MASTER

PERFORMANCE OF TYPE 316 STAINLESS STEEL
IN SODIUM-POTASSIUM EUTECTIC ALLOY
During 32,600 Hours Service

by

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ABSTRACT

The Waste Calcining Facility at the Idaho Chemical Processing Plant of Idaho Nuclear Corporation utilizes a fluidized-bed calciner for converting highly radioactive aqueous waste into granular solids. Heat has been supplied to this calciner by circulating sodium-potassium (NaK) eutectic alloy at 760°C through a bayonet heat exchanger in the fluidized-bed of solids.

Service test examinations were performed on the Type 316 stainless steel loop for circulating the NaK eutectic alloy. These examinations of the stainless steel loop revealed the cumulative effects of 32,600 hours of operation at temperatures of 590 to 780°C during eight years service. Although Type 316 stainless steel performed satisfactorily, the results showed that changes in mechanical properties and metallurgical effects occur with circulating non-isothermal NaK in contact with Type 316 stainless steel. Some mass transfer of alloying elements from the hot regions of the Type 316 stainless steel loop to the colder regions was observed. The mitigation of these effects is discussed.

SUMMARY

The Waste Calcining Facility (WCF) at the Idaho Chemical Processing Plant employs a fluidized bed calcination process for converting highly radioactive aqueous waste into granular solids. Heat was supplied to the calciner by circulating sodium-potassium (NaK) eutectic alloy at 760°C through a bayonet heat exchanger in the fluidized bed of solids. Construction material for the NaK loop in the WCF was Type 316 stainless steel; the bayonet heat exchanger is Type 316 stainless steel modified with columbium and tantalum; the semi-elliptical heads on the NaK expansion tanks are Type 318 stainless steel. On March 19, 1969, the loop was shut down in preparation for the installation of an in-fluidized-bed combustion heating system. When shutdown occurred, this loop had been in service for 1,407 hours below 600°C and 31,182 hours above 600°C with 52 starts from room temperature.

As part of the overall program of surveillance on the NaK loop, service tests were made on several fittings and on a portion of the loop piping after 16,300 hours of loop operations. The results of these observations were reported on during the March, 1967 NACE Conference and subsequently published in Material Protection, Vol. 7, No. 5, pp. 35-39 (May 1968).

This paper presents data on the performance of construction materials for the NaK loop in the WCF over its entire lifetime as well as the last 16,300 hours of service. The Types 304L, 316, and 318 stainless steel alloys performed in a satisfactory manner. After 32,600 hours of service at or near 760°C, the tensile strength of Types 316 and 318 stainless steels remained high, but deterioration of elongation and impact strength values occurred. After 16,300 hours service, Type 304L stainless steel in 760°C NaK remained more ductile with higher elongation and impact values than Type 316 stainless steel. Carbide precipitation and sigma phase formation were identified in each of these austenitic stainless steels. Although difficult to quantitatively estimate, there appeared to be more carbide precipitation in Type 304L stainless steel than in Type 316 stainless steel after 16,300 hours high temperature NaK service. The Type 316 and Type 318 stainless steels appeared to have significantly more sigma phase formation than the Type 304L. General corrosion damage was limited to a two-mil thick band of decarburized alloy on the inside surface of the pipe and a 0.2-mil thick film of oxide on the outside surface. Although brittle fractures frequently occurred on Type 316 stainless steel at stress gradients, fractures were absent when working stresses were lowered. After repeated failures, the replacement of one Type 316 stainless steel fitting with a Type 304L stainless steel fitting eliminated further fractures.

I. INTRODUCTION

The Idaho Chemical Processing Plant recovers enriched uranium from spent aluminum-uranium reactor fuels⁽¹⁾ by a solvent extraction process. In the Waste Calcining Facility (WCF) at this plant, Figure 1, highly radioactive waste solutions resulting from this reprocessing are sprayed into a heated bed of fluidized solids where the salts are converted to oxides⁽²⁾. These free-flowing granular solids are produced continuously and are continuously conveyed to permanent storage bins from the calcination reaction vessel through a pneumatic solids transport system. Simultaneously, water vapor and volatile decomposition products are carried over with the fluidizing air to the WCF off-gas cleaning system before being released to the atmosphere. Formerly heat was supplied to the calciner by circulating sodium-potassium (NaK) eutectic alloy through a bayonet heat exchanger in the fluidized solids. Type 316 stainless steel was used as the construction material for this NaK loop. At the time of shutdown for installation of an in-bed heating system, the NaK loop of the WCF had been in service 32,600 hours. This represents the longest period of operation on record of a Type 316 stainless steel loop with NaK at elevated temperatures. However, some failures occurred during the first 16,300 hours of operation which necessitated extensive analyses of the nature and origin of the failures. In the course of those investigations, it was clear that the failure was not general; that is, the unstressed, straight runs of pipe did not suffer failure. Rather, failures have occurred in fittings, which, upon close analysis, were shown to have been subjected to considerable external stress. Accordingly, a sophisticated thermal stress analyses was conducted on the high temperature NaK loop in the WCF to avoid excessive external stresses. These results suggested

Figure 1 Fluidized bed waste calcining facility

certain piping alterations which were made. The Type 316 stainless steel NaK loop in the WCF served without failure during subsequent 16,300 hours of operation.

As part of an overall evaluation of construction materials suitable for handling liquid metals at high temperatures, service tests were conducted on several fittings and on a portion of the Type 316 stainless steel piping after abandonment of the NaK loop in the WCF. Metallurgical, chemical, X-ray and mechanical tests were used during this evaluation of the effects of exposure to NaK at 760°C with an interpretation thereof.

It should be noted that while pure sodium systems undoubtedly will not behave exactly like the NaK system studied here, and while all austenitic stainless steels will not respond exactly like the Type 316 stainless steel, the same basic mechanisms leading to failure are more or less in action in all such systems. Valuable guidance toward the behavior of other liquid metal systems may be found in the experience reported.

II. NaK LOOP IN THE WASTE CALCINING FACILITY

Liquid NaK (77.2 percent potassium - 22.8 percent sodium) was pumped through three-inch diameter, Type 316 stainless steel, Schedule 40 pipe in a loop which included an oil-fired radiant heater and a fluidized bed heat exchanger for the 48-inch diameter calciner ⁽²⁾ (Figure 2). The loop piping was fabricated from Heat X 22326 at Ellwood Works, National Tube Division, United States Steel Corporation. The NaK temperature in the heater reached a maximum of 760°C, and decreased to about 600°C at the outlet of the fluidized bed heat exchanger. The equipment in the loop also included an electromagnetic pump, expansion tank, and an oxide removal system. The expansion tank were Type 316 stainless steel vertical cylindrical vessels with semi-elliptical Type 318 stainless steel heads that permit the NaK to expand when heated; this increase in volume amounts to about 25 percent of the NaK volume at ambient temperature. Thermal insulation used on this loop was designed to be compatible with NaK at 760°C service temperature, and consisted of a 2-inch layer of molded Aerogel (Johns-Mansville Corporation) in contact with the piping and an outer 2-inch layer of 85 percent magnesia.

III. WORK PREVIOUSLY REPORTED

Before discussing the observations made after the last 16,300-hour service period, it is convenient to restate certain published observations from the first period of service. Tensile strength remained high on Type 316 stainless steel that was exposed in NaK at 760°C during the first period of loop operation; however, elongation and subsized Izod impact values were significantly reduced. Other service-associated effects that were observed in the Type 316 stainless steel were the formation of sigma phase throughout essentially the entire cross-section of the loop piping.

FIGURE 2

NaK System Flow Diagram

Precipitation of carbides at the grain boundaries was observed, but the associated general corrosion damage was limited to a two-mil thick band of decarburized alloy on the inside surface of the pipe in the high temperature zone and a 0.2-mil thick film of oxide on the outside surface.

Details of these observations are contained in Idaho Nuclear Corporation report, IN-1185.(4)

IV. EXPERIMENTAL PROCEDURE

Service test examinations were conducted on several fittings and on portions of piping that were exposed for varying time periods in circulating non-isothermal NaK.

A. Materials

1. Type 316 Stainless Steel

Service test examinations were conducted on three pieces of 3-inch schedule 40 Type 316 stainless steel piping - all of which were installed upstream from the NaK heater in the ICPP Waste Calcining Facility (WCF). One piece of pipe was in service during the first 16,300 hours of service at 1,120 hours below 600°C and 15,180 hours above 600°C with 37 starts from room temperature. This pipe was replaced by another which was in service during the last 16,300 hours of the NaK loop operation. During this latter time period, the replacement pipe was in service for 300 hours below 600°C and 16,000 hours above 600°C with 15 starts from room temperature. The third piece of pipe that was examined was installed before the initial start-up and remained in NaK service until the loop was abandoned. This pipe was in service for 1,410 hours below 600°C and 31,190 hours above 600°C with 52 starts from room temperature.

2. Type 304L Stainless Steel

An examination was conducted on a 3" x 3" x 3" Schedule 80 Type 304L stainless steel tee fitting which replaced a 3" x 3" x 1½" schedule 40 Type 316 stainless steel tee. This fitting permitted the liquid metal to circulate through the loop and also through a 3" x 7½" x 3½" high Type 316 machined reducer into the NaK expansion tank. The tee fitting was in service during the last 15,567 hours of the NaK loop operation of which 261 hours were below 600°C and 15,307 hours were above 600°C with 13 starts from room temperature.

3. Type 318 Stainless Steel

The 0.5-inch thick walled lower semi-elliptical Type 318 stainless steel head on the NaK expansion tank was examined after 32,600 hours of NaK loop operation of which 1,410 hours were below 600°C and 31,190 hours were above 600°C with 52 starts from room temperature.

B. Test Methods

For results reported in Section V the following experimental techniques were used:

1. Hardness - Clark diamond pyramid hardness tester on polished cross-sections
2. Microstructure - photographs of polished cross-sections
3. Identification of sigma phase, search for other new phases - X-ray diffraction
4. Carbon and nickel analyses - standard chemical methods
5. Ductility - ASIM A 376, Seamless Austenitic Steel Pipe for High-Temperature Central-Station Service, "Flattening Test"
6. Tensile Strength - a special sheet tensile specimen was cut from exposed pipe wall, as shown in Figure 3, and a tube tensile specimen (Figure 5) was prepared from unexposed tubing from the same heat.
7. Impact strength - a substandard size specimen (Figure 4) was cut from the pipe wall with the longitudinal axis of the specimen parallel to the longitudinal axis of the pipe. The axis of the ground notch was perpendicular to the surface of the pipe. The standard Izod "V" notch impact test was conducted in air at room temperature.

V. RESULTS & DISCUSSIONS

A. Type 316 Stainless Steel

The principal effect that was shown from the post-test evaluation of Type 316 sections from the NaK containment piping system was carbon depletion at NaK-pipe wall interface. The presence in the piping of sigma phase formation as evidenced by metallographic examination and accompanying embrittlement are indicative of a fundamental change in the microstructure of the alloy due to exposure at elevated temperatures. General corrosion damage was nil on each specimen after their service periods of 32,600 or 16,300 hours.

Positive identification of sigma phase was accomplished by X-ray diffraction analysis. A sample of the pipe tee was dissolved in 2:1 hydrochloric-nitric acids. The undissolved residue gave an X-ray diffraction pattern which corresponded to the American Society for Testing Materials (ASIM), X-ray Powder Data File No. 7-356 for sigma phase in molybdenum-titanium 18:8 stainless steel. The residue containing sigma was further dissolved in 48 percent hydrofluoric acid leaving a second residue which was identified by X-ray diffraction as epsilon iron, Fe_2C , that corresponded with ASIM, X-ray File No. 6-0670.

Figure 3 Sheet tensile specimen.

Figure 4 Impact test specimen.

18" Overall Length
OD 0.540"
ID 0.364

INC-A-12328

Figure 5 Tube tensile specimen.

The results of mechanical tests at 22°C, 500°C, and 760°C in air are recorded in Table I. At 22°C, the observed tensile and yield strengths of specimens from the 32,600-hour exposed sections compare favorably with values obtained from specimens of unexposed tubes of the same heat of Type 316 stainless steel and with published values of the unexposed alloy. Further, the observed tensile and yield strengths of the specimens from the sections which were exposed for the two different time periods compare favorably with the published values of unexposed Type 316 stainless steel at 500°C. The observed elongation percentages of the pipe exposed for 32,600 hours and 16,300 hours were 60 and 63 percent, respectively, lower than the percentage obtained from specimens of unexposed tubes from the heat of Type 316 stainless steel that was tensile tested at 22°C. When tested at 500°C in air, the elongation percentages of pipe sections that were exposed to NaK during the two time periods were 75 percent lower than the average published percentage for the unexposed alloy. Izod impact test results show that specimens of the pipe which were in high temperature NaK service absorbed 66 percent less kinetic energy in breaking than similarly tested specimens from unexposed piping.

Flattening test, ASTM A 376 Seamless Austenitic Steel Pipe for High Temperature Central Station Service, showed that exposed pipe remained ductile. However, a pipe section that was exposed in NaK service at 760°C for 16,300 hours broke when flattening continued until the opposite walls of the pipe met.

Post-test microhardness surveys of the Type 316 pipe sections from the NaK loop in the WCF had measured averaged diamond pyramid hardness (DPH) values of 158 and measured averaged Rockwell superficial 15-T scale (1/16-inch ball, 15, kilogram load) values of 89 which correspond to Rockwell B - scale of 86.

A metallographic examination of the piping indicated carbide precipitation at the grain boundaries. Sigma phase transformation as shown in Figure 6 appeared to be disbursed at concentrations equal to or less than four percent after 16,300 hours service. A band of decarburization, as in the piping during the first 16,300 hours of service, was found on the NaK side of the pipe wall, Figure 7. Type 316 piping that was exposed for the entire 32,600 hours service in the NaK loop of the WCF shows, Figure 8, about three times more sigma phase than that observed in piping that was exposed for 16,300 hours.

The results suggest that sigma phase transformation in Type 316 stainless steel when in NaK service at 760°C increases with increasing service time; although, the observed hardness values appeared to be quite constant through the 32,600 hours total exposure time. The impact strength of the alloy appears to decline to a minimum level within something less than 16,000 hours service and remains at that level for an indefinite time period. Although the general corrosion loss of Type 316 piping was nil, almost complete carbon depletion occurred at the NaK piping interface.

TABLE I

MECHANICAL PROPERTIES OF TYPE 316 STAINLESS STEEL

	Tensile Strength (Ksi) ³	Yield Strength (Ksi) 0.2% Offset	Elongation in 2 in. (%)	Flattening Test (ASIM A 376)	Subsize Izod Impact (Ft-lb.)
<u>Published Values</u>					
at 22°C	70-110 ¹	28-55 ¹	40-70 ¹	Satisfactory	NA ²
at 500°C	50-80 ¹	18-45 ¹	45-55 ¹		
at 760°C	30-34 ¹	18-35 ¹	20-60 ¹		
<u>Tests of Unexposed Steel⁴</u>					
at 22°C	80	35	63	Satisfactory	10.2
at 760°C	29	25	54		
<u>Measured Values (after 1st 16,300 Hours in NaK Service</u>					
at 22°C	96	51	30	Failed	3.6
at 760°C	36	15	14-16		
<u>After Last 16,300 Hours in NaK Service</u>					
at 22°C	107	58	23	Failed	3.4
at 500°C	76	48	11		
<u>After 32,600 Hours in NaK Service</u>					
at 22°C	98	56	25	Failed	2.9
at 500°C	70	45	11		

(1) ASM Handbook, Vol. 1, 8th Ed., pp 504

(2) There are no published values since this is not a standard test

(3) Kilo pounds per square inch

(4) Using specimens from the same heat of steel from which the WCF piping was fabricated

Figure 6 Cross section of 3-inch schedule 40 Type 316 stainless steel pipe after 16,300 hours at 760°C. Total sigma is about four percent.

0.5 M KOH <1 second etch 1500X
Sigma stained; carbide phase unoutlined.

Figure 7 Decarburized zone of inside edge of 3-inch schedule 40 Type 316 stainless steel pipe after 16,300 hours of service.

10% oxalic acid etch 750X

Figure 8 Cross section of 3-inch schedule 40 Type 316 stainless steel pipe after 32,600 hours at 760°C. Total sigma is about 12 percent.

0.5 M KOH <1 second etch 1500X
Sigma stained; carbide phase unoutlined.

B. Type 304L Stainless Steel

The service test evaluation of Type 304L stainless steel that was exposed in flowing NaK showed carbon depletion at the NaK-metal interface. There were significant amounts of carbide precipitation at the grain boundaries and only trace quantities of sigma phase formation in the cross-section of the tee, as evidenced by metallographic examination, Figure 9 and 10. These observations are suggestive of only minor changes in micro-structure of the alloy due to exposure at 760°C over 15,600 hours of service.

The post-service examination indicated that the general corrosion damage on the tee was nil. The concentration of sigma phase was estimated at less than one percent while carbide phases were present in concentrations of about two percent. The band of decarburization found on the NaK side of the wall of the tee is shown in Figure 11, it appears to be about 1 mil thick.

The results of mechanical tests at 760°C in air are recorded in Table II. The observed tensile and yield strengths as well as elongation percentage of specimens from the pipe tee compare favorably with published values of the exposed alloy. Izod impact test results show that specimens of the tee which were in high temperature NaK service were ductile and not brittle.

Sections of the Type 304L stainless steel tee from the NaK loop in the WCF had averaged diamond pyramid hardness (DPH) values of 195 which corresponds to Rockwell B-scale of 90.

C. Type 318 Stainless Steel

The observed effect that was most significant from the evaluation of the Type 318 stainless steel was almost complete absence of carbon depletion at the NaK-metal interface. Sigma phase formation which was identified in cross-sections of the columbium-molybdenum austenitic stainless steel alloy and accompanying embrittlement are indicative of fundamental change in the micro structure of the alloy due to exposure at elevated temperatures. General corrosion damage was undetectable on the steel after 32,600 hours of service.

The results of mechanical tests at 220°C and 500°C in air are recorded in Table II. At both test temperatures, the observed tensile and yield strengths of Type 318 stainless steel specimens were generally about 30 percent higher than published values for the unexposed alloy. When tested at 220°C and 500°C, the observed elongation percentage of the exposed sections were about 87 and 88 percent lower, respectively, than the average published percentages for unexposed alloy. The Izod impact test with a subsized specimen gave a relatively low result, 1.2 foot-pounds, for a stainless steel.

Figure 9 Cross section of Type 304L stainless steel pipe tee after 15,600 hours at 760°C.

0.5 M KOH $\frac{1}{2}$ second etch 200X
Sigma phase is darkened; carbide phase is outlined.

Figure 10 Cross section of Type 304L stainless steel pipe tee after 15,600 hours at 760°C.

0.5 M KOH $\frac{1}{2}$ second etch 1500X
Sigma phase is darkened; carbide phase is outlined.

Figure 11 Decarburized zone of the NaK side of 3" x 3" x 3" schedule 80 Type 304L stainless steel pipe tee after 15,600 hours of service

10% oxalic acid etch

750X

TABLE II

MECHANICAL PROPERTIES OF TYPES 304L & 318
STAINLESS STEEL FITTINGS

	Tensile Strength (Ksi) ³	Yield Strength (Ksi) 0.2% Offset	Elongation in 2 in. (%)	Flattening Test (ASIM A 376)	Subsize Izod Impact (Ft-lb.)
<u>Published Values</u>					
<u>304L</u>					
at 22°C	75-95 ¹	30-60 ¹	42-75 ¹	Satisfactory	NA ²
at 760°C	18-25 ¹	10-30 ¹	20-60 ¹		
<u>318</u>					
at 22°C	75-95 ¹	45-55 ¹	30-55 ¹	Satisfactory	NA ²
at 500°C	70-80 ¹	40-50 ¹	25-60 ¹		
<u>Measured Values</u> After Last 15,600 Hours in NaK Service					
<u>304L</u>					
at 22°C				Not Tested	>12
at 760°C	23	17	43		
<u>Measured Values After</u> 32,600 Hours in NaK Service					
<u>318</u>					
at 22°C	116	70	5.5	Not Tested	1.2
at 500°C	99	70	5.0		

(1) ASM Handbook, Vol. 1, 8th Ed., P. 504

(2) There are no published values since this is not a standard test.

(3) Kilo pounds per square inch.

Figure 12 Cross section of 0.5 inch thick OD semi-elliptical Type 318 stainless steel lower head on the NaK expansion tank after 32,600 hours at 760°C. Total sigma is greater than 15 percent.

0.5 M KOH $\frac{1}{2}$ second etch 1500X
Sigma stained; carbide phase unoutlined.

The microhardness survey of the Type 318 section had measured diamond pyramid hardness (DPH) values of 242 and measured average Rockwell superficial 15-T scale values of 93 which correspond to Rockwell B-scale of 100.

VI. CONCLUSIONS

The results of this work suggest that Types 304L, 316, and 318 stainless steel alloys are suitable for materials of construction for non-isothermal relationship between the failure of pipe fittings and applied stress on the components of loop, applied stress should be minimized in the design of any future loops.

The presence of *sigma* phase in Types 316 or 318 stainless steel, which increases in concentration with increasing exposure time at temperatures above 600°C, does not appear to greatly affect the servicability of the steel as long as the *sigma* particles are small and dispersed. Embrittlement that is usually associated with *sigma* phase formation may cause failures in areas of high external stress. When *sigma* phase inhibition is desirable, the use of fully austenitic low-carbon stainless steels is suggested. Owing to significantly greater yield and ultimate tensile strengths after 32,600 hours of exposure, Types 316 and 318 stainless steels are favored for construction materials for NaK loop service. Where inhibition of brittleness is desirable, Type 304L is useful because it was shown to have retained its impact strength and the lowest *sigma* phase concentration after 15,600 hours in NaK service. To inhibit decarburization with associated corrosion losses in NaK service, Type 318 (Mo,Cb) stainless steel is suggested because of the alloy resists precipitation of carbides in the grain boundaries.

VII. REFERENCES

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