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CORROSION INVESTIGATIONS OF REDOX PILOT PLANT EQUIPMENT AT OAK RIDGE NATIONAL LABORATORIES

By
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November 3, 1949

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CORROSION INVESTIGATIONS OF REDOX PILOT PLANT EQUIPMENT AT OAK RIDGE NATIONAL LABORATORIES

INTRODUCTION

Two particularly corrosive conditions have been recognized to exist in the separations technology for processing highly radioactive materials. The first is encountered during the dissolving operation wherein the dissolver vessel is exposed to concentrated nitric acid at elevated temperatures. The second is encountered when contaminated vessels are subjected to decontamination. Of these, the second is known to be by far the more corrosive of the two since the most successful decontamination cycles involve the use of hydrofluoric acid or its salts.

Since the Oak Ridge National Laboratories depend upon the direct, or contact-type of equipment maintenance, a prerequisite of which is essentially the complete removal of radioactivity, they have had considerable experience with decontamination and its resultant corrosion problems.

During the months of August and September much of the O.R.N.L. Pilot Plant equipment was decontaminated and disassembled for inspection in preparation for further use. The author visited that site in order to examine the effects of corrosion upon this equipment. The observations made are the subject of this report.

SUMMARY

With one notable exception, i.e., the dissolver (Vessel A-1, Cell No. 1), the corrosion encountered in the pilot plant at the Oak Ridge National Laboratories was quite small. with exception of the dissolver (Vessel A-1, Cell No. 1).

The dissolver showed considerable corrosion of the inside bottom dollar weld and of those welds securing the slug basket to the bottom of this vessel. Several components of the dissolver, such as the "slug crash plate" and service tubes, also showed weld corrosion. /end

While present construction materials are satisfactory; extreme care should be exercised during fabrication to insure superior weldments and satisfactory heat treatment.

DETAILS

The Oak Ridge National Laboratories pilot plant has been in operation for several years. In 1944 the Bismuth Phosphate Process development was begun. At the conclusion of this program, the equipment was cleaned and converted for use in the study of the Code 25 recovery process, a solvent extraction process study which was completed in October 1947. Following this study the equipment was decontaminated and converted for use in the study of the Redox process which included one combined plutonium and uranium cycle and one uranium decontamination cycle. These runs, which began in September 1948, were initially run at 5% Hanford level, were increased to 30% Hanford and finally to full Hanford level at which a series of six runs were made. In preparation for additional studies of the Code 25 process this equipment was again decontaminated and partially dismantled for inspection during August and September 1949.

Those vessels and auxiliary equipment decontaminated and dismantled at the time of the author's visit are discussed below:

CELL I VESSELS

Dissolver (Vessel A-1)

This vessel was fabricated from ½" plate of du Pont specification 820-B stainless steel which is essentially T-309 SCb (25-12 SCb) stainless. It was thought a 25-16 Cb welding rod was employed. This would be borne out by a spectrochemical analysis made on drillings from the inside bottom dollar weld which reported the following: Cr 25%; Ni 13% and Cb ± 1%.

The vessel had been dismantled and its interior could be closely inspected. It was etched throughout, particularly toward the bottom where the liquid phase (55% HNO_3) of the dissolving operation was contained. All interior metal surfaces had a dull, grayish apperance due to corrosion, as compared to the relatively bright, metallic-gray outside surface. Several rough pits, where inclusions apparently had been etched out, were observed; however, there was no evidence of local corrosion at these points.

Both exterior and interior welds were undercut. In the case of the latter, this undercutting was aggravated by subsequent exposure to operation and decontamination conditions. In addition, the interior welds were etched, with the greatest degree of etching towards the bottom. However, these welds were all sound except those securing the slug basket to the bottom dollar and the bottom dollar-tank wall weld. These exceptions were rough, blackened (likely by the oxalic acid decontamination cycle), cracked, pitted, and at their worst, had a spongy appearance. Apparently they were somewhat anodic to the base metal.

The bottom dollar weld was attacked to the greatest degree. (See Appendix C: Vessel A-1, Dissolver - Interior, p. 9). It was cracked some three-quarters of its length and at one point the fissure appeared to extend through to the root of the exterior weld exposing what looked to be a cavity between the roots of the interior and exterior welds. This cavity, judging from its appearance, was more likely the result of poor penetration during welding than of subsequent corrosion, although such crevices invite corrosion.

These welds, i.e., the bottom dollar and slug basket welds, which were attacked, also experienced the severest corrosion conditions during both process operation and the decontamination cycles.

During normal process operation, a batch operation, the metal slugs are dissolved in this vessel using initially 55% HNO_3 at approximately 100°C. As the operation proceeds the temperature probably increases somewhat before it decreases and the HNO_3 is diluted. The decontamination cycles vary considerably. The last time this vessel was decontaminated nitric acid, ammonium acid fluoride, ammonium silicofluoride, sodium hydroxide, sodium dichromate, oxalic and citric acids were used. Appendix A, "Decontamination Cycles", p. 7 , gives details of these decontaminants and their effectiveness. Total decontamination time was approximately 12 days during which hydrofluoric acid compounds were used some 1 ½ days. Hydrofluoric acid is known to be corrosive to stainless steel even in presence of strong oxidizing agents such as nitric acid.

What percentage of this corrosion was due to process operation and what percentage was due to the decontamination cycles is unknown along with the nature of the decontamination employed on previous occasions. However, on the basis of corrosion tests with welded stainless steel in boiling conc. nitric acid and of a superficial examination of the dissolver in the Hanford 321 Bldg., which has not been subjected to thorough decontamination, we may assume that the decontamination cycles were responsible for the greatest percentage of this corrosion.

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The dissolver slug guide [1] (du Pont 820-B, essentially T-309 SCb, stress relieved) was etched overall. The welds, in general, were in better condition than those of the dissolver vessel, but were rough etched, particularly toward the bottom where several pits with porous sides were observed.

The reflux condenser [2] (T-347, not stress relieved) was somewhat etched and dull in appearance except for bright welds which were made with T-309 SCb welding rod. Several of the welds which tacked the condenser coils together, were cracked, but this was apparently due to a combination of welding stresses and rough handling rather than to corrosion.

The dissolver utility tubes [3] were reportedly fabricated of butt-welded T-347 stainless tubing. The tube seams were well etched, contained a few pits and showed indication that failures would result. Hand-welds, used to plug the ends of the thermocouple tube, failed, allowing solution leakage which resulted in the loss of the thermocouple proper. Comparable welds on the sparger showed signs of attack, as did those welds which joined the three tubes of the liquid level tube unit.

The dissolver vessel had been checked for contamination and the following readings were reported:

(a) Center of dissolver slug basket against bottom dollar, 90 mr/hr.
(b) Center of dissolver, 15 mr/hr.
(c) Top edge of dissolver slug basket, 26 mr/hr.

(1) See Appendix C, p. 10, Vessel A1: Dissolver Slug Guide

(2) See Appendix C, pp. 11-12, Vessel A2: Reflux Condenser.

(3) See appendix C, p. 13, Vessel A-1; Dissolver Utility Tubes and Gasket Section, (a) Dip Tubes, (b) Liquid Level Tubes, (c) Chemical Addition Tube, (d) Sparger, (E-E_1), Thermocouple Sheath-sectioned, (f) Polythene gasket section.

B: See Appendix B, p. 8, Spectrochemical Analysis Vessel A-1 Welds, of utility tubes and welds and of column packing.

Filter Tank (Vessel A-11, T-347 not stress relieved)

This tank was equipped with micro-metallic grade G porous stainless steel filters which had gradually become covered with "crud" with a resulting loss in efficiency to the point where they merely served as stainless screens. In order to check column efficiency under these circumstances, operations were continued and it was found that the column handled the solutions in a satisfactory manner.

The tank had never been sufficiently decontaminated to allow it to be torn down and inspected, thus no corrosion data is available.

Miscellaneous Vessels

Other tank vessels in this cell including the 1-A column were not available for inspection. The 1-A column had been given a severe-decontamination treatment, but the level of activity had not been reduced sufficiently to allow first hand inspection. Further work was contemplated.

CELL II VESSELS:

IB Column (T-347)

This unit has been decontaminated to a level of 30-40 mr/hr. The packing, ¼" and ½" Raschig rings fabricated of 18-8 stainless steel was unaffected except for slight tarnishing. Some corrosion of welds, where inclusions were found and thought to be the contributing factor, was experienced in T-347 transfer lines. Several minor failures developed at points such as these; however, they were satisfactorily repaired by welding after the particular line had been drained.

A Milton-Roy piston pump failure, at first thought to have been caused by corrosion, was traceable to a manufacturing defect in the form of a thin section of the pump casting.

Teflon gaskets were employed with all columns and, as anticipated, gave excellent service.

IC Column (T-347)

No failures or indications of potential failures were observed.

The columns were decontaminated by blowing "live" steam in at the bottom and adding the decontamination chemicals at the same time. This technique proved rather effective. Straight HNO_3 washes for column decontamination were found to be but a little more effective than straight "live" steam because film formation on packing and column walls was not cut by straight nitric acid.

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Concentrator (Vessel B-5, duPont 820-B, T-309 SCb)

A T-309 SCb stainless steel tank was employed for this vessel merely because one was available, otherwise T-347 stainless would have been specified. The welds of this vessel are only slightly etched and in much better condition than those of the dissolver (Vessel A-1). A greasy film on the interior was attributed to the failure of a grease seal in the agitator gear reduction unit and apparently had no effect on corrosion.

ID Column (U-Extraction) and IE Column (Strip)

These columns had not been dismantled for inspection; however, their packing is in excellent condition. Both are fabricated of T-347 stainless steel.

MISCELLANEOUS VESSELS

Of the remaining vessels inspected, no unusual evidence of corrosion was observed. The IBF feed tank (Vessel B-7), the IDW collection tank (Vessel B-37) and the neutralized waste tank (Vessel B-30) were not dismantled and could not be inspected; however, no corrosion is anticipated. No records are available on Vessel B-8.

CONCLUSIONS

In general, Redox process vessels can be successfully decontaminated by the methods employed at the Oak Ridge National Laboratories. Exceptions as discussed elsewhere in this report may be experienced since the prolonged use of some of these decontaminants will attack stainless steel vessels, especially in the weld areas. The following recommendations are made:

(a) Authorize a test program to study decontamination with a view towards combining maximum decontamination with minimum corrosion.

(b) Establish rigid specifications for not only the fabrication of all process vessels but also for thorough inspection both during and after fabrication with particular emphasis on welds and heat treatment.

(c) The specification of seamless tubing for all lines or utility tubes which will come in contact with corrosive chemicals.

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APPENDIX A

DECONTAMINATION CYCLES (EXCERPT FROM NOTES OF E. C. STEWART, O.R.N.L., REPORT PENDING)

Al-DC*	Solution	Time Hrs.	Temp. °C	Volume Gals.	Volume Liters	U Gamma/Ml	Beta Ct/cc/m	Gamma Ct/cc/m	Gamma Mr/ml
1	55% HNO_3	24	95-105	36.3	137	137	1.44×10^9	296×10^6	1.23×10^6
2	55% HNO_3	24	95-105	42.5	160	19.5	8.8×10^5	364×10^4	1.35×10^5
3	55% HNO_3 (1)	24	95-105	43.7	165	0.60	1.9×10^5	112×10^5	5.33×10^4
4	55% HNO_3 (1) (2)	33	95-105	40.1	150	-	7.6×10^5	-	1.65×10^4
5	55% HNO_3	24	95-105	41	155	90.0	2.14×10^6	637×10^4	2.86×10^4
6	29% HNO_3 (3)	3	95-105	78.6	297	35.0	3.75×10^5	361×10^4	1.43×10^4
7	20% HNO_3-2% NH_4F-HF	¼	54	47.1	178	14.1	2.64×10^7	-	2.18×10^4
8	4% Oxalic Acid	1	95-100	95.6	361	24.0	2.69×10^7	-	4.4×10^4
9	1% NH_4F-HF (1)	7	60	50	189	5.52	3.34×10^7	-	4.33×10^3
10	4% NaOH	24	95-102	60	227	13.0	1.2×10^6	-	1.99×10^3
11	11% HNO_3 + 2.2% Citric (4)	¼	60	12	46.5	0.47	5.3×10^6	-	2.5×10^3
12	24% HNO_3 + 3.3% $Na_2Cr_2O_4$	24	95-105	50	189	18.4	1.98×10^7	-	1.78×10^3
13	5% HNO_3 + 4% $(NH_4)_2SiF_6$	8	60	55	208	0.66	8.47×10^4	-	2.86×10^3
14	55% HNO_3	16	120-125	42	159	0.09	5.98×10^5	-	2.59×10^4
15	42.8% NaOH + 13% [illegible]tric	2½	80- 90	92½	350	0.17	4.74×10^4	-	880
16	Same	16	80- 90	92½	350	0.15	1.80×10^4	-	48.4
17	42.8% NaOH + 13% Citric	16	80- 90	92½	350	-	-	-	-
18	Same	8	95-105	92½	350	-	5.68×10^3	-	-
19	30% NaOH + 11% Citric	16	95-105	105	396	-	6.44×10^3	-	139
20	Same plus 1.2% $(NH_4)_2SiF_6$	16	95-105	115	436	0.44	1.84×10^3	-	11.0
21	1% NH_4-HF	4	30- 35	95	359	0.92	875		60.0
22	3.5% HNO_3 + 0.6% (NH_4F-HF)	4	30- 35	80	303	0.28	2.4×10^3		500

Total: 202 Curies Removed

(1) Intermittent refluxing in condenser permitted for 3 hrs, 20 minutes.
(2) Solution sampled after refluxing.
(3) Same solution as sample 5 but diluted and sparged for 3 hours.
(4) Added to tank via off-gas line through packing.
(5) Off-gas line flush - sampled in dissolver

* Al-DC: Vessel AI (Dissolver) decontamination sample numbers.

APPENDIX B

SPECTROCHEMICAL ANALYSIS OF VESSEL A-1 WELDS, OF UTILITY TUBES AND WELDS AND OF COLUMN PACKING

	Cr%	Ni%	Cb%	Mo%	Ti%
A-1 Dissolver: Bottom Dollar Weld	25	13	M	-	M
Liquid Level Tube -					
Base Metal	23.49	12.69	M-S		
Seam	21.36	12.76	M	-	-
Hand Weld	12.64	11.30	M	-	-
Thermocouple Sheath					
Base Metal	23.49	12.69	M	-	-
Seam	20.49	12.50	M	-	-
End Weld	17.21	8.21	M	-	-
Sparger					
Base Metal	22.10	11.91	M	-	-
Seam	22.34	12.96	M	-	-
End Weld	12.21	9.43	M	-	-
1/4" Raschig Ring	21.97	8.70	-	-	-
1/2" Raschig Ring	17.35	7.98	-	-	-

Note: M = moderate, 1% to 0.01%

S = strong, >1%

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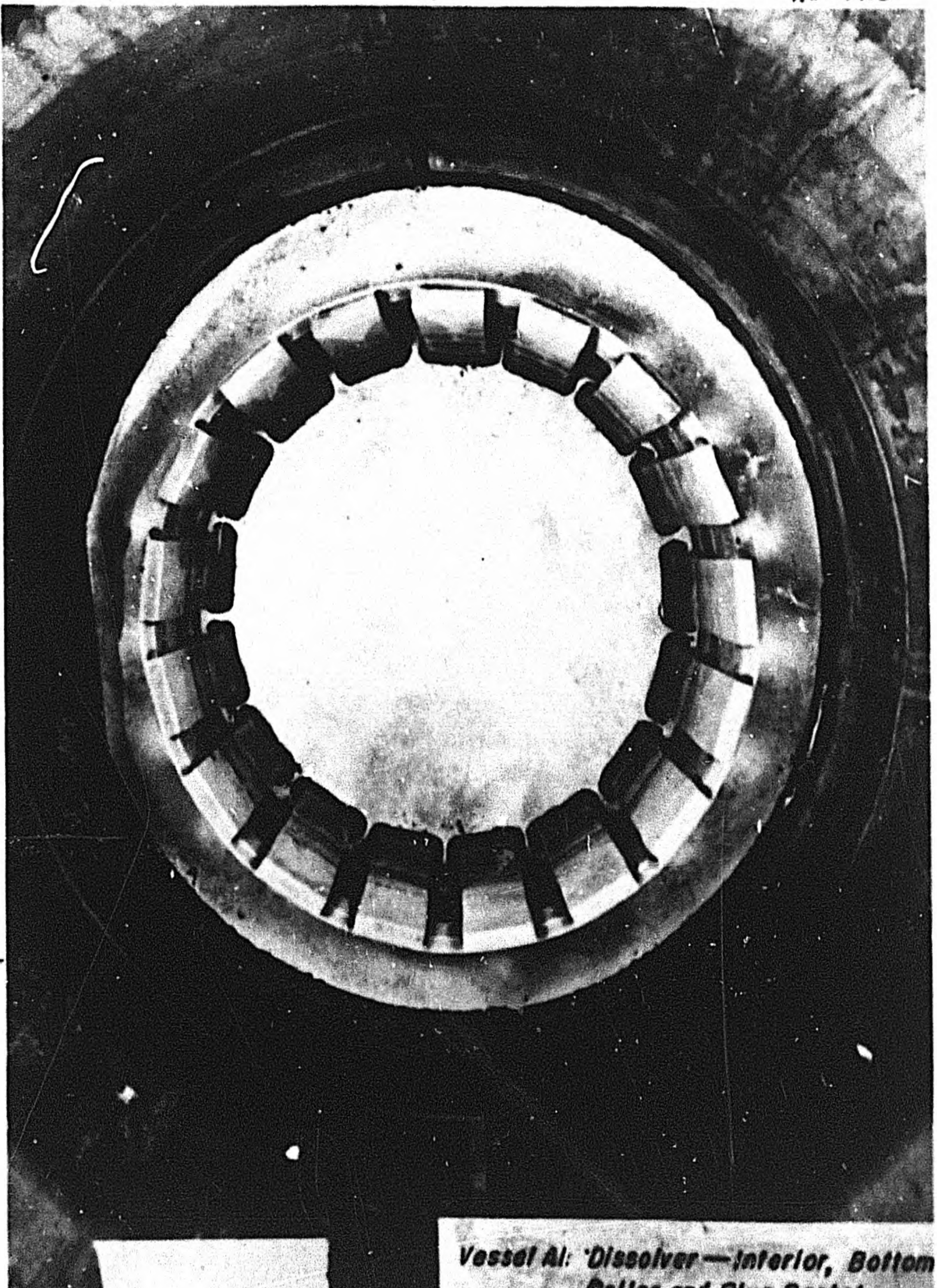

Vessel Al: Dissolver — Interior, Bottom Collar and Slug Basket.

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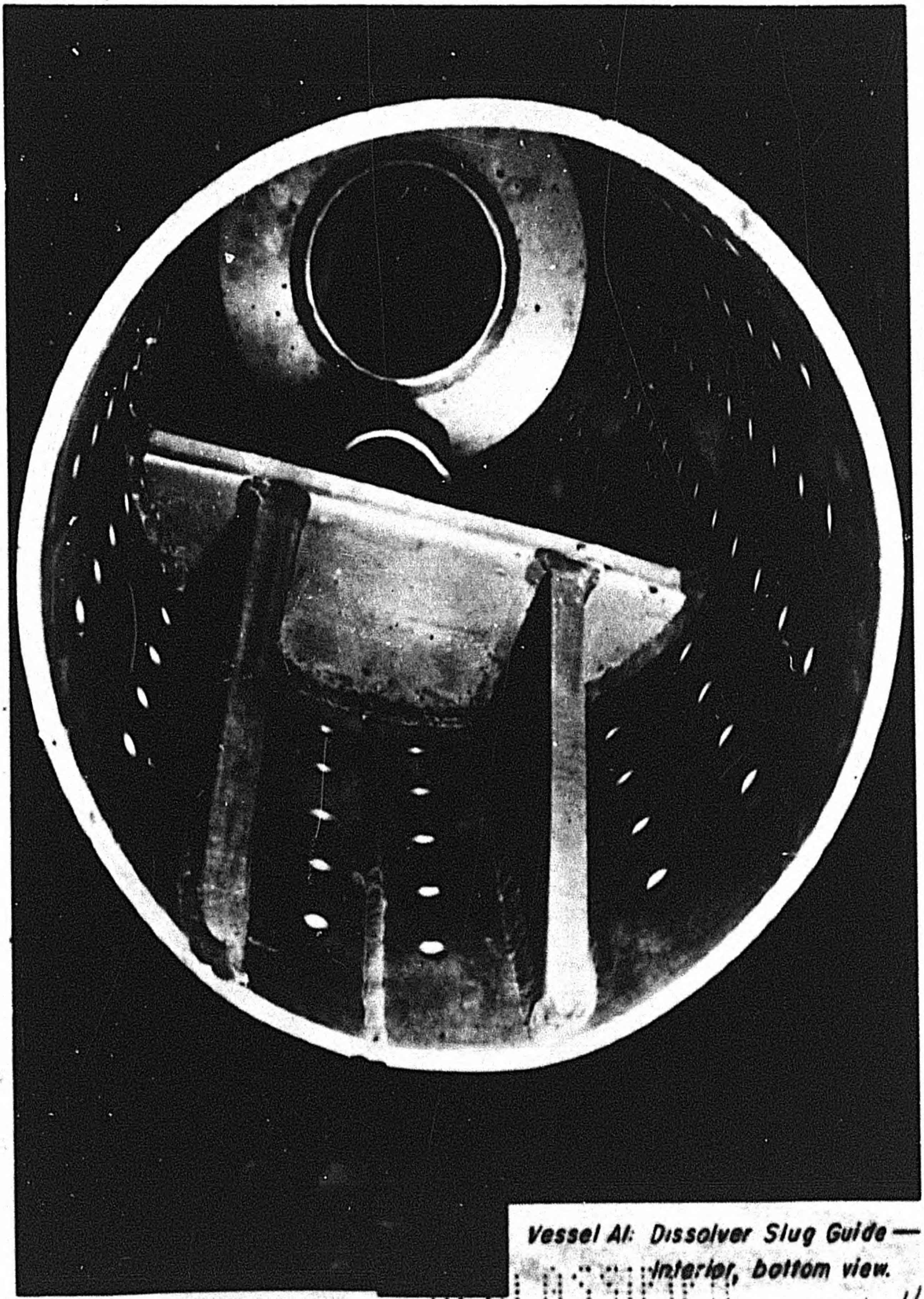

Vessel A1: Dissolver Slug Guide — Interior, bottom view.

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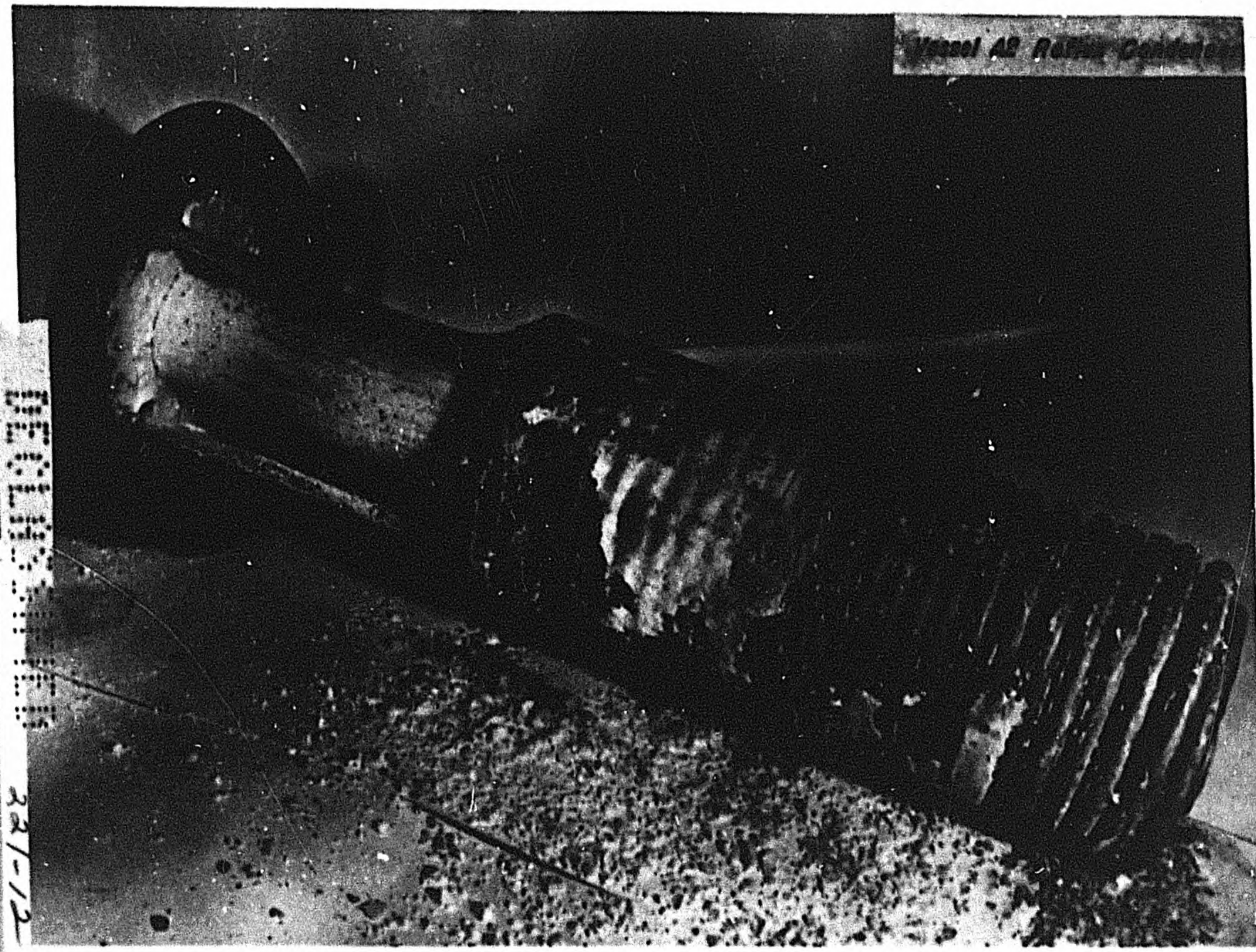
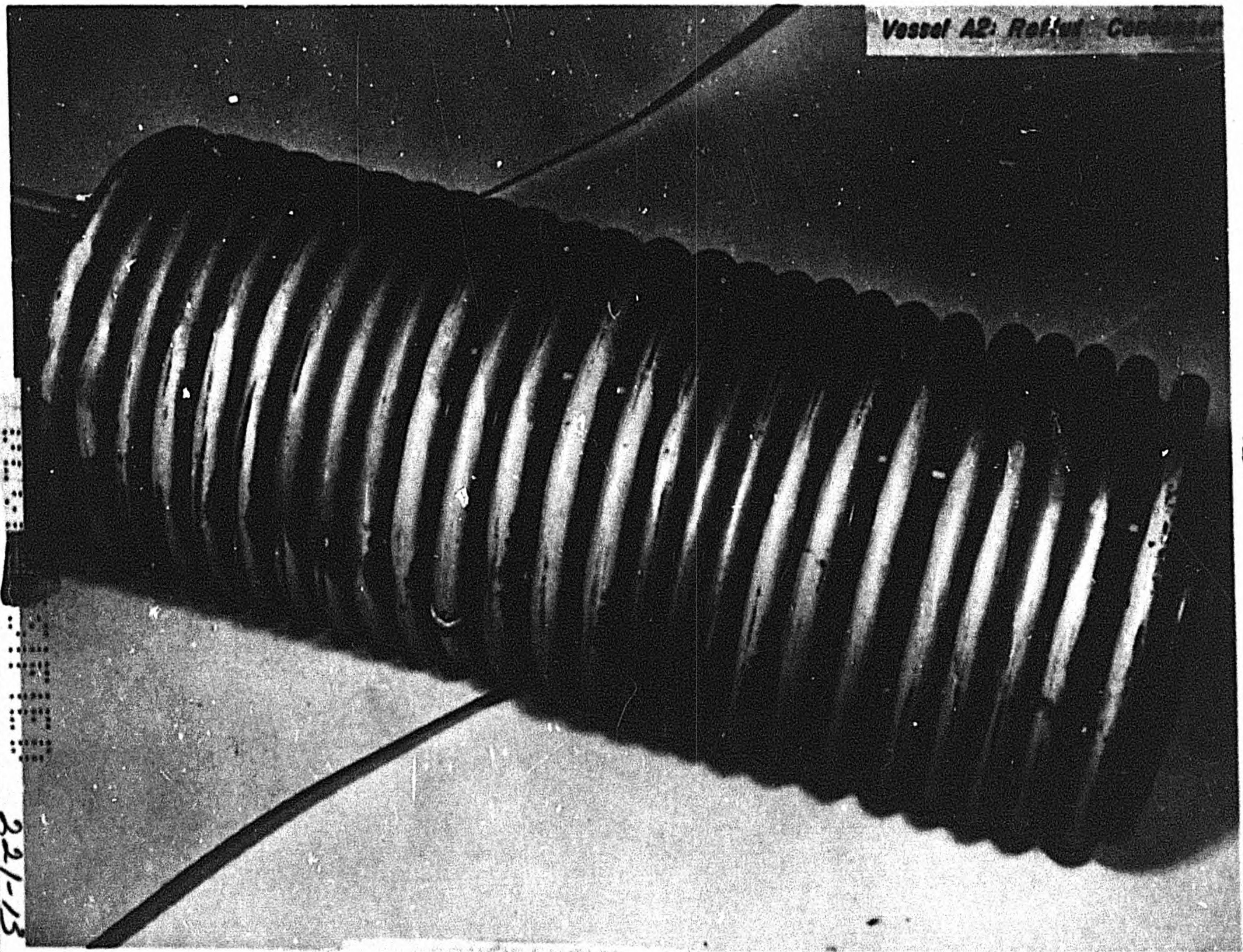

Vessel A8 Reflux Condenser



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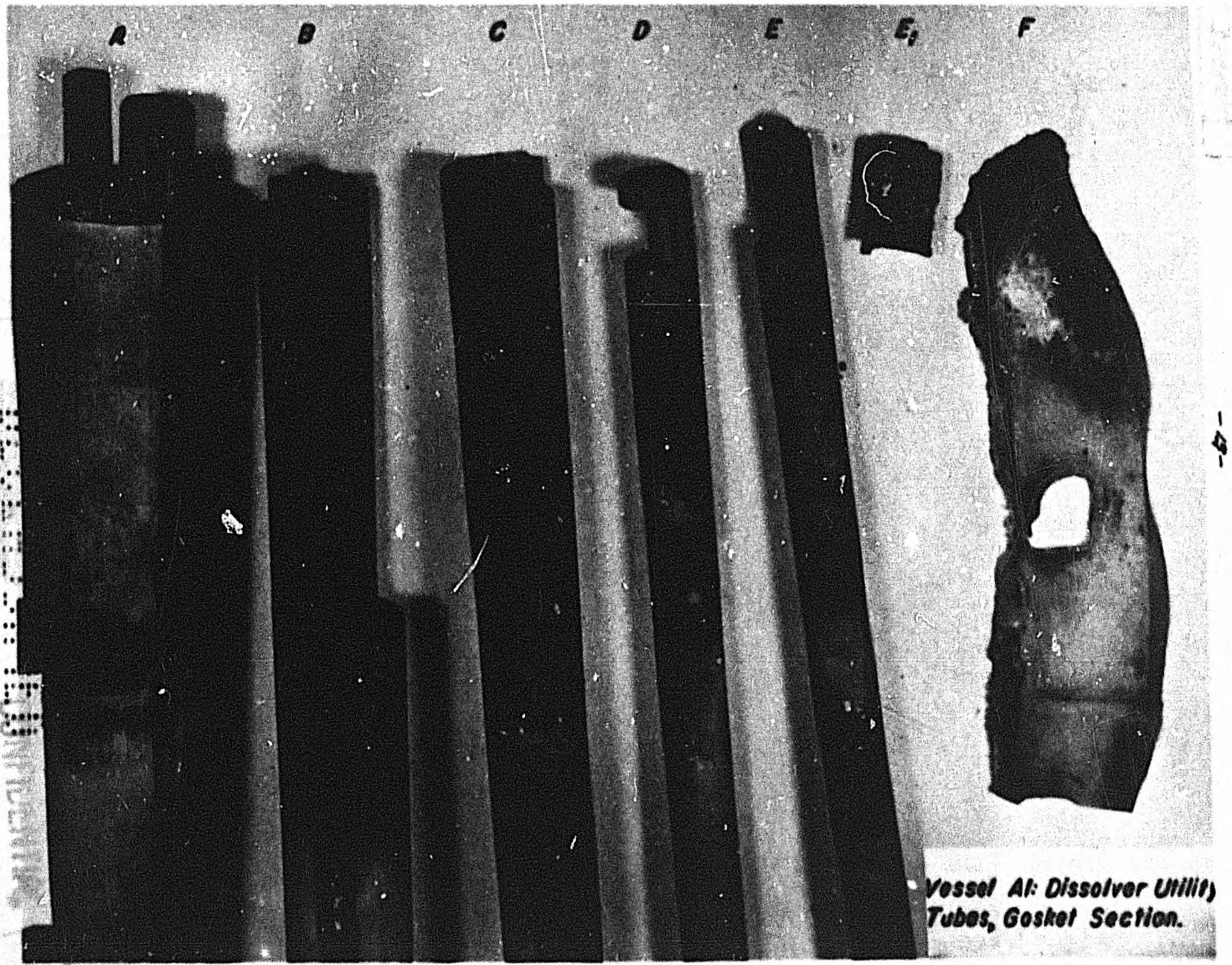

Vessel Al: Dissolver Utility Tubes, Gasket Section.

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CORROSION INVESTIGATIONS OF REDOX PILOT PLANT EQUIPMENT AT OAK RIDGE NATIONAL LABORATORIES. W. W. Koenig. Nov. 3, 1949. 13p. (HW-14955) SECRET

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END