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TOPICAL REPORT

on

EXAMINATIONS OF PORTIONS OF THE REACTOR
BUILDING SPRAY SYSTEM PIPING FROM
THE ARKANSAS NUCLEAR PLANT NO. 1

to

U.S. ATOMIC ENERGY COMMISSION

February 7, 1975

by

Warren E. Berry, William N. Stiegelmeier,
and Walter K. Boyd

Work Performed Under Contract W-7405-Eng-92
Task Agreement No. 65 for the
U.S. Atomic Energy Commission

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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PDR FOIA
BELL84-316 PDR

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ABSTRACT

An examination has been made of a cracked welded joint from the 10-inch Type 304 stainless steel piping in the recirculating line of the Reactor Building Spray System in the Arkansas Nuclear Plant No. 1. Cracks were observed at six joints within an 8-day period after the system was operated for 6 to 7 months with H_3BO_3 (2300 ppm B) at ambient temperature. Chemical analyses revealed the piping was within chemical specifications for Type 304 stainless steel. Metallographic examination revealed stress-corrosion cracking that initiated on the inside surface of the pipe and propagated intergranularly through the sensitized microstructure (chromium carbide precipitation at grain boundaries) of the heat-affected zone adjacent to the weld. Microprobe and scanning electron microscope analyses revealed up to 1000 ppm chlorine on the tarnish film at the heat-affected zone on the inner surface of the pipe as well as areas of chlorine on the fracture surface itself. Also found at the heat-affected zone were appreciable quantities (to 1 percent) of sodium, aluminum, silicon, calcium, magnesium, potassium, and titanium. Activity analyses revealed Co 58 and Fe 59 deposits on the surface which were transported from elsewhere in the system. Examination of radiographs from several sources revealed that the cracks coincided with areas of weld repair or high heat input and thus were caused by high residual stresses from welding. Chloride ion was the probable corrodent. Its source is not known definitely, but the chloride could have become concentrated by an ion-exchange process on the tarnish film at the heat-affected zone even from a bulk solution concentration of <100 ppb. Aluminum corrosion products (as found in this area) would contribute to this concentrating mechanism.

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INTRODUCTION

Cracking has been observed adjacent to welds in the 10-inch-diameter Schedule 10 Type 304 stainless steel piping in the recirculating lines in the Reactor Building Spray System of the Arkansas Nuclear Plant No. 1. The pipes carry a solution of reagent-grade H_3BO_3 in deionized water. Leaking-type failures occurred within 6 to 7 months after solution was added to the piping.

As part of the overall failure analyses, the AEC Regulatory Operations has asked Battelle's Columbus Laboratories to examine a portion of one of the cracked areas to determine the nature and the probable cause of the cracking. This report presents the results of this investigation which was conducted under Contract W-7405-Eng-92 Task Agreement No. 65 for the U.S. Atomic Energy Commission.

BACKGROUND

The Arkansas Nuclear 1 power plant has recently undergone the power ascension test phase of operation. On November 8, 1974, a leak was noted at a crack adjacent to a weld in the 10-inch-diameter piping that comprises the circulating lines for the Reactor Building Spray System. Five more crack-type leaks were noted by November 15, 1974.

The pipes were welded Type 304 stainless steel. The final heat-treating step in the fabrication of the pipe was an air quench from 2000 F. The reported composition of the stainless steel fell within the specifications for Type 304. The pipe was installed (welded) in September, 1971. It is not insulated. It is located in an auxiliary area near pumps outside the containment. The area is not air-conditioned and thus could become humid on occasion.

The pipes contain boric acid (H_3BO_3) at a specified level of 2300 ppm boron, pH \sim 5.5, and temperature of 70 to 100 F. The boric acid was introduced into the pipes in April, 1974. Chemical analyses revealed that the boron content was maintained as specified. Analyses also indicated that chloride and fluoride contents were <0.1 ppm. Two of the leaks occurred in the circulating system and four occurred in a line isolated from the circulating system, but full of borated water. Three of the leaks were in an open area, the other three were beyond a penetration.

The piping was supplied by Swepco, who also supplied the 2-, 4-, 6-, 8-, 12-, and 14-inch piping in Arkansas Nuclear 1. The A and B decay heat lines (also 10-inch diameter) were fabricated from the same heat of steel as the 10-inch spray system line that exhibited cracking. However, no cracking has been observed in any of the other lines.

Many radiographs were made of the welds in the spray system and the A and B decay heat lines. These were checked with the original radiographs made at the time of installation. In all, radiographs were examined for some 35 field welds and some 25 shop welds. All six cracking failures were in field welds: two were at areas of weld repair, three were at areas of high heat input, and the sixth showed nothing unusual. Good correlation was obtained between the circumferential location of the cracks and the circumferential location of the weld repairs or high heat inputs. No other indications of weld repair or high heat input were found other than those associated with the cracks.

An area where cracking was observed on November 10 was repaired on November 11 and cracking was observed adjacent to the repair weld on November 15, 1974. The repair was a TIG weld (Type 308 weld rod) done with argon backing, while the original welds also were TIG but with nitrogen backing. The original pipe was cut back and reground to effect the repair.

Two segments of pipe were supplied to Battelle for examination: one piece, including about 4 inches of the circumference, that contained the girth (field) weld but no cracks and a second piece, including about 1 inch of the circumference, that contained a crack adjacent to the weld. Both pieces came from the circumferential weld associated with Leak No. 2 as designated on-site. The crack itself was less than 3 inches long and was located between 5:00 and 6:00 where the top of the installed pipe is designated as 12:00. The large piece had not been penetrant-checked nor cleaned in any way and exhibited a very slight amount of gamma radioactivity. The small piece containing the crack had been ultrasonically cleaned in a dishwashing product, Calgonite 211. This product contains Na_2SiO_3 and Na_3PO_4 and is reportedly high in chloride content.

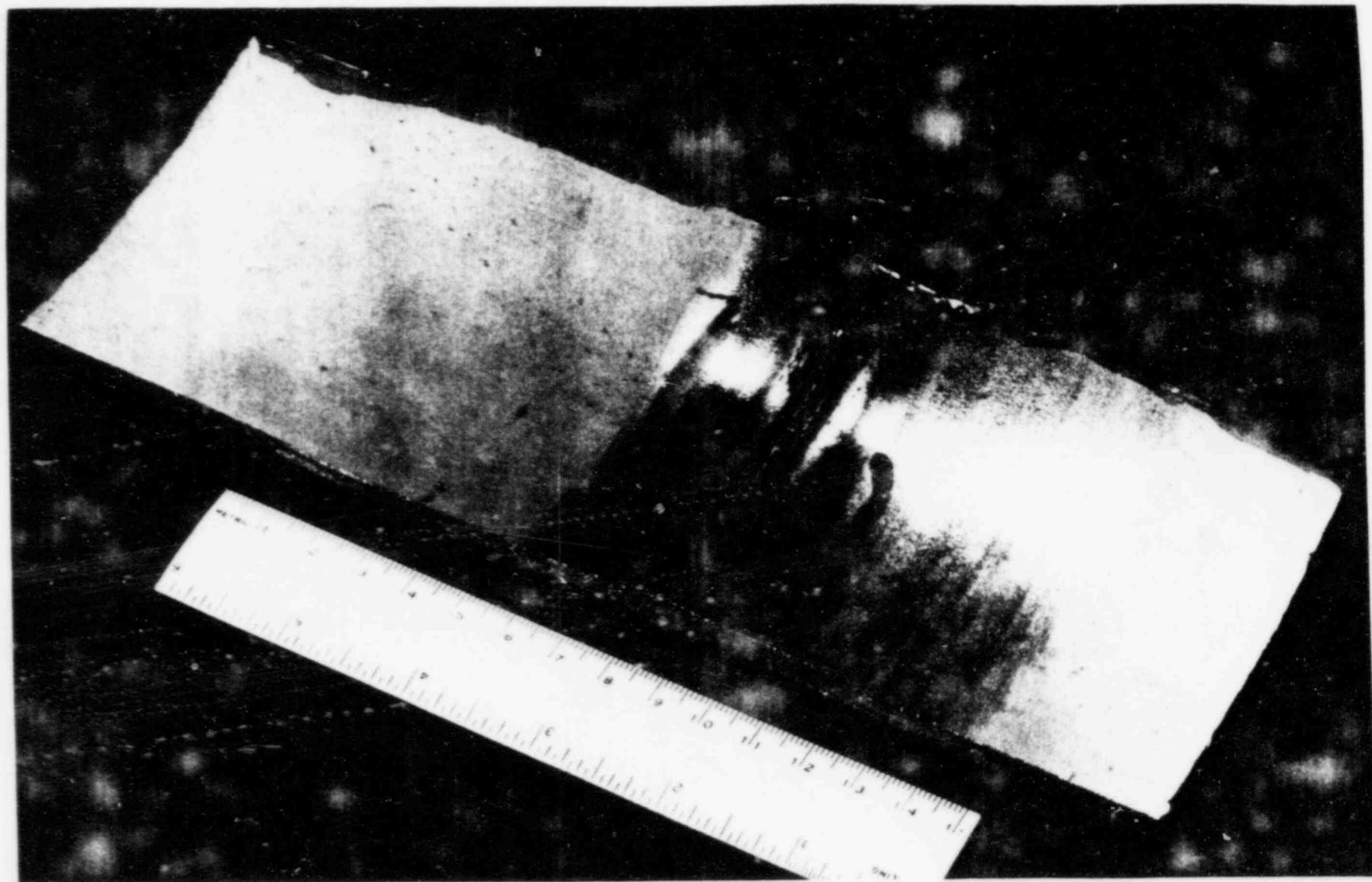
RESULTS

Appearance

The appearance of the large noncracked piece is shown in Figures 1 and 2. On the inside of the pipe, the weld and an area about 1/8 inch wide on either side of the weld were covered with a dark brown film. A tarnish film extended outward on either side and to about 1/2 inch away from the center of the weld. Bands of deep blue tarnish were located about 3/8 inch from the center of the weld. On the OD surface, the weld bead was covered with a brown tarnish, the deep blue tarnish bands were \sim 3/8 inch from the center of the weld, and the tarnish extended about 3/4 inch from the center of the weld. Note that the pipe was wire-brushed or ground on either side of the weld, probably as part of the weld preparation.

An enlargement of the cracked area in the small piece is shown in Figure 3. Although not readily apparent from the photograph, the crack is just adjacent to the dark blue tarnish band on one side of the weld suggesting that it initiated in the heat-affected zone adjacent to the weld.

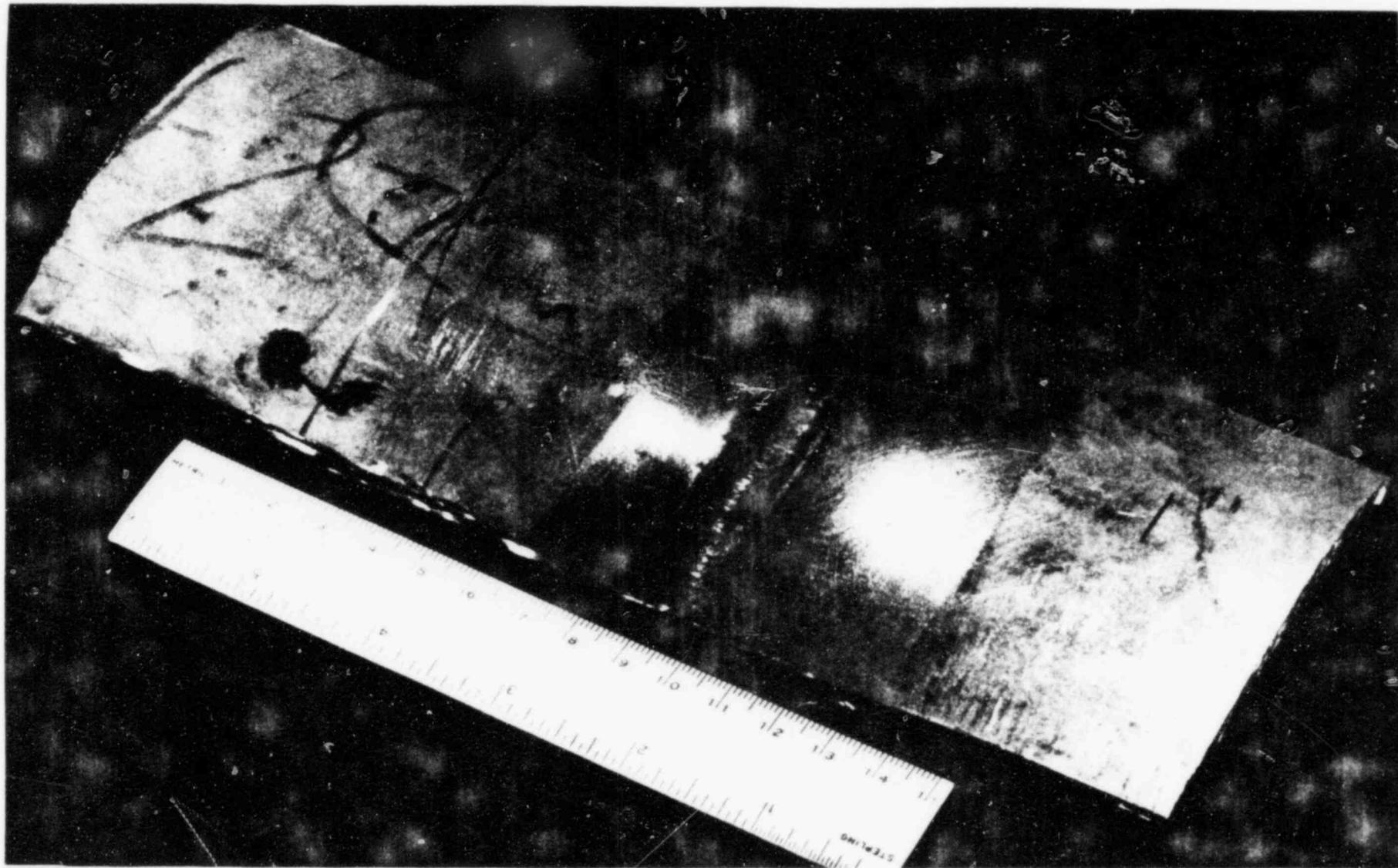
A visual examination at 20X of the ID and OD surfaces of both pieces of the pipe revealed what appeared to be incipient intergranular attack. A



5019

FIGURE 1. APPEARANCE OF INSIDE SURFACE OF THE NONCRACKED PIECE OF SPRAY SYSTEM PIPING AS RECEIVED AT BATTELLE

Note the ground areas on either side of the weld and the bands of tarnish in the heat-affected zone.



5

5018

FIGURE 2. APPEARANCE OF OUTSIDE SURFACE OF THE NONCRACKED PIECE OF SPRAY SYSTEM PIPING AS RECEIVED AT BATTELLE

See Figure 1.



5X

C-4596

FIGURE 3. CRACK ON THE INSIDE SURFACE OF THE SMALL PIECE OF SPRAY SYSTEM PIPING AS RECEIVED AT BATTELLE

Note that the crack is just adjacent to the band of blue tarnish.

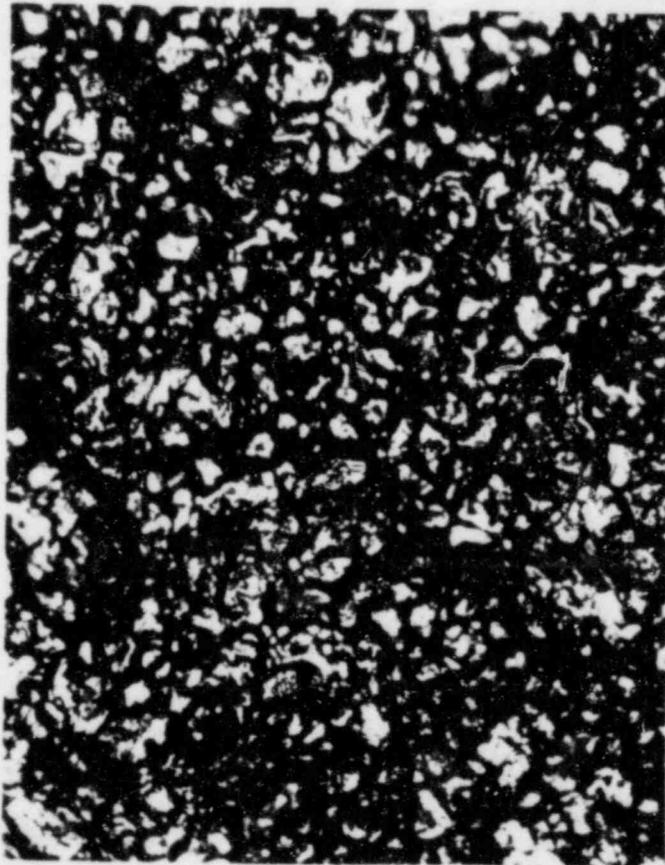
typical area is shown in Figure 4. This suggests that the stainless steel sheet probably was acid-pickled after final mill annealing to remove the surface oxide. A typical solution used for this purpose in the past contains 1 to 2 percent HF and 12 to 14 percent HNO₃. No such attack was noted in the ground areas, indicating that this attack occurred before welding in the field.

Metallography

A photomacrograph is shown in Figure 5 of a cross section through the crack shown in Figure 3. The piece was etched electrolytically in 10 percent oxalic acid. If the photograph is examined closely, the sensitized portion (grain-boundary carbides) of the heat-affected zone can be seen. The crack is located near the outer edge of the heat-affected zone away from the weld. Note that the crack is wider at the inner surface and appears to be propagating from the inner surface to the outer surface.

A photomicrograph showing the crack at higher magnification is presented in Figure 6. Note that the crack propagated at grain boundaries, but was not very branching. Based on the greater width of the crack at the inner surface and the direction of the limited amount of branching, it appears that the crack initiated on the inside surface and propagated toward the outside surface. Also note that the pattern of carbide precipitation produced large sensitized grains at the inner and outer surfaces and small sensitized grains in the center of the cross section. As will be discussed later, the crack is probably a stress-corrosion crack. This type of cracking is an electrochemical phenomenon under these conditions and, thus, large grains at the surface would create a greater tendency to initiate cracking because of the large cathode (grain)-to-anode (grain boundary) ratio.

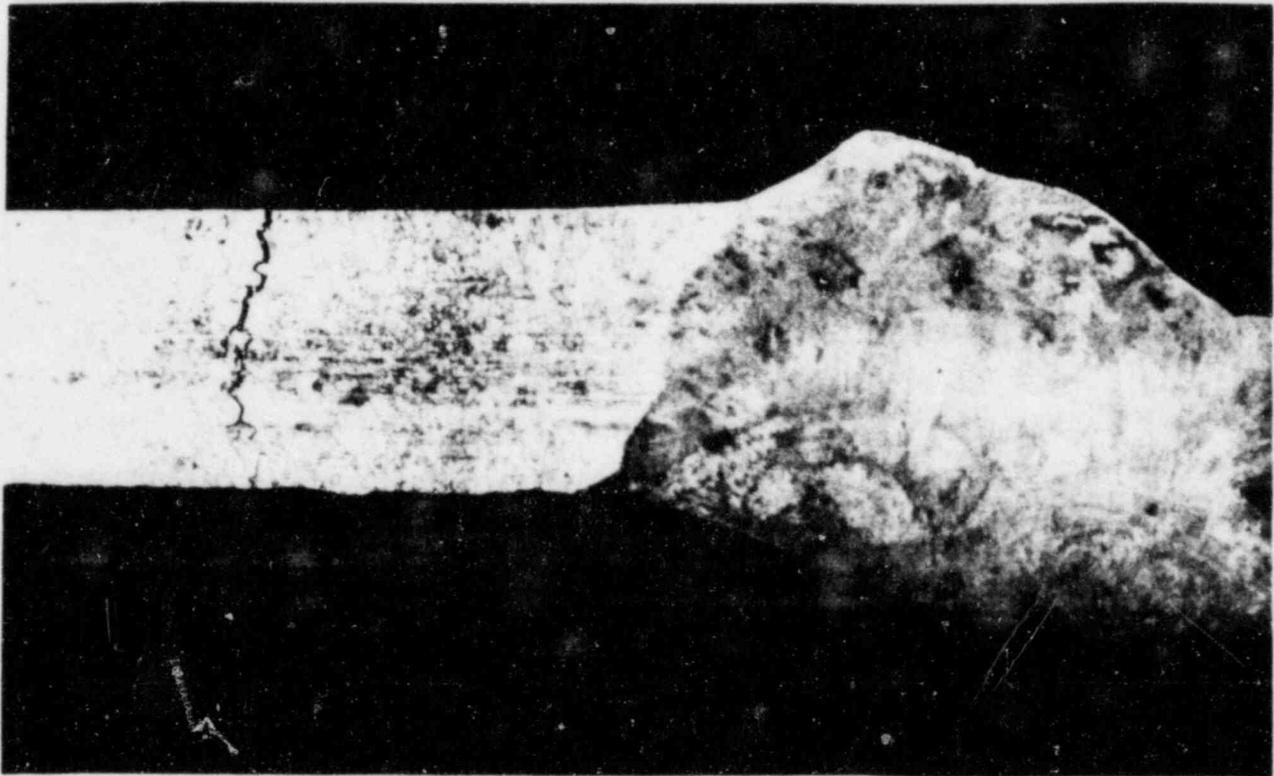
The microstructure of the pipe was examined in cross section along the entire length (about 5 inches) of the pieces received at Battelle. Partial sensitization (discontinuous carbide precipitation at grain boundaries) was observed in the center of the cross section of the pipe wall along the entire length. In some places, the partial sensitization extended almost to the inner and outer surfaces of the pipe wall. Examples are shown in Figures 7 and 8. Note the partial sensitization, particularly in the center of the cross section



100X

C-4597

FIGURE 4. APPEARANCE OF INTERGRANULAR
ATTACK OBSERVED ON BOTH
SURFACES OF BOTH PIECES OF
SPRAY SYSTEM PIPING



10X

Etchant: Electrolytic 10 Percent Oxalic Acid

C-4598

FIGURE 5. PHOTOMACROGRAPH OF ETCHED CROSS SECTION THROUGH CRACK SHOWN IN FIGURE 3

Inside surface of pipe is at top of photograph. Note that crack propagates through the outer edge of the heat-affected zone (where grain-boundary carbides are evident in the microstructure).



50X

Etchant: Electrolytic 10 Percent Oxalic Acid

C-4599

10

FIGURE 6. PHOTOMICROGRAPH OF CRACK SHOWN IN FIGURES 3 and 5

Inner surface is at right of photograph. Note that the crack propagates intergranularly and appears to have initiated on the inside surface of the pipe. Note also that the grain-boundary carbide precipitation resulted in large sensitized grains on both surfaces and small sensitized grains in the middle of the cross section.



50X

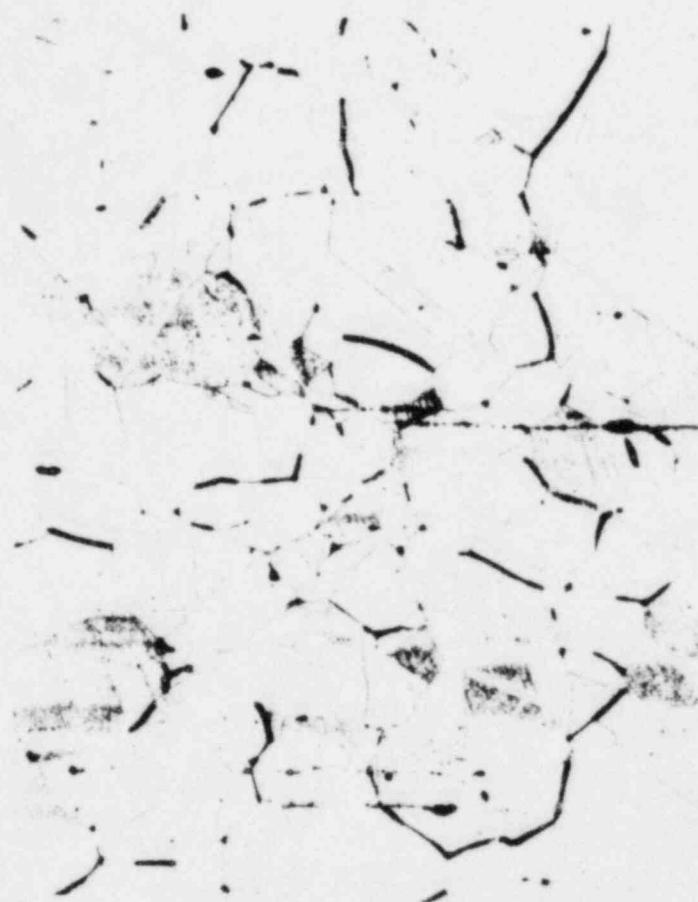
Etchant: Electrolytic 10 Percent Oxalic Acid Followed by
Light Polish Followed by Swab With Aqua Regia

C-4600

11

FIGURE 7. APPEARANCE OF REPRESENTATIVE CROSS SECTION OF PIPE WALL AWAY FROM WELD AREA

Note partial sensitization is greater at center but also occurs near the surface in isolated areas.



200X

C-4601

Etchant: Electrolytic 10 Percent
Oxalic Acid

FIGURE 8. PHOTOMICROGRAPH SHOWING ENLARGEMENT OF CENTER PORTION OF TUBE WALL CROSS SECTION AWAY FROM THE WELD

Note the partial sensitization (discontinuous carbide precipitation at grain boundaries). Also see Figure 7.

and the large grains at either surface. This partial sensitization suggests that the pipe was not rapidly quenched after the final anneal at 2000 F or the center of the pipe was not heated to 2000 F. The large grains near either surface might be the result of surface heating of the sheet during the final anneal in the mill. If the sheet were severely cold-worked before the final anneal, the hotter outside surface could have recrystallized more rapidly, which would account for the large grains. Failure to reach the annealing temperature in the center of the sheet would account for the partial sensitization as well as the smaller grain size in the center of the sheet. As a check on this hypothesis, a microhardness traverse was made across the wall of the specimen. The results are summarized below.

Location	Hardness	
	Measured, Knoop, 500-g load	Converted, Rockwell B
Inside edge ↓	135	68
	145	73
	162	79
Center zone of small grains ↓	160	79
	162	79
	165	80
Center zone ↓	171	82
	169	82
Outside edge ↓	138	70
	142	72
	148	74

Note that the small-grained center zone of the pipe wall was harder, thus lending support to the possibility that the large grains were formed because of localized heating of a cold-worked structure.

The cross sections of the pipe wall away from the weld area also were examined for the nature of the etching attack observed on both the inner and outer surfaces of the pipe. This attack was found to be incipient grain-boundary corrosion ≈ 0.5 mil deep. An example is shown in Figure 9. As mentioned earlier, this attack probably occurred as the result of pickling to remove heat-treating



200X

C-4602

Etchant: Electrolytic 10 Percent
Oxalic Acid

FIGURE 9. CROSS SECTION THROUGH THE INTER-
GRANULAR ATTACK NOTED ON THE
INSIDE AND OUTSIDE SURFACE OF THE
PIPE AWAY FROM THE WELD

Note that the attack was only about 0.5 mil
deep and apparently occurred at grain
boundaries.

oxide scales. Note from Figure 6 that no such intergranular attack was evident in areas near the weld where the pipe had been ground or wire-brushed prior to welding (Figures 1 and 2). Apparently, this weld preparation step removed the metal that included the incipient grain-boundary attack.

Analyses

Base Metal

Chemical analyses were obtained on the wrought metal piping. Carbon and nitrogen were determined by wet chemistry procedures. All other elements were determined by X-ray fluorescence. The results are presented in Table 1 along with the ladle analyses and check analyses provided by Swepco Tube Corporation who furnished the pipe. Note that the analyses of the wrought material are within the specifications for Type 304 stainless steel, although the 0.078 percent carbon value is just below the 0.08 max specification. Nitrogen also was determined at Battelle because high nitrogen contents can lead to increased sensitization and increased susceptibility to stress-corrosion cracking. The 0.035 percent nitrogen for this heat is within the usual range of 0.03 to 0.05 percent for Type 304 stainless steel.

Surface Deposits

The ion microprobe was used to analyze the oxide films in the inner surface of the uncleaned piece of piping and one half of the fracture surface of the crack that was broken out of the cleaned piece of piping. The results were semiquantitative and are presented in Table 2 for the heat-affected zone adjacent to the weld, the weld itself, and the fracture surface. Note that small quantities of chlorine and fluorine were detected in the oxide films. The amounts were less than 100 ppm in all areas except at the heat-affected zone where chlorine ran 100 to 1000 ppm. (Both chlorine and fluorine are known to produce stress-corrosion cracking of stressed sensitized stainless steel at ambient temperatures.)^{(1,2)*} Also note the high contents (to 1.0 percent) of

* References are listed on page 26.

TABLE 1. CHEMICAL ANALYSES OF TYPE 304 STAINLESS STEEL HEAT
USED FOR THE 10-INCH PIPING IN THE ARKANSAS
NUCLEAR 1 REACTOR BUILDING SPRAY SYSTEM

Source	Composition, percent									
	C	Cr	Ni	Mn	Si	Mo	Co	P	S	N
Ladle analyses ^(a)	0.080	18.43	9.17	1.45	0.63	0.390	0.05	0.019	0.005	--
Check analyses ^(a)										
Base metal	0.057	18.29	8.89	1.53	0.39	--	--	0.011	0.012	--
Battelle analyses										
Base metal	0.078	19.0	9.3	1.55	0.70	0.41	<0.1	0.015	0.01	0.035

(a) Results provided by Swepeco Tube Corporation (Heat No. 800201).

TABLE 2. SEMIQUANTITATIVE ION-MICROPROBE ANALYSES
OF SELECTED AREAS ON PIECES FROM THE 10-
INCH PIPE

Element	Mass Number	Concentration at Areas Noted ^(a)		
		Heat-Affected Zone ^(b)	Center of Weld ^(b)	Fracture Surface ^(c)
Lithium	6, 7	Trace	Trace	Trace
Boron	10, 11	Trace	Low	Trace
Carbon	12	Low	Trace	Trace
Fluorine	19	Trace	Trace	Trace
Sodium	23	Medium	Low	Low
Magnesium	24	Medium	Medium	Low
Aluminum	27	Medium	Low	Medium
Silicon	28	Medium	Low	Medium
Chlorine	35	Low	Trace	Trace
Potassium	39	Medium	Medium	Low
Calcium	40	Medium	Medium	Medium
Titanium	48	Medium	Low	Low
Chromium	52	Major	Major	Major
Manganese	55	Low	Low	Low
Iron	56	Major	Major	Major
Nickel	58	Major	Major	Major
Copper	63	Low	Trace	Trace

- (a) Trace = Detected but <0.01 percent (<100 ppm).
 Low = 0.01 to 0.1 percent (100 to 1000 ppm).
 Medium = 0.1 to 1.0 percent (1000 to 10,000 ppm).
 Major = >1 percent (>10,000 ppm).

(b) Inner surface of uncleaned piece.

(c) Fracture surface of crack in small piece that had been cleaned ultrasonically.

sodium, magnesium, aluminum, silicon, potassium, calcium, and titanium at the heat-affected zone. In fact, these elements plus chlorine and copper were higher in the heat-affected zone than in at least one (and usually both) of the other areas analyzed. By the same comparison, boron, magnesium, and potassium were higher at the weld, while aluminum and silicon were higher on the fracture face. This indicates a greater degree of contamination at the heat-affected zone where the cracking initiated. Note that no phosphorus was found on the fracture surface. The lack of phosphorus indicates that the silicon on the fracture surface probably did not come from the detergent used to clean the cracked specimen. (The detergent contained Na_2SiO_3 and Na_3PO_4 .) Also note aluminum and silicon were the only two contaminants found at high levels at both the heat-affected zone and the fracture surface.

Radioactivity Analyses

Radioactivity levels on the inner surface of the uncleaned piece of pipe were determined as follows:

- (1) A gamma-ray spectrum was run on a 2 x 1/4 x 3/16-inch sample using a 3 x 3-inch NaI(Tl) well crystal and 400 channel analyzer. Standards and background were also run for comparison.
- (2) An alpha spectrum was taken on a Si surface barrier detector in vacuum, along with a standard and background count.
- (3) The sample was scrubbed with a nylon brush using a ~20 percent radiac solution, rinsed, dried, and recounted for gamma. Weights before and after were recorded.

Although monitoring the pipe weld sample (304 SS) with a sensitive lab monitor revealed no activity, a long time count (40.0 min) in an efficient 3 x 3-inch NaI(Tl) well crystal revealed six gamma rays as follows (see Figure 10):

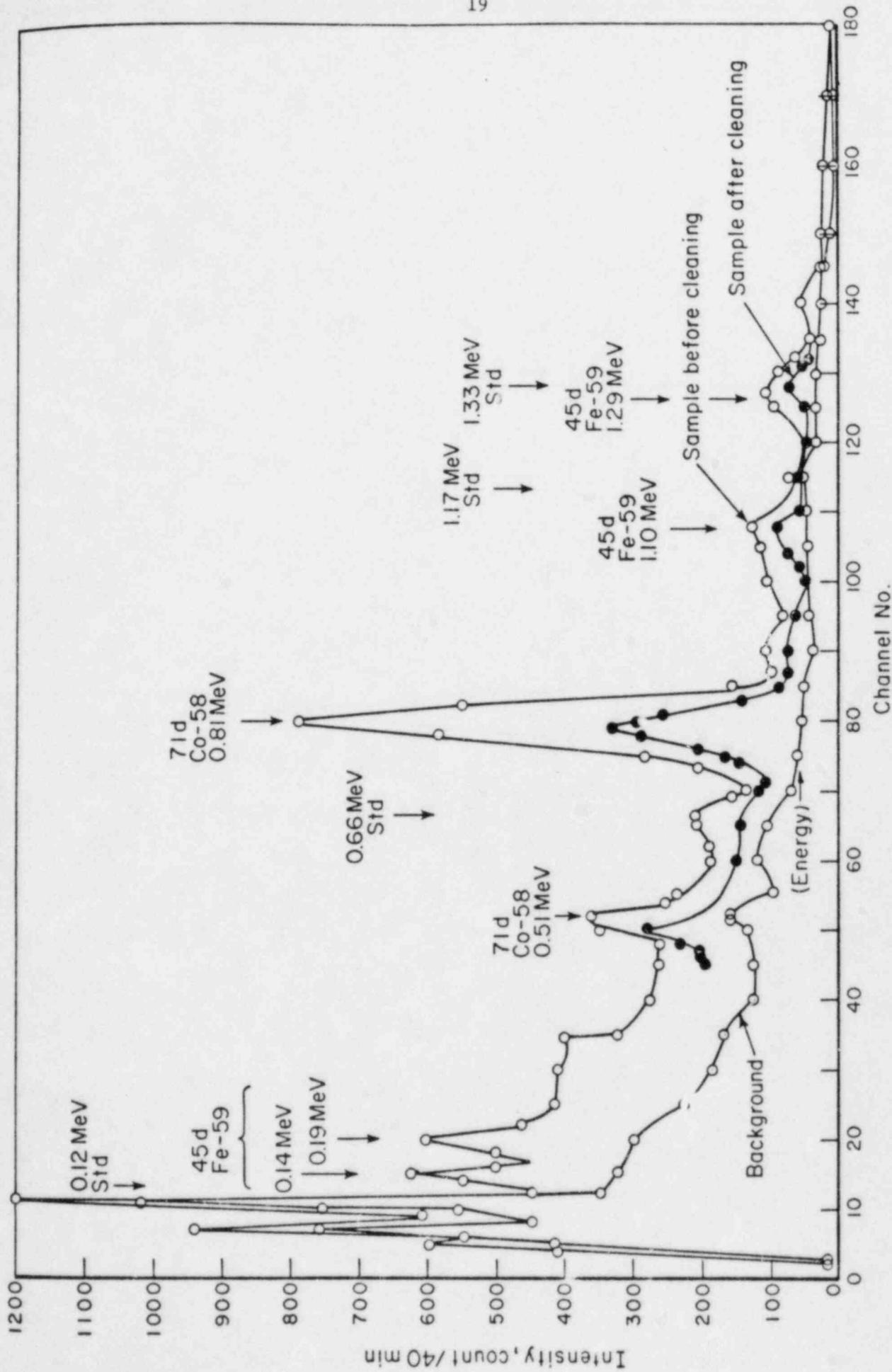


FIGURE 10. GAMMA-RAY SPECTRUM OF INNER SURFACE OF 10-INCH PIPE

<u>γ Energy, MeV</u>	<u>Isotope</u>	<u>Half-Life</u>
0.81	Co 58	71 d
0.51	Co 58	71 d
1.10	Fe 59	45 d
1.29	Fe 59	45 d
0.19	Fe 59	45 d
0.14	Fe 59	45 d

There is no doubt that these activities were present when compared with the low background count. Note that no Cr 51 was detected. If the stainless piping had been activated, one would expect to find Cr 51 in the gamma spectrum.

An examination for alpha activity revealed no alpha activity present.

No beta count was attempted due to (1) the difficulty in resolving maximum beta energies, (2) interference from two Fe 59 betas and one Co 58 positron, and (3) the lack of sufficient activity to obtain a suitable absorption curve.

After the alpha and gamma spectra were obtained, the sample was scrubbed with a nylon brush using a ~20 percent radiac solution to determine whether the activity was removable. These results also are included in Figure 10 and are summarized below.

	<u>As Received</u>	<u>After Cleaning</u>	<u>Loss</u>
Approx. Co 58 Activity ^(a) , dpm ± 25%	690	260	62%
Sample Weight, grams	9.5717	9.5693	0.0024 g

(a) Measured from 0.81 MeV gamma.

Since no Cr 51 was found on the surface and a large percentage of the activity was removed by scrubbing, it is concluded that these elements were transported from elsewhere in the system and were deposited on the inner surface of the pipe.

SEM Examinations

The scanning electron microscope (SEM) also was used to examine and analyze the fracture surface. SEM photographs of the fracture surface near the inner and outer surfaces of the pipe wall are shown in Figure 11. Note the "rock-candy" structure that is typical of intergranular cracking. Dispersive X-ray analyses of a spot of "debris" just left of center and at the bottom of Figure 11a (inner surface) revealed appreciable quantities of chlorine, sodium, aluminum, silicon, sulfur, potassium, and calcium as well as iron, chromium, and nickel. Analyses of other areas near the inner surface revealed the same general results except little or no chlorine was detected.

On the other hand, analyses of the fracture surface near the outer edge revealed aluminum, sulfur, and calcium plus a trace of silicon and the expected iron, chromium, and nickel. Analyses of a bare (abraded) metal surface revealed only traces of aluminum and silicon in addition to the three major elements.

Thus, the SEM results show that the fracture surface near the initiation site (inside surface) was contaminated with chlorine, aluminum, and silicon as well as sodium, calcium, and potassium. These contaminants were largely absent where the crack penetrated the outside surface of the pipe. This distribution would be expected if contamination on the inner surface of the pipe was responsible for crack initiation.

DISCUSSION

The observed cracking failure appears to be intergranular stress-corrosion cracking that initiated on the inside surface of the pipe at the heat-affected zone and propagated through the sensitized microstructure in the area. The stresses were probably residual tensile stresses that were intensified by repair welding and/or high heat input in localized areas. The good correlation between crack location and weld repair or high heat input locations further is indicative of a high localized residual stress. Intergranular stress-corrosion cracking in heat-affected zones adjacent to welds in Type 304 stainless steel



108X

SEM-879



108X

SEM-880

a. Inner Surface at Bottom
(Initiating Edge)

b. Outer Surface at Top

FIGURE 11. SEM PHOTOGRAPHS OF THE FRACTURE SURFACE OF THE CRACK SHOWN IN FIGURES 3, 5, AND 6

Note the "rock-candy" structure that is typical of intergranular stress-corrosion cracking.

pipng also has occurred in other applications such as the Dresden-1 nuclear plant.⁽³⁾

The probable corrodent was chloride ion detected in reasonably high quantity at the heat-affected zone of the weld and on the fracture surface where cracking initiated. There is precedence for low chloride contents (less than 5 ppm) in boric acid to cause stress-corrosion cracking of sensitized stainless steel. In studies conducted by the Oak Ridge National Laboratory in 0.28 M H_3BO_3 (pH 4.5) and 5 ppm chloride, 4 of 4 heavily sensitized Type 304 stainless steel specimens cracked in exposures of up to 2 months at 180 F, with several days' exposure initially at temperatures of the order of 212 F.⁽⁴⁾

The source of the chloride ion is not readily apparent. It is tempting to postulate that the chloride ion may have been introduced during preoperational treatments with, say, tap water. Chloride trapped in oxides during this period could have been released when the boric acid was introduced. The finding of calcium and magnesium in the oxide films also suggests tap water. However, two observations tend to disprove this supposition, namely, that (1) the repaired area which was reground (and thus cleaned) failed by cracking 4 days after repair, and (2) water standing in the pipe probably was not the cause because several of the cracks were reported to have occurred at the top or the top half of the pipe.⁽⁵⁾

Surface contamination during welding might also account for the chlorides. These contaminants might have been introduced during welding or weld preparation (as from grinding wheels or contaminated degreasing fluids). However, if all welding procedures were followed as outlined in the Bechtel General Welding Standard GWS-SN, there should have been no contamination during the TIG welding.

A third, and most likely, source of the chlorides is the boric acid solution itself. The boric acid reportedly was analytical grade very low in chloride. Furthermore, the boric acid solution analyzed <0.1 ppm chloride. However, experience at the Savannah River Laboratory has indicated that even with such low chloride levels in solution, chlorides could become concentrated by ion exchange in corrosion products and cause stress-corrosion cracking of sensitized Type 304 stainless steel.⁽⁶⁾ The corrosion product at Savannah River was aluminum hydroxide (or hydrated aluminum oxide) which deposited at etched grain

boundaries in the stainless steel. It is significant that appreciable aluminum (0.1 to 1 percent) was found at the heat-affected zone and on the fracture surface. Aluminum and silicon were the only two contaminants that were found in common in high quantities at the two areas. The chloride may not have come from the boric acid itself but may have come from an additional source of contamination, since the radiochemical analyses indicated a transport of material (Co 58 and Fe 59) from a foreign source to the inner surface of the pipe.

Another possible corrodent is the boric acid itself. The Oak Ridge results indicate that boric acid does not cause stress-corrosion cracking of sensitized stainless steel if there is insufficient chloride present.⁽⁴⁾ However, the current electrochemical theories of stress-corrosion cracking propose that stress-corrosion cracking occurs at critical potentials or over critical potential ranges. These vary for different materials and different environments. Surprisingly, several environments, previously thought to be nonaggressive, have been shown to produce cracking at certain potentials. These potentials usually are well removed from the free corrosion potential that is assumed by the metal in the environment. Thus, cracking does not occur under the usual service conditions. However, galvanic coupling to a dissimilar metal could shift the potential into the critical range for cracking. In some cases, the dissimilar metal could conceivably be the weld bead. Oxide films may produce a similar effect. In fact, studies conducted at Battelle on oxide-coated pipe steel have shown that the oxide itself will maintain the pipe steel in the critical potential range for stress-corrosion cracking in caustic and carbonate-bicarbonate solutions.⁽⁷⁾ The tarnish film on the sensitized heat-affected zone of the stainless steel pipe might produce a similar effect in boric acid solutions. Thus, although the probability is low that boric acid alone can cause stress-corrosion cracking of weld-sensitized stainless steel, the possibility can not be ruled out until such factors as those described above have been investigated.

CONCLUSIONS

The following conclusions can be made as to the leaks in the 10-inch recirculating line of the Arkansas Nuclear 1 Reactor Building Spray System based

on the results of this examination together with information obtained from on-site examinations and construction and operation records.

- (1) The leaks were caused by stress-corrosion cracks that initiated on the inside surface of the Type 304 stainless steel pipe and propagated intergranularly through the sensitized microstructure of the heat-affected zone adjacent to the circumferential field welds.
- (2) The source of the stress was residual stresses associated with welding and, in particular, high residual stresses from weld repairs or high heat input during welding.
- (3) The corrodent responsible for the cracking appears to be chloride ions. The source of the chloride ions is not known, but even at low levels (<100 ppb) in the solution, it is possible that they could have become concentrated to high levels in the tarnish film over the heat-affected zone either by ion exchange with the tarnish film or with aluminum corrosion products that deposited on the tarnish film.

ACKNOWLEDGMENT

This research was performed under Contract W-7405-Eng-92 Task Agreement No. 65 for the Division of Regulatory Operations of the U.S. Atomic Energy Commission. Liaison was maintained with Mr. Alan R. Herdt of Region II Regulatory Operations whose technical assistance and guidance have been greatly appreciated.

REFERENCES

- (1) Ward, C. T., Mathis, D. L., and Staehle, R. W., "Research in Progress: Intergranular Attack of Sensitized Austenitic Stainless Steel by Water Containing Fluoride Ions", *Corrosion*, 25 (9), 394-396 (September, 1969).
- (2) Copson, H. R., "An Appraisal of the Resistance to Stress-Corrosion Cracking of Iron-Nickel-Chromium Alloys in Pressurized Water and Related Environments", paper presented at the Polytechnic Institute of Brooklyn Seminar on Corrosion in Nuclear and Conventional Power Plant Systems, New York, New York (May 22-23, 1969).
- (3) Cheng, Craig F., "Intergranular Stress-Assisted Corrosion Cracking of Austenitic Alloys in Water-Cooled Nuclear Reactors", paper presented at the 5th European Congress on Corrosion, Paris, France (September 24-28, 1973).
- (4) Griess, J. C., and Creek, G. E., "Design Considerations of Reactor Containment Spray Systems, Part X, The Stress-Corrosion Cracking of Types 304 and 316 Stainless Steel in Boric Acid Solution", USAEC Report ORNL-TM-2412 (Pt. 10) (May, 1971).
- (5) Personal communication from Alan R. Herdt, Division II of AEC Regulatory Operations.
- (6) Rideout, S. P., "Stress Corrosion Cracking of Type 304 Stainless Steel in High Purity Heavy Water", Proceedings Second International Congress on Metallic Corrosion, National Association of Corrosion Engineers, Houston, Texas (1966), pp 159-171.
- (7) Berry, Warren E., "Stress Corrosion Cracking. Laboratory Experiments", paper presented at 5th Symposium on Line Pipe Research, Houston, Texas (November 20-22, 1974), American Gas Association, Inc., Catalogue No. L30174.