status of workplan activities for alloy 230

USC alloy (participant)	Evaluation planned	Results and status	Comments	Follow-on activities
Alloy 230 (B&W)	Cold U-bend trials	13.3, 20, and 33.3%	Good; some ovality	P-Creep at ORNL
	Tubewelding trials	625 filler; 622, 52, 72 WOL	Good; field test loops fabricated	Fabricate demonstration article
	Machining trials	Completed	Good; field test loops fabricated	Fabricate demonstration article
	Strain/Rx/Pptn trials	1500 and 1600°F	100, 250, 400, and 550	Assess microstructures
	Swaging trials	Planned Spring 2005	Machined tubes to 0.2 in. wall	Assess microstructures
	Demonstration article fabrication	Planned Spring 2005	Design completed	Fabricate; display TBD

Source: (Ref 17)

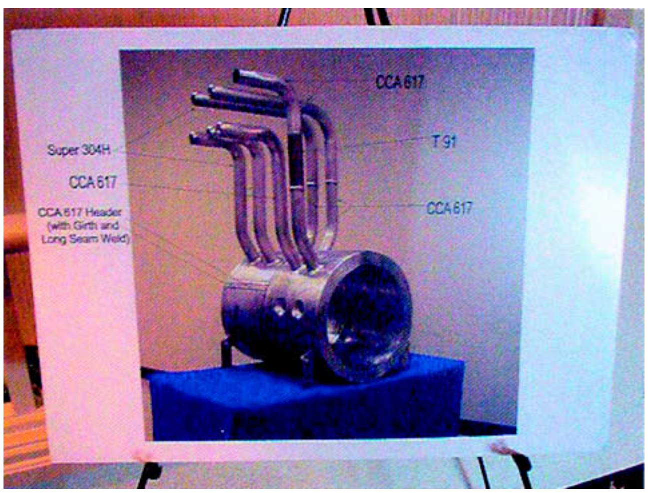


Fig. 12 Mock-up header section used to demonstrate the fabrication techniques developed in the study. Source: (Ref 1)

to that, they were included in the Main Committee ballot. Feedback is being awaited.

4. Follow-On Work

The USC boiler project that is currently in progress has made substantial progress in laying the groundwork for the selection and use of materials that can operate under steam conditions up to 760 °C (1400 °F). However, much more work is needed to support a national program to move into high-efficiency USC power generation. Most of the design issues and integration with BOP has yet to be worked out. Further studies are needed in the materials area with respect to the weldability of high-strength alloys, oxidation and exfoliation in boiler tubes, the investigation of weld strength reduction factor, and many others. Most importantly, parallel technology has to be developed for steam turbines and BOP components. Another major area that is gaining attention is called *oxyfuel combustion technology*.

Oxycombustion, which is also known as oxyfuel combustion, is a technology under development that involves burning fuel in the presence of essentially pure (i.e., 95 to 99.5%) oxygen rather than air, and recycling flue gas to the combustion chamber to moderate temperature (thus performing the same role of nitrogen in air). There are two major advantages to this technology. The first is that in the absence of nitrogen from air, the amount of nitrogen oxides that forms when fuel is combusted are significantly lower. The absence of nitrogen from air in the flue gas also means that the flue gas is almost pure carbon dioxide, which then can be captured at a much lower cost than from a conventional power plant. This second point is the more important of the two if carbon dioxide emission regulations are ever put into place in the future. Most of the materials issues that need to be addressed with respect to this technology are the same as those being addressed in the current USC boiler project. Exceptions may exist in the areas of more severe hot corrosion and corrosion due to more intense streams of CO_2. These issues are being addressed in a follow-on program.

5. Summary

The technical and economic feasibility of designing a USC 750 MW boiler operating at a temperature of 760 °C (1400 °F) and a pressure of 35 MPa (5000 psi) with existing materials technology is encouraging. This plant would be capable of achieving a net plant efficiency of about 45% HHV. With a double-reheat configuration, a plant efficiency of 47% could be achieved. Materials needed for the construction of various parts of the boiler have been identified. Studies pertaining to mechanical properties, steamside oxidation resistance, fireside corrosion resistance, weldability, fabricability, and the use of coatings/claddings are nearing completion. Design approaches that are less conservative and more robust have been explored, with a view to extending the range of applicability of the available materials to higher temperatures and stresses.

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