ELECTRIC SYSTEM SUPPORT
DUKE POWER COMPANY

Diversified Services

METALLURGY DUKE POWER FAILURE ANALYSIS

ATTACHMENT 3

# Catawba - RN System
# Corrosion in Stainless Steel Welds

## Metallurgical Analysis Report

Prepared for: Ernie McElroy
CNS - Mech/Comp Engineering

xc: Joel Reeves - CNS
Mark Pyne - NGD/GO
Steve Davenport - NGD/GO
Norm Stambaugh - NGD/GO
David Ward - CNS
Donna Keck - NGD/GO
Tony Mauldin - CNS
Mary Maner - ESS/Environmental
John Derwort - ESS/Environmental

Prepared by: S Anderson Date 4/24/95

Susan Anderson
Engineer - ESS/DSD Metallurgy Lab
Duke Power Company

Reviewed by: C. R. Frye Date 4/24/95

C. Rod Frye
Engineer - ESS/DSD Metallurgy Lab
Duke Power Company

Metallurgical Analysis Report #1812

9505230287 950511
PDR ADOCK 05000413
P PDR

**Equipment Description:**
RN system, stainless steel piping - various locations

**Background Information:**
Leaks were first found in 4" Sch 40 pipe (SA312 TP304) adjacent to butt welds. Samples were taken from lube injection strainer piping in the RN pump house, leading to the upper bearing motor cooler and oil cooler. The piping had been installed 4-5 years ago. The lines see constant flow at 70-80°F; flow rate was reportedly <100 gpm, or <3 fps in a 4" line. Three samples were provided, but ~12 leaks were reported in the same area.

During subsequent inspections, a number of leaks were found at socket welds, primarily those joining 2" lines to SA182 TP304 elbows. Several samples were provided from the lines leading to radiation monitor 2EMF458. The flow rate was likely low, because a strong odor was reported (as would be produced by stagnation) when the lines were cut for sample removal.

All samples were provided in service water within 24 hours of removal for proper bacteriological sampling. The piping sections were then allowed to dry.

---

## 1. BUTT WELDS

Ring sections from welds 0RN216-9, 0RN225-18, and 0RN227-13 were provided; the welds were not individually identified. Each leak was reportedly on the underside of the horizontal piping.

- One sample had a distinct pinhole on the OD, 1/16" from the weld toe (Figure 1). Smaller pinholes were nearby, indicating the pit had tunnelled. The pit site was covered by a tubercle on the ID, which was sampled for bacteriology. Circular traces up to 3/4" diameter indicated where two other tubercles had been located; pitting was visible at one site. Those two tubercles formed ~3" away on either side of the leak, on the same side of the weld.

- One sample had two red-brown tubercles 3" apart on opposite sides of the weld ( Figure 2). The growths were 3/4" diameter at their bases. A pinhole leak occurred at the taller conical tubercle. The other one had grayish-green material along a hollow center path. A darker, hemispherical tubercle 1/4" diameter lay between them. This sample was left intact for NDE use.

- The third sample contained only one 5/8" diameter trace of a tubercle location. The only leak path found was two 1/16" discontinuous cracks in the HAZ (heat-affected zone) on the OD, 1/16" from the weld toe.

Metallography
The samples containing one and three tubercles/traces showed cavernous subsurface pits at the leak sites (Figures 3-4). The pits had pinhole ID penetrations. One tunnelled to the OD; the other progressed about halfway through-wall, at which point transgranular cracking became the propagation mode (Figures 5-6). A non-leaking tubercle site revealed a small round cavernous pit 1/16" deep.

The ID openings were 3/16" to 3/8" from the ID toe of the weld. The massive pit in Figure 3 covered ~1/4" axially and was probably similar in circumferential length. The opening of the pit/crack was in straw-tinted oxide on the far side of the blue tint band.

The crack network below the pit shown in Figure 4 was bent apart to reveal the crack surfaces. No chloride was detected; some sulfur-containing material was found near the crack tips. The interior surface of the cavity had a faceted appearance.

The composition of a removed tubercle and the deposit at a tubercle trace were checked qualitatively using EDS (energy-dispersive spectroscopy). The tubercle was lightweight, frail, and full of hollow areas. Sulfur was identified in both the tubercle and trace, along with metal oxides and sediment (Figure 7). The sulfur was most readily detectible in the green-gray portion of the tubercle.

Bacteriological Sampling
Two complete tubercles (one of which had detached) and the nearby interior surfaces were sampled. Only slime bacteria were cultured from the detached tubercle. Slime and three types of iron-oxidizing bacteria (Siderocapsa, Sphaerotilus, and Gallionella) were cultured from the tubercle taken directly from the pipe wall.

## 2. SOCKET WELDS

Numerous leaking welds were supplied for examination, including:

2RN441-1 (90° elbow)
2RN442-13 (45° elbow)
2RN442-25 (attached reducing insert to tee - had 3 leaks)
2RN442-23 (attached 2" pipe to tee, pipe led to blind flange)
2RN442-22 (90° elbow)
2RN442-15 (45° elbow)
2RN442-21 (90° elbow)

Typical leaks are shown in Figure 8 - occurring near the center of the bead and leaving a rusty streak on the OD. Figure 9 shows three leaks in 442-25 spaced ~120° apart and the neighboring leak in 442-23.

Deposits protruded from the socket joint at each leak (Figure 10), with the leak located near the center of the deposit arc. Some joints contained deposit but were not leaking, implying that corrosion was occurring but hadn't yet penetrated to the OD. This deposit material was shown by EDS to contain sulfur and was similar in texture and composition to tubercles from the butt welds.

Metallography

Three leaks sectioned (2RN441-1, 442-13, and 442-25) showed similar characteristics - lack of fusion at the weld root, and extensive preferential corrosion of one phase of the filler metal (Figures 11-12). Water was able to leak through this torturous pathway. The sponge-like metal structure remaining eventually corroded away, leaving a void.

Sections through the ends of the deposit arc for 2RN440-22 (shown in Figure 10) showed a lack of fusion but no corrosion. Active corrosion must have be confined to near the leak at the center of the arc, producing deposits massive enough to fill the joint for ~150°. Arc length affected by corrosion was estimated as 1/4" or less.

The one atypical leak occurred in 2RN442-15, where pitting took an intergranular path through the forging (Figure 13). The weld root was sound and was unattacked. A tunnelling pit extended from the intergranular attack to the weld, and subsequently corroded by the same preferential attack seen in most socket welds (Figure 14). A thin network of grain-boundary carbides was seen around the pit in the forging, indicating sensitization. The pipe had larger but discontinuous carbides and a much smaller grain size than the forging.

Bacteriological Sampling

Deposits protruding from the socket joints were sampled, but the deposit within the joints was not accessible. A soupy mix of sediment and organic matter provided in one pipe was also sampled. No preliminary results were available.

---

**Discussion:**

Type 304 stainless steel can pit if its protective oxide layer is breached. Sulfide and chloride ions can penetrate the oxide and form a local anodic site. The site normally will repassivate and remain protected, but it cannot do so if local dissolved oxygen is depleted. Biological activity and thick deposits can reduce the amount of oxygen reaching the surface. The anodic reaction occurring at the site can then continue, lowering the local pH in the process. The corrosion is thus is self-accelerating, typically producing cavernous pits (corrosion rate faster inside than at surface).

MIC (microbiologically-influenced corrosion) of stainless steel base metal has a distinctive form of subsurface cavities with pinhole surface penetrations. Preferential attack of two-phase weld metal is also indicative of MIC activity. The presence of tubercles implies some organic activity. Attack occurred on the underside of horizontal pipe and in the bottom of sockets, where deposits naturally settle. By most indications, the underlying cause of the attack in these stainless steel welds was MIC.

Iron bacteria are known to promote tubercle formation. Sulfate-reducing bacteria were (likely) also present. SRB can reduce sulfate to sulfide, which can pit stainless steel.

Attack has occurred only at welds, which is typical for MIC in stainless steel. The exact reason for this preference is unknown; it may be easier for bacteria to colonize in the HAZ due to oxide film characteristics. MIC can occur in stainless base metal but it is less common.

Several corrosion mechanisms were observed - pitting, stress-corrosion cracking, and intergranular attack. The corrosion followed the "path of least resistance" - that is, whatever mechanism was thermodynamically favored under a given condition. Pitting occurred under tubercles and in sockets. There was probably more residual stress in the butt weld which underwent SCC than in welds which simply pitted through-wall, as SCC began after the wall was reduced by half. Pitting was intergranular in sensitized material, rather than galvanic (cavern-shaped); after the limit of the sensitized area was reached, classic galvanic corrosion reappeared. Regardless of form, the corrosion was initiated by localized acidic and or/low oxygen conditions created by the bacterial colonization.

The SCC agent did not appear to be chloride, although iron bacteria reportedly can concentrate chloride. Transgranular SCC of 304 stainless has been reported in solutions containing large amounts of hydrogen sulfide at low pH levels. SRB can produce hydrogen sulfide as a metabolic by-product.

This situation was not created by a material or welding process problem. Poor fusion in some socket welds likely created a niche for colonization; sensitization in others allowed for reduced corrosion resistance. Neither condition would lead to this type of corrosion without the environmental changes caused by colonization.

For correction, the pits must be ground out and repaired. There is no way to arrest the attack, since the cavernous pit shape creates its own aggressive environment. The corrodent (bacteria) must be removed from the environment. Not enough is known about weld conditions which attract bacteria to warrant changing processes.

In a once-through untreated cooling system, any water treatment must be short-lived or biodegradable. A biocide which is biodegradable or which dissipates would be ideal. Chlorine injections should be considered only if no other biocide is available; while chlorine conveniently dissipates and has been used at other nuclear sites, deliberate introduction of chloride into a welded stainless system is not recommended.

## 3. CNS RL CORROSION STUDY OF 1989-91

A corrosion coupon study in the low-pressure service water (RL) at CNS included several welded stainless steel coupons, specifically to test for MIC of this type (see Metallurgy Reports from File #788). No bacterial attack (or corrosion of any kind) was observed on any of the stainless coupons; however, SRB and iron bacteria were found to be present on most coupons. The final report of 8/13/91 stated that "under different conditions and geometries, the potential for MIC in the service water system remains."

Study factors which differed from in-service conditions included:

- A flow velocity of 4 fps in a 3/4" diameter PVC tube, flowing around a 1/2"-wide coupon - likely increased local velocity; sediment and some organic matter deposited on coupons, but tubercle formation might have been prevented
- Coupons were machined from welded blocks and ground to 120 grit finish, leaving no surface oxide or typical weld bead geometry
- Coupons were purchased, not made by DPCo welders under DPCo procedures
- No residual stress remained in coupons

Welded spool pieces which would simulate realistic stresses and geometries were reportedly installed as of the final report of that study, but their evaluation was not pursued.

## 4. RE-EVALUATION OF LEAK AT 1RN-C97

In April 1994, a pinhole leak was found in a 4" diameter stainless RN to KF line at weld 1RN523-7. The pipe had been installed in 1989. Laboratory evaluation of the leak discovered a cavernous subsurface defect (Metallurgy Report #1650).

Pertinent observations of that incident include:

- Leak occurred in a vertical pipe run, 3/8" from toe of weld on OD
- Line normally sat isolated, was used for clam flushing
- Mid-wall cavern had two chambers plus a linear axial portion; defect occupied 0.15" arc length, 1.25" axial length
- No tubercle on ID, but reddish-brown deposit streak present; EDS showed sulfur
- Transgranular stress-corrosion cracks present, traveling outward from mid-wall cavity toward both OD and ID
- Leak occurred through cracks rather than pit; no chloride found
- Cavity had unusual texture, resembling delamination, as did much of the corrosion near the OD surface

This lab concluded that the cavity was an isolated manufacturing defect. MIC was considered to be a possible cause of the defect but was discounted because it did not show characteristics typical of anecdotal MIC attack in stainless steel. The factors

which appeared to discount MIC were:
- lack of tubercle or significant biological growth on ID
- delaminated texture of interior void
- long axial portion of void, which extended down center of pipe wall
- presence of cracking, especially traveling toward the ID

We have now seen that cracking can accompany MIC attack, but it has been observed as an extension of pitting. A tubercle might have been present and been washed away when the flush was performed. The axial gap at mid-wall and the laminated texture of the cavity would be very unusual features for MIC attack, but it is possible that bacteria contributed to the corrosion.

---

**Conclusions:**

Leaks in the RN stainless steel welds were attributed to microbiologically-influenced corrosion (MIC). Typical attack in butt welds was cavernous pitting in the HAZ under tubercles; in socket welds, corrosion through one phase of the stainless filler metal.

The leaks were highly localized, even within a single weld; no link-up of corrosion sites was observed. Leaks may continue to occur at sites where attack has already begun.

Future bacterial colonization needs to be minimized to reduce the continued formation of new pit sites. Careful use of biocides should be considered. Biocide treatment likely will not reach into existing pits, but removing the tubercles may slow the corrosion.

If the Metallurgy Lab can be of further assistance, please call us at (704) 875-5275.

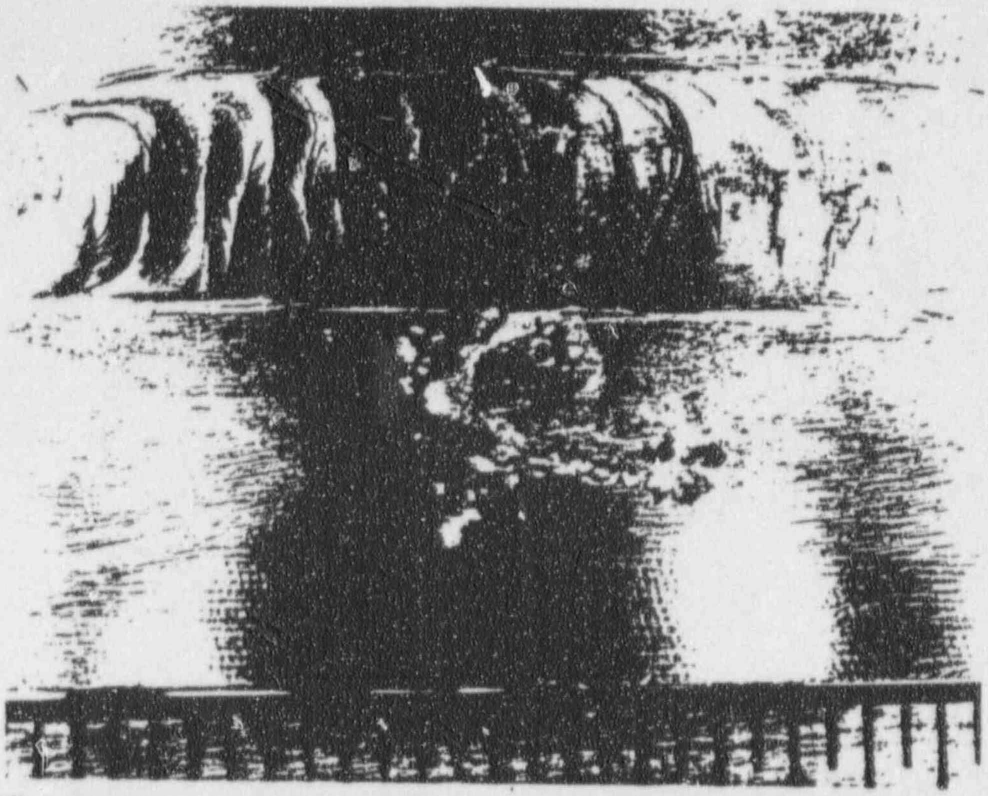


Figure 1 OD appearance of a butt weld leak showing pinholes near toe of weld. One butt weld leaker showed a crack on the OD rather than a pinhole. Gauge = 1/16". Ma-3327.

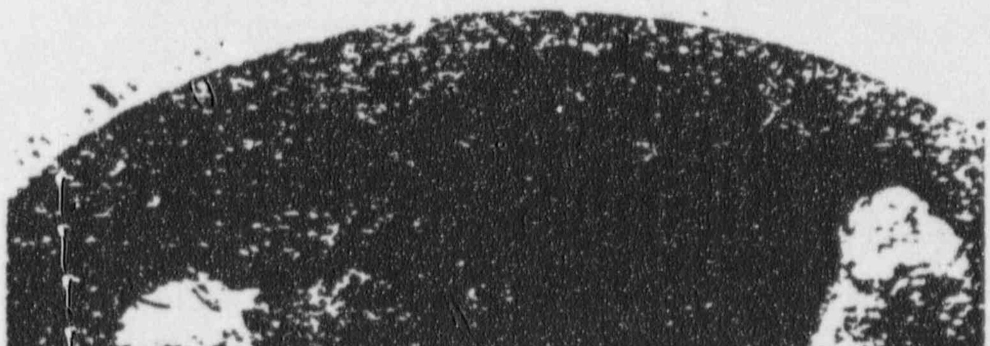


Figure 2 Intact tubercles on either side of the butt weld. Leak occurred under one tubercle; pitting was occurring under the other. Smaller tubercle between was of different size and color. Ma-3330.

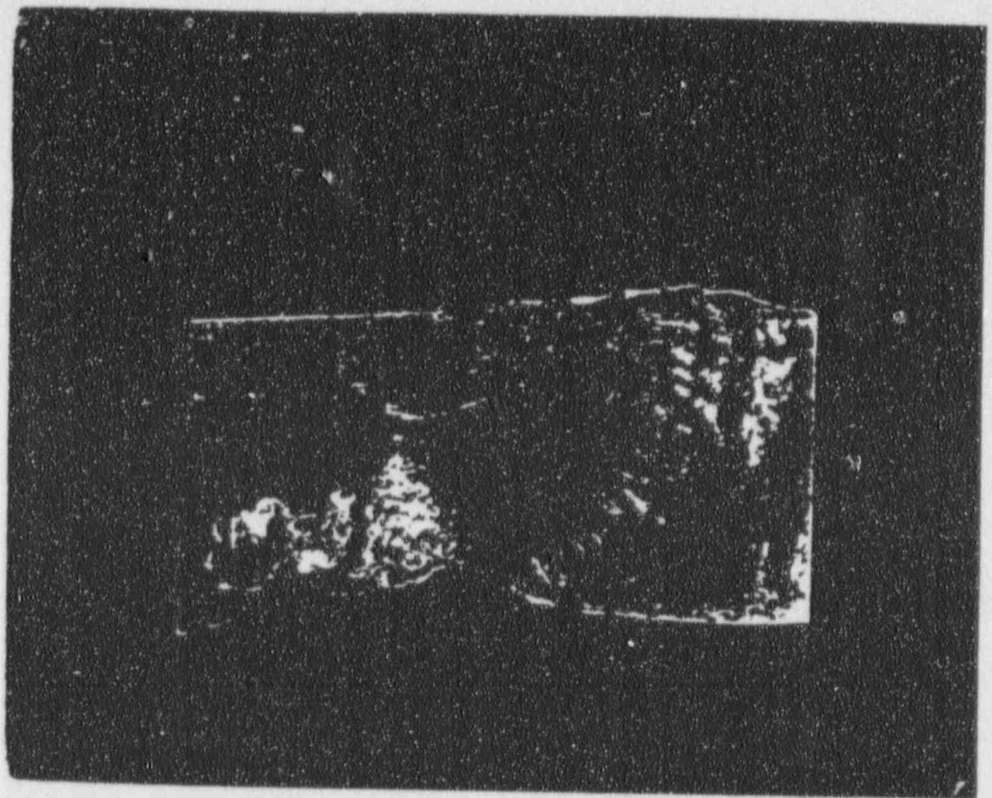


Figure 3 Mounted/etched cross-section through pit in Figure 1 showing cavernous subsurface pits. Pits began at ID (top) and tunnelled toward OD. Pinhole ID and OD penetrations. (5X) Ma-3342.

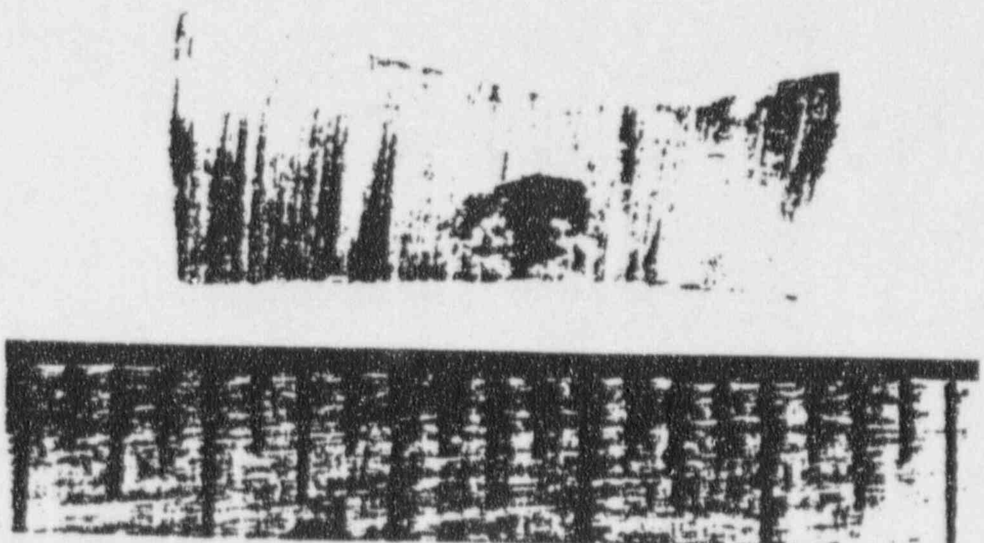


Figure 4 Cross-section (as saw-cut) through butt weld HAZ where tubercle trace appeared. Leak was located at this site but pit penetrates only halfway through wall. Gauge = 1/16". Ma-3341.

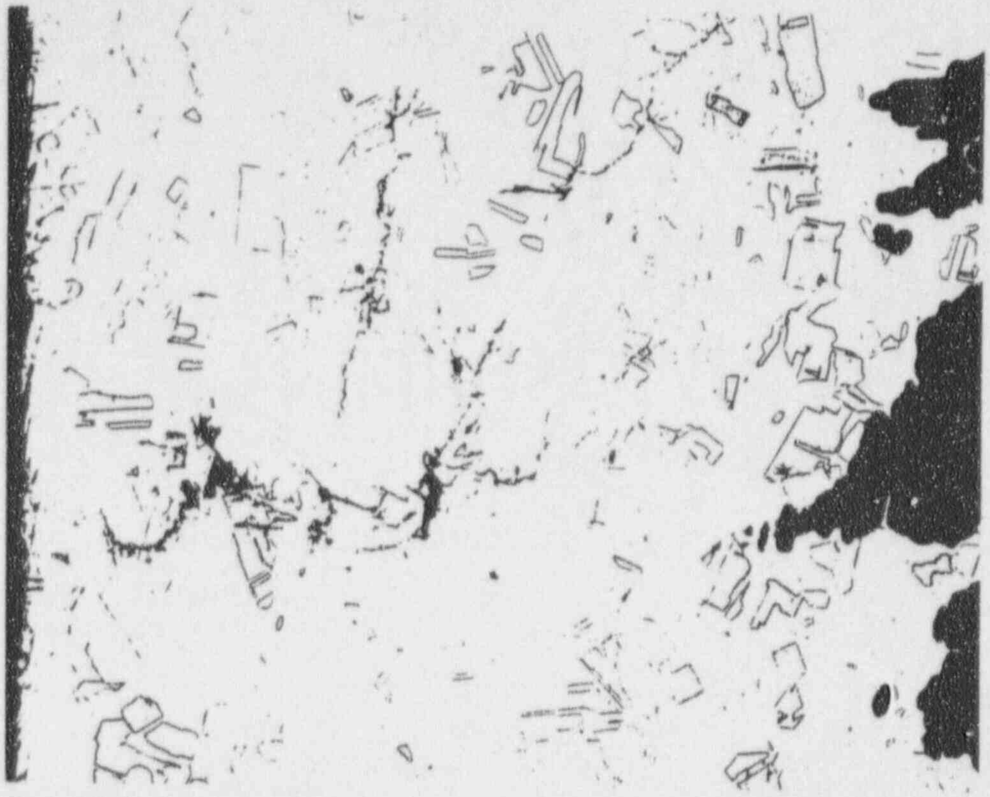


Figure 5 Detail of pit in Figure 4 after metallographic preparation. Crack network is visible between irregular bottom of pit and OD wall. Cracks are branching and transgranular. (32X) Oxalic acid. Mi-3319.

Figure 6 Detail of one arm of pit in Figure 5 showing cracks growing directly from the pit itself. Cracks are the same as those in the large network shown above. (100X) Oxalic acid. Mi-3321.

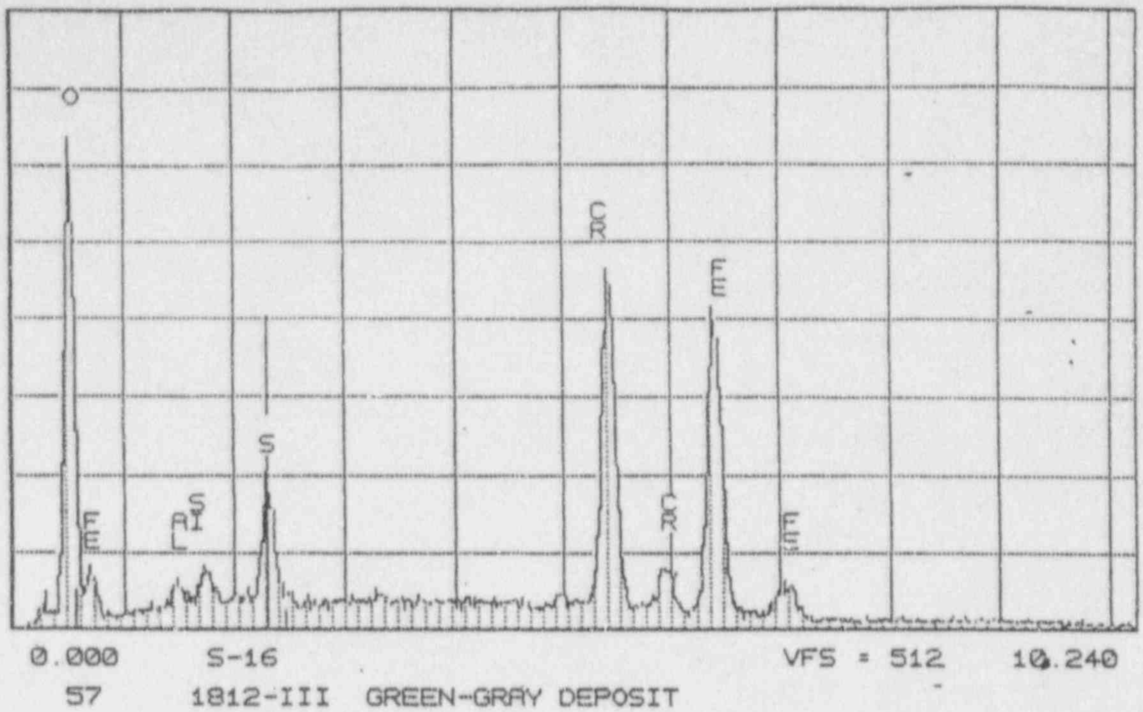



Figure 7 Typical EDS spectrum produced by greenish-gray material at center of tubercle. A distinct sulfur peak is present along with sediment and metal oxides.

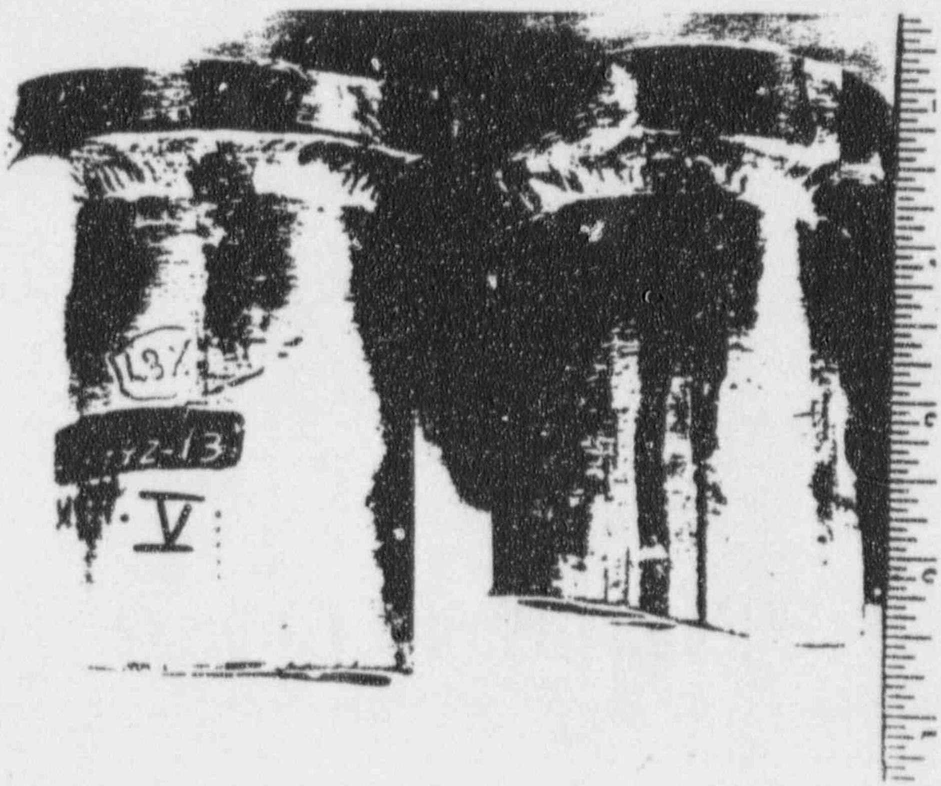


Figure 8 Typical appearance of leaks in socket welds 2RN443-13 (left) and 2RN441-1 showing leak through weld bead and rusty streak on OD. Ma-3345.

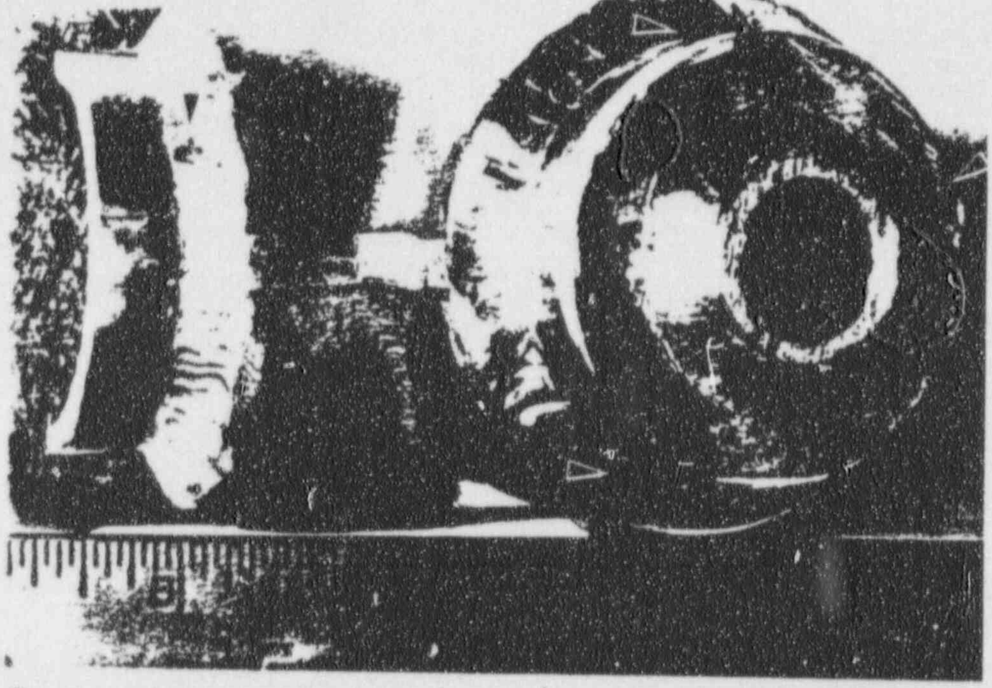


Figure 9 Section of tee showing leak on underside of 2RN442-23 (left) and 3 leaks on 2RN442-25 (one hidden) which attached the reducing insert. Ma-3351.

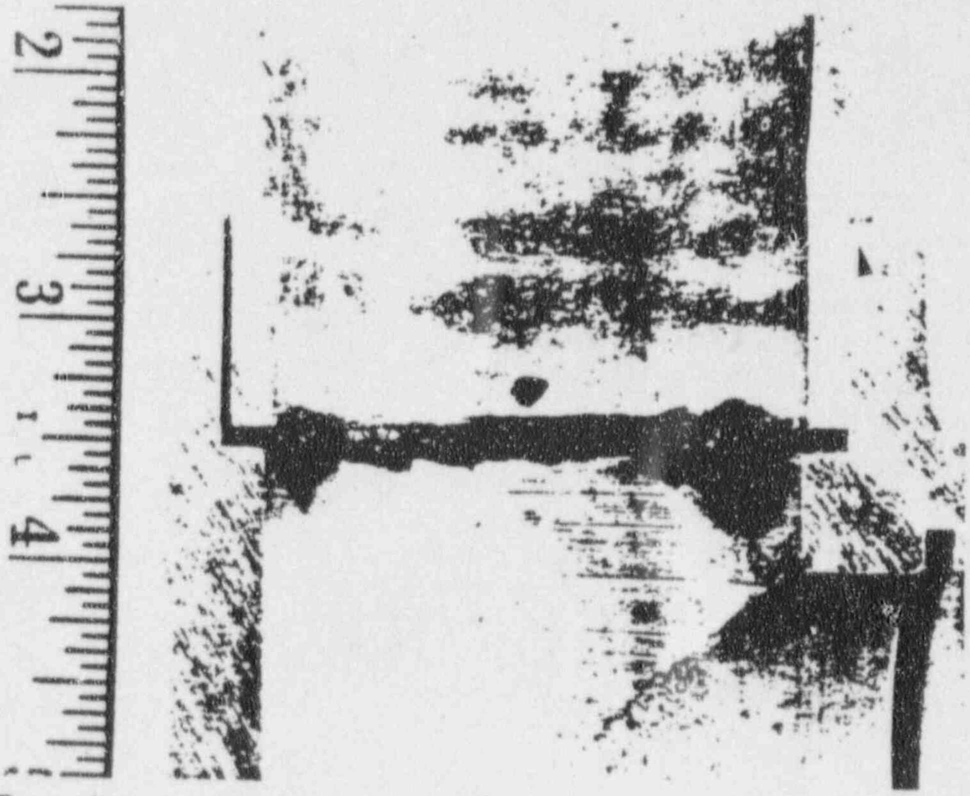


Figure 10 Deposit protruding from socket joint behind 2RN440-22. Leak occurred at center of deposit arc. Adjacent socket joint is clean. Note lack of fusion at weld root (arrow). Ma-3347.

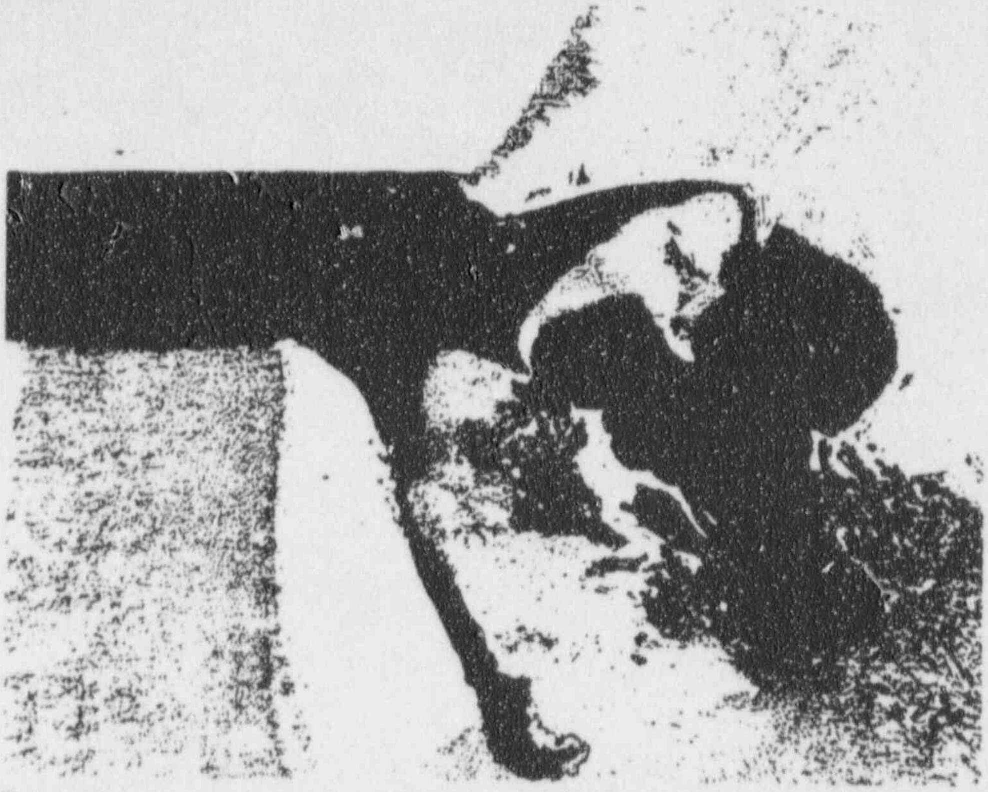


Figure 11 Corrosion at root of weld 2RN441-1. Path is through one phase of weld metal; sponge-like structure remaining eventually corrodes away to form pit. Lack of fusion evident. (32X) Oxalic acid. Mi-3328.

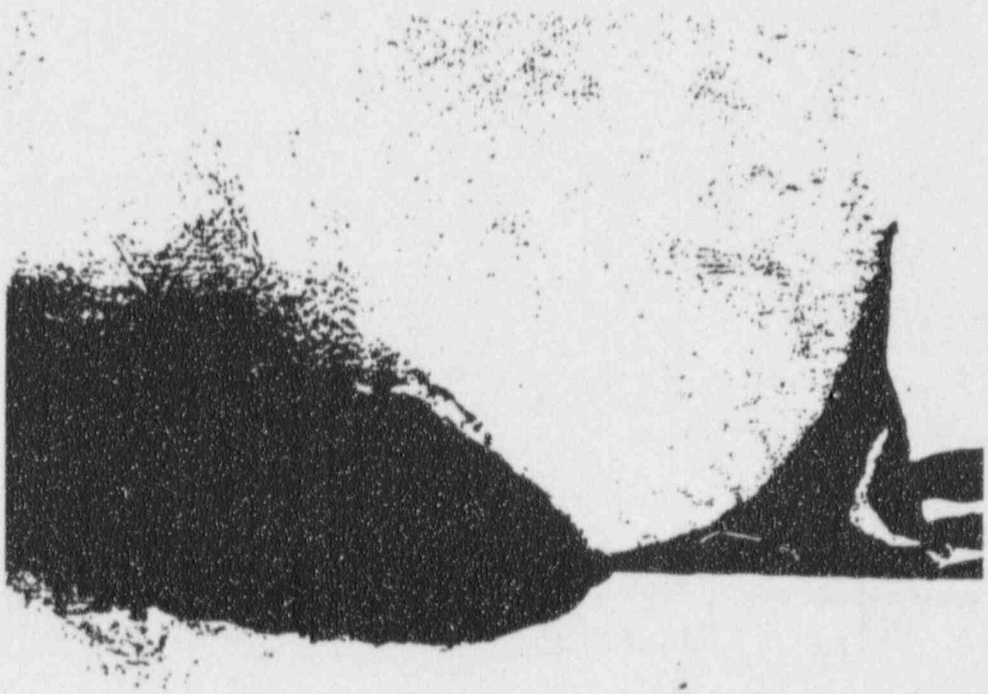


Figure 12 Corrosion at root of weld 2RN442-13. Lack of fusion also evident, but corrosion took different path than in Figure 11. Same preferential attack in weld metal. (32X) Oxalic acid. Mi-3329.

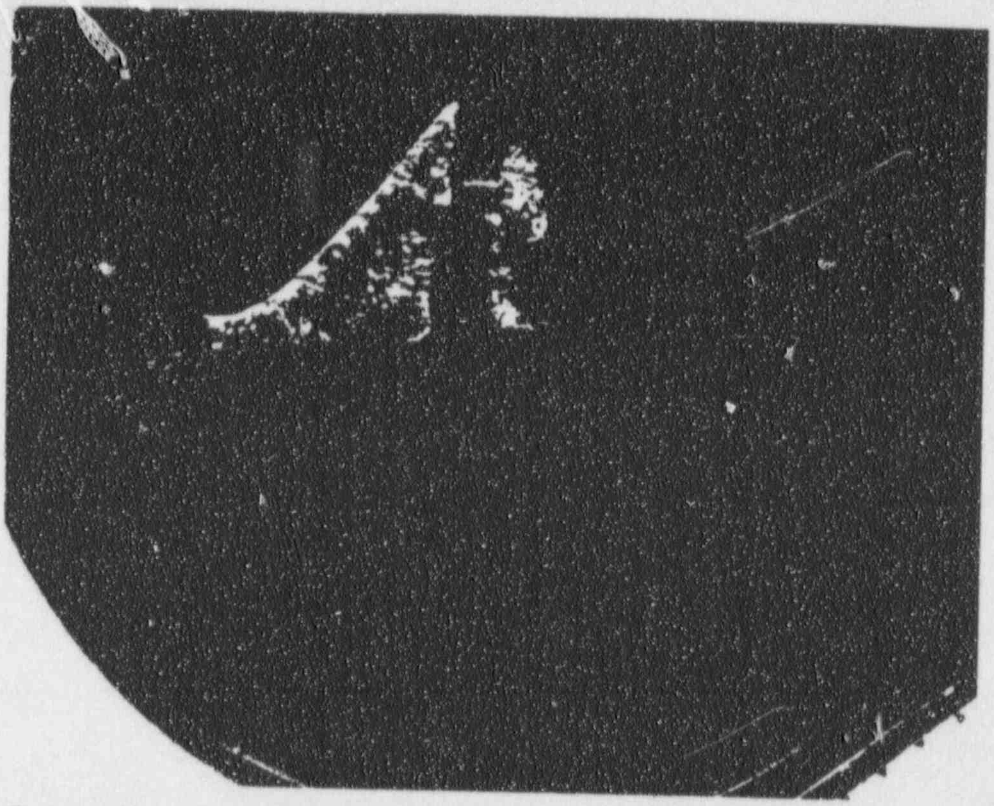


Figure 13 Cross-section through 2RN442-15 showing pitting attack through elbow; weld root is unattacked. "Finger" from pit connects to weld metal at ~2/3 through-wall; see detail below. (3X) Oxalic acid. Ma-3353.

Figure 14 Detail of Figure 13 showing intergranular pit in forging, pit tunnelling toward weld metal, and preferential attack in weld which led to leakage. (32X) Oxalic acid. Mi-3332.

May 1, 1995

# CNS Stainless RN Piping - Flaw Sizing

## Addendum to Metallurgy Report #1812

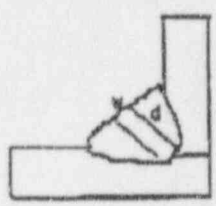
To: Ernie McElroy / Fred Willis / Joel Reeves - CNS
David Ward / Tony Mauldin - CNS
Mark Pyne / Steve Davenport - NGD/GO
Norm Stambaugh / Donna Keck - NGD/GO
Mary Maner / John Derwort - ESS/Environmental

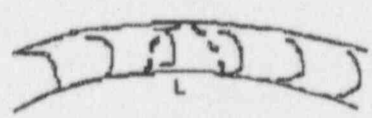
Characterization of typical flaw sizes was requested for use in fracture mechanics calculations. A description of each attack site examined is included, followed by a generalization of the typical form in each type of weld.

### SOCKET WELDS

Eight socket welds were sectioned for flaw size characterization. A corrosion path which began at the root and traveled outward through the weld metal was seen in five of the eight samples. The corrosion occurred preferentially along one phase. The typical geometry and dimensions were as shown:

W = 0.15"
D = 0.25"
L = 0.38" max

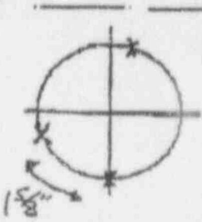




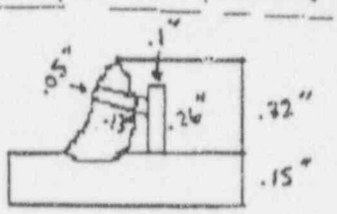

Path probably has this shape.

The sampled welds which were leaking were 2RN441-1, 2RN442-13, 2RN442-25, and 2RN442-21. Weld 2RN442-20 had deposit in the socket joint but was not leaking; sectioning showed that similar corrosion was occurring. Length (L) in that case was less than 0.25".

The leak in 2RN442-25 was only one of three separate leak sites in that weld. The mechanism and geometry of the other two were not investigated, but were assumed to be similar. The leaks were distributed as shown.



Weld 2RN440-22 contained one leak. The corrosion path was primarily through the 90° elbow, then switched to the weld metal. This complicated geometry is shown here. The circumferential length (L) was 0.38" or less.




Weld 2RN442-15 (45° elbow) had two leak sites 0.5" apart visible on the exterior of the weld, and pinholes in the elbow as well. Sectioning revealed it to be pitted through both the weld and the fitting, as in 2RN440-22 above. The arc was sectioned in five locations 1/4" apart, each showing some form of attack. While the forms of attack were not proven to be linked, it must be assumed that they are linked in some way. The arc length of this defect should thus be considered to be 1.25".

Weld 2RN442-23 (underside of the 2" line to the blind flange) had attack in both the tee and weld, similar to the geometry above. Again, the attack sites appeared to be distinct, but there may have been some link-up on a microscopic scale. The arc length where pitting was actually visible was 0.5". NOTE: Minor surface attack had occurred along nearly 180° of the socket, indicating that active corrosion had the potential to attack an arc of that size. The pitting was limited to the small arc as described.

**BUTT WELDS**

Only two of the three original samples had been retained for further study. The sample which had stress-corrosion cracks extending from a cavernous pit was 3/16" in arc length; the pit itself was 0.16" through a 0.25" wall.

The other sample contained three tubercle sites, each 3" of arc length apart, with the leaker located at the bottom center. The two non-leaking sites contained much smaller pits than the leak site. The axial length was 0.30" and the circumferential arc length was 0.25" maximum.

Bacteriological Sampling - Update

Cultures were taken from deposits growing out of socket joints where leaks were located. In one case, both iron-oxidizing bacteria (Gallionella and Sphaerotilus) and slime were identified, while only slime was identified at two other socket sites. Sludge poured out of the reducing insert section and swabbed from the cap of the blind flange were positive for iron-oxidizers and slime.

All bacteriological culture reports performed for this investigation are attached.

Summary

The circumferential arc lengths of the socket weld flaws were typically 3/8"; however, some linkup of adjacent flaws appeared to have occurred in some cases. The flaw length may have encompassed 1.25" in one weld. The mode of the attack in these welds (along one phase of the filler metal or through sensitized areas of the fittings) created elaborate crack paths which were difficult to characterize.

The leaks at the butt welds were highly localized, cavernous pits. The pits were self-contained and did not link up in any way. Cracking which occurred at one pit site was also concentrated at the pit location.

Bacteriological sampling confirmed the presence of iron-oxidizing bacteria in the sludge in and on the pipe. The bacteria were cultured at only one of three socket joints. Since the material protruding from the joints was somewhat removed from the active corrosion site deep in the socket, the absence of iron-oxidizers does not eliminate them from consideration as a corrosive agent. In fact, corrosion by iron-oxidizers remains the most likely explanation for the observed weld attack.

If the Metallurgy Lab can be of further assistance, please call us at (704) 875-5275.

S Anderson
Sue Anderson
Engineer - APT/Metallurgy Lab
ESS Diversified Services