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CORROSION MONITORING OF STORAGE BINS FOR RADIOACTIVE CALCINES

ABSTRACT

Highly radioactive liquid waste produced at the Idaho Chemical Processing Plant is calcined to a granular solid for long term storage in stainless steel bins. Corrosion evaluation of coupons withdrawn from these bins indicates excellent performance for the materials of construction of the bins. At exposure periods of up to six years the average penetration rates are 0.01 and 0.05 mils per year for Types 304 and 405 stainless steels, respectively.

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I SUMMARY

The high-level waste at the Idaho Chemical Processing Plant (ICPP) is generated during the reprocessing of spent nuclear fuel. The fuel comes from nuclear reactors using highly-enriched uranium-235 fuel. This waste is primarily the first-cycle raffinate from the solvent extraction of dissolved fuel solutions, and is self-heating. The second- and third-cycle solvent extraction wastes are handled as high-level waste also.

Management practice for high-level waste at the ICPP is to store the liquid waste safely for a period not to exceed five years, calcine the liquid to a dry solid, and store the solid safely in engineered bins of Types 405 and 304 (0.06 percent carbon maximum) stainless steels where it will be retrievable at all times(1,2). After exposure of specimens in the radioactive dry solids for periods up to six years, the average-projected 500-year penetration rates are 20- and 5- mils for Types 405 and 304 stainless steels.

II INTRODUCTION

High-level radioactive aqueous wastes resulting from the solvent extraction of uranium from nuclear fuel elements are calcined to granular solids in the Waste Calcining Facility (WCF) at the Idaho Chemical Processing Plant (ICPP). The granular solids are stored in stainless steel bins which in turn are contained inside buried concrete vaults. This arrangement provides double containment and methods for detecting failure of the primary containers, or seepage of surface or ground water through a fissure in the concrete vault. The calcined product from the WCF is spherical and granular in nature.

The original waste storage facility, consisting of four annular bins, has been filled with approximately 7,500 cubic feet of calcined solids. The second storage facility consists of seven cylindrical bins, and has a storage capacity of approximately 30,000 cubic feet. The third set of bins of 40,000 cubic feet capacity is similar in design to the second facility. These bins were placed in service in 1973.

During October 1973, corrosion coupons were removed from two bins in the second solids storage facility. One bin contained alumina calcine solids and the other zirconium calcine solids, described in Section III.

III CALCINE PRODUCT

The WCF at the ICPP has been solidifying high-level wastes in a fluidized-bed calciner since December 1963. As of January 1974, over 1,510,000 gallons of aluminum-type waste and 1,089,000 gallons of zirconium-type waste had been calcined to give a total of 42,500 cubic feet of solids. The original process was developed for solidifying high-level waste from the processing of aluminum-clad test reactor fuel. The process has been modified to calcine fluoride-bearing zirconium waste, stainless steel sulfate waste, and ammonium nitrate-containing waste. The WCF is a vital unit in an integrated program of spent fuel storage, fuel reprocessing, and waste management at the ICPP(3).

In the calciner, the liquid waste is pneumatically atomized from three nozzles at 85-140 gph into a heated, 6-ft-deep, fluidized bed of solidified granular waste at 400-500°C. The process is endothermic; therefore the bed is heated by in-bed combustion of an oxygen-atomized stream of kerosene.

Typical physical and chemical properties of calcined solids from acid aluminum waste and fluoride-bearing zirconium waste are given in Table 1.

IV CALCINE STORAGE FACILITIES

A. ICPP First Calcine Solids Storage Facility.

The first solids storage unit was provided with the initial WCF installation. It was designed to maintain all of the stored material below the calcination temperature (400°C) and to prevent, if possible, the evolution of radioactive fission products. Accordingly, storage for calcined waste was provided by four units located underground in a concrete vault. Each one, as shown in Figure 1 was made up of a central cylinder and two progressively larger concentric bins with annular spaces between each section. The outermost bin is enclosed by a carbon steel shell which leaves a 1-1/2-inch-wide annular space between the bins and the shell. The capacity of each unit is 1950 cubic feet, and the total capacity for the four units is 7800 cubic feet. The design pressure range for each unit is from -3.75 psig to +3.75 psig at a design temperature of 350°C. These units were fabricated from Type 405 stainless steel plate whose thicknesses varied from 1/8 to 5/16-inch.

B. ICPP Second Calcined Solids Storage Facility.

The second solids storage facility consists of a circular concrete vault holding seven vertically-arranged cylindrical metal bins. Each bin has forged and dished heads and is 12 feet in diameter. The bins are 42 feet high and are arranged as shown in Figure 2 . All junctions are welded, and each weld has been 100 percent radiographed. The bins, which were constructed with Type 304 (0.06 percent carbon maximum) stainless steel plate, have 1/4-inch thick walls which includes a 1/8-inch allowance for corrosion protection. The design pressure range is ± 3.75 psig at a maximum design temperature of 500°F. Each bin has a 4580-cubic foot capacity for a total capacity of 32,060 cubic feet. This capacity is roughly equivalent to 2,000,000 gallons of liquid waste, assuming a volume reduction factor of 9 to 1 and a 10 percent void space at the top of the bins.

V TEST PROCEDURE

Existing corrosion information on metal alloys suitable as possible construction materials for calcined-solids storage bins has been obtained from tests lasting 10 years or less. Because little was known about the corrosive effects of the solids on metal alloys, a long-term corrosion testing program was started in support of the ICPP.

A. Coupon Installation

During January 1966, 160 coupons were hung on ten stainless steel cables in two empty storage bins of the second calcined solids storage facility; one bin was scheduled to contain zirconium-type solids and the other aluminum-type solids. Each cable has 16 coupons, four each of four different alloys---AISI Types 405, 304, and 304L stainless steels, and Type 1025 carbon steel. The cables are supported from blind flanges on the bin access risers. Corrosion coupon locations in the solids storage bins are shown in Figure 3. The schedule provides that one cable from each bin be withdrawn on the 5th, 10th, 20th, 40th, and 80th year of solid storage, and that the samples will be examined and measured for corrosion effects. The test results will be used for more accurate determination of the expected lifetime of the bins and for the design of future solids storage bins.

B. Waste Calcine Bin Corrosion Coupons

The best method of obtaining corrosion data in a calcine storage bin is to provide for surveillance of the corrosion in the environment of the bin itself during use. Accordingly, welded cylinders and plates of AISI Types 304, 304L, 405, and 1025 carbon steel were fabricated from mill certified steels. All coupons were exposed in the bins in their as-welded metallurgical condition.

The cylinders were fabricated from 1/8-inch thick plate into 6-inch-high welded tubes. Then, discs were welded to the cylinder ends, so as to cover each end of the cylinders. Finally, a 1/2-inch eye was welded onto each of the ends of the cylinders, using 1/8-inch diameter drill rod. All welding was performed by the tungsten inert gas (TIG) welding process, using the appropriate welding electrode for the four different alloys. Figure 4 shows the design of the cylindrical test coupons.

The plate coupons were fabricated from 1/4-inch-thick materials. Using the TIG welding process, 1-1/2-inch wide strips were butt-welded together so that the coupons were 3-inches wide by 5-inches long with a weld deposit parallel to the long edges of the coupons. The appropriate welding electrode was used to weld coupons for the four different alloys. Figure 5 shows the dimensions of the plate test coupons.

C. Corrosion Coupon Removal

The main hazard involved in withdrawing the coupons from the storage bins in the WCF at the ICPP was the spread of radioactive contamination.

To reduce the likelihood of contamination spread, a minimum of 7-inches water vacuum was maintained inside the bins when the flange covers were removed from the access risers. During withdrawal from the risers, the cables with their coupons were pulled into a 7-inch diameter by 75-foot long polyethylene tube that contained the contamination.

D. Corrosion Coupon Decontamination Sequence

Before corrosion observations were made, radioactive contamination was removed from the Types 304 and 304L stainless steel coupons by decontaminating them in a proprietary boiling alkaline permanganate solution for 45 minutes followed by 15 minutes alternating nitric acid and water rinses.

Tests on Type 304L stainless steels have shown the corrosion to be 0.0007 mils per hour for the sequence(4). AISI Type 1025 carbon steel and Type 405 stainless steel in 100°C alkaline permanganate solution followed by water rinses both corrode at 0.001 mils per hour rates(5). The effect of decontamination was subtracted from the observed corrosion.

VI RESULTS

During October 1973, corrosion coupons were removed from two solid storage bins in the second solids storage facility. One bin contained aluminum calcine and the other, zirconium calcine. A corrosion evaluation of these coupons was performed after they were decontaminated.

A. Results From Coupons In The Aluminum Calcine Bin

The results of measurements of corrosion coupons that were immersed in radioactive aluminum calcine solids for approximately six years indicate that the projected 500-year corrosion loss on storage bins, if fabricated from AISI Types 304L, 304, 405, or 1025 carbon steel, would be 1-, 1-, 7-, and 12-mils, respectively. The estimated corrosion coupon exposure temperature was taken as the mean of the reading of a thermocouple that was very near the suspended coupons. The 1971 - 1973 mean for this calcine was 65°C. The average corrosion rates on the welded plates of the various alloys that were exposed in the aluminum calcine are listed in Table 2.

Figure 6 is a photograph of the welded plates that were exposed in the aluminum calcine.

B. Corrosion Samples In The Zirconium Calcine Bins

Measurements of corrosion rates on coupons that were immersed in radioactive zirconium calcine product for about 2 years indicate a projected 500-year corrosion loss on bins that were fabricated from AISI Type 304L, 304, 405, and 1025 carbon steel of 4-, 5-, 20-, and 35- mils, respectively. The coupon exposure temperature of 38°C was estimated from the mean of the readings of a thermocouple that was very near the suspended coupons. Physical and chemical properties of the calcined solids from the fluoride-bearing raffinate are given in Table 1. The average corrosion rates on welded cylinders and plates of the various alloys that were exposed in the zirconium calcine product are listed in Table 3.

Figure 7 is a photograph of the welded plates that were exposed in the zirconium calcine.

VII CONCLUSIONS

1. A corrosion allowance independent of the thickness requirements for structural and abnormal stress must be specified as a part of the design criteria for the construction of future solids storage bins. Based upon data from the corrosion coupons that were withdrawn from the zirconium calcine storage bin, corrosion allowances for Types 304L, 304, 405, and AISI 1025 carbon steel at 95 percent confidence level assuring a projected 500 year service life, are 5-, 7-, 40-, and 50- mils, respectively. Accordingly, with these corrosion allowances, any of these alloys would be suitable for storage of zirconium calcine.

2. Based upon data on corrosion coupons that were withdrawn from bins that contained aluminum calcine solids, corrosion allowances to provide the required 500 year life are 1-, 1-, 7- and 12-mils for Types 304L, 304, 405, and AISI 1025 carbon steel, respectively. Thus, each of these alloys is suited for aluminum calcine product storage service.

3. For a proposed service life of 500 years, the existing ICPP Type 304 (0.06 percent carbon maximum) stainless steel bins for storage of dry aluminum and/or zirconium calcine solids will not exceed, at 95% confidence level, a metal loss of 5 ± 2 mils.

4. Owing to the very low observed corrosion rates, a revised schedule for withdrawing corrosion coupons from the storage bins to reflect observations nearing the 500 year terminal service life of these bins is recommended. Accordingly, one cable from each bin should be withdrawn at the end of the 10th, 100th, 250th, and 450th year of solid storage service.

VIII REFERENCES

1. Plan for the Management of AEC-Generated Radioactive Wastes, Division of Waste Management and Transporation, January 1972 (WASH -1202, P-35).
2. ID Waste Management Plan For FY-1975. Idaho National Engineering Laboratory, July 1974, (IDO - 10050).
3. Cyril M. Slansky, High-Level Radioactive Waste Management Program At The Idaho National Engineering Laboratory. Presented at the symposium on High-Level Radioactive Waste Management; 167th National ACS Meeting - Los Angeles, California, March 31 - April 5, 1974 (TO BE PUBLISHED)
4. B. C. Musgrave et al, Chemical Development For EBR-II Fuel Process 1967 - 1969, April 1970, (IN-1285, P 26).
5. Technical Data Bulletin No. 136-13, Turco Products, Inc., Wilmington, California.

TABLE 1

TYPICAL PROPERTIES OF CALCINER PRODUCT

Physical properties	Aluminum Calcine	Zirconium Calcine
Mass median particle diameter, mm	0.56 to 0.70	0.6 to 0.8
Bulk density, g/cc	1.0 to 1.2	1.7
Composition (wt%):		
Zirconium as ZrO_2	-	21.4
Calcium as CaF_2	-	54.2
Aluminum as Al_2O_3	88 to 89	21.9
Sodium as Na_2O	1.3 to 2.0	
Nitrogen as N_2O_5	3.9 to 4.1	1.9
Mercury as HgO	2.9	-
Water	2.0	0.6
Gross fission product oxides	0.6	0.6

TABLE 2

CORROSION EXPERIENCE IN

ALUMINUM CALCINE PRODUCT

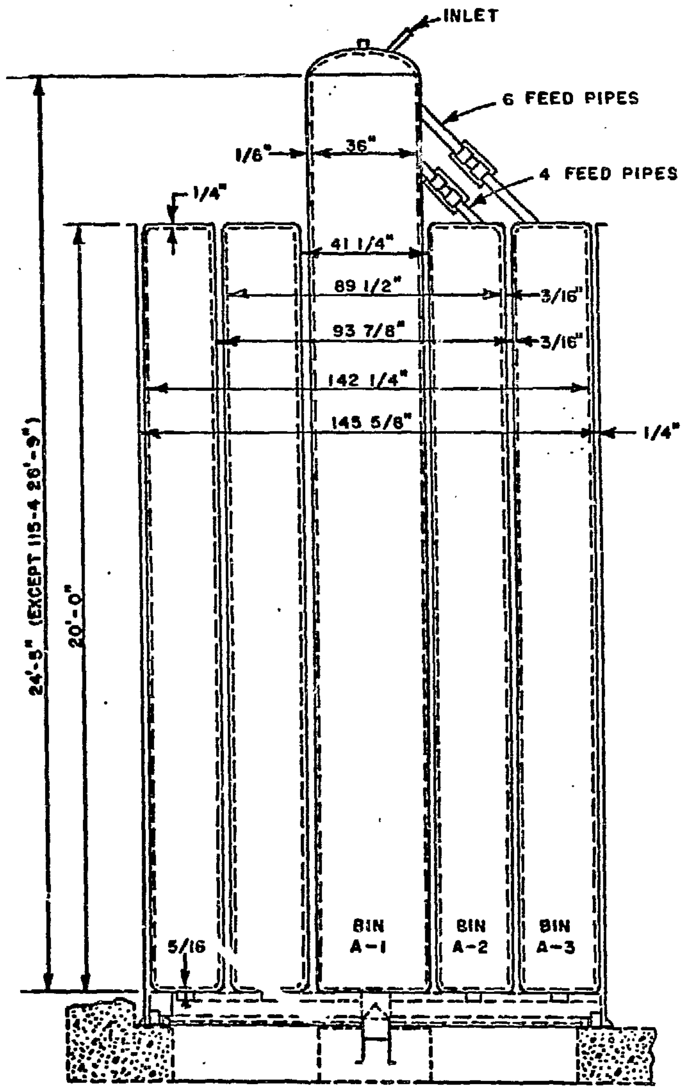
Exposure time 6 - Years

Type Alloy	Average Corrosion Rate (Mils per Year)	Projected Corrosion After 500 Years Service (Mil)
AISI 1025	0.024	12
AISI 405	0.014	7
AISI 304	0.003	1
AISI 304L	0.003	1

TABLE 3

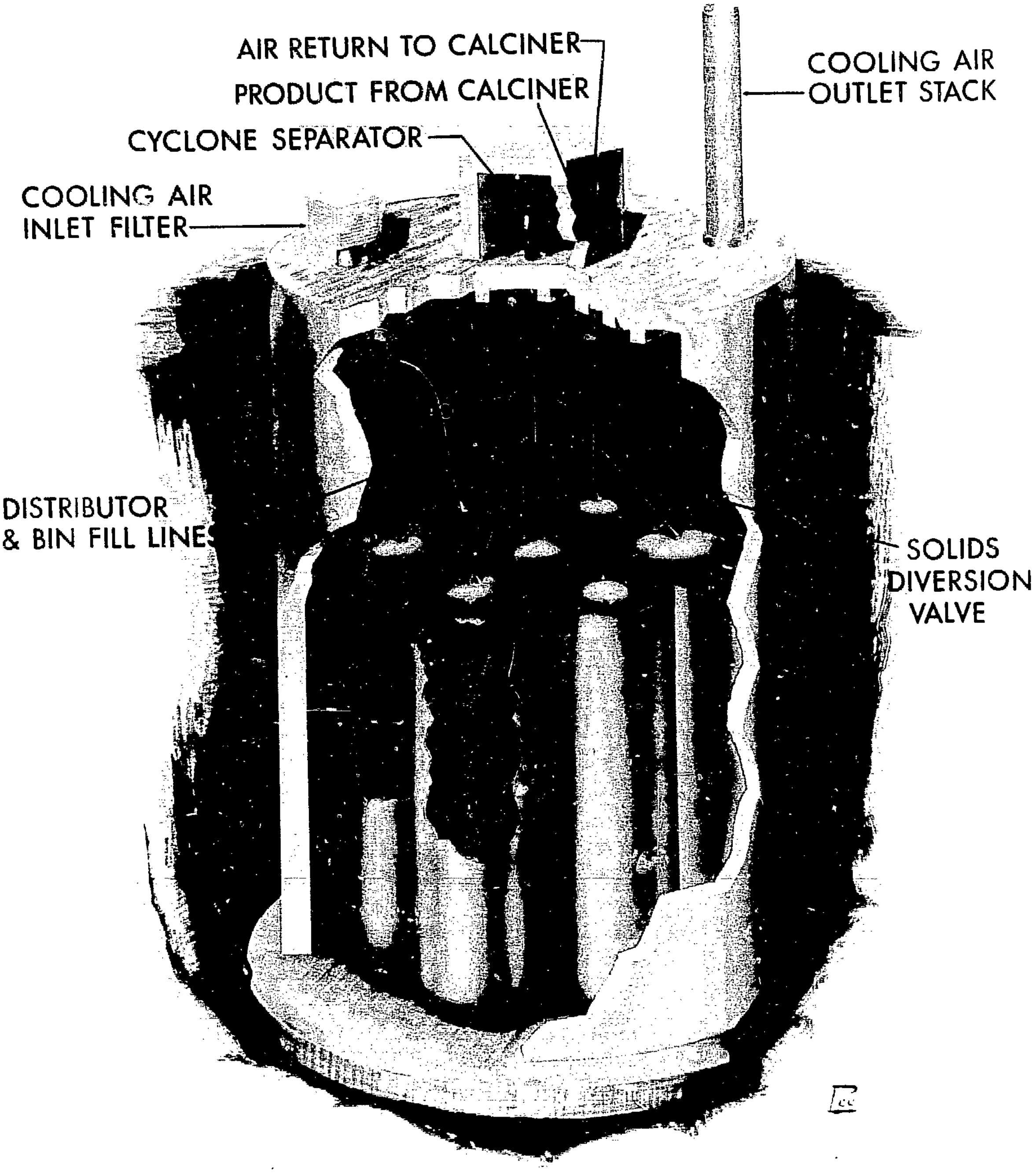
CORROSION EXPERIENCE IN ZIRCONIUM CALCINE PRODUCT

Type Alloy	Type Coupon	Average Corrosion Rate (Mil Per Year)	Projected Corrosion After 500 Years Service (Mil)	Corrosion Allowance at 95% Confidence Level (Mil)
AISI 304L	Plates	0.010	4.9	5
	Cylinders	0.007	3.7	
AISI 304	Plates	0.008	4.0	7
	Cylinders	0.012	5.9	
AISI 405	Plates	0.032	16.0	40
	Cylinders	0.052	27.0	
AISI 1025 (0.25% C)	Plates	0.079	40.0	50
	Cylinders	0.056	28.0	



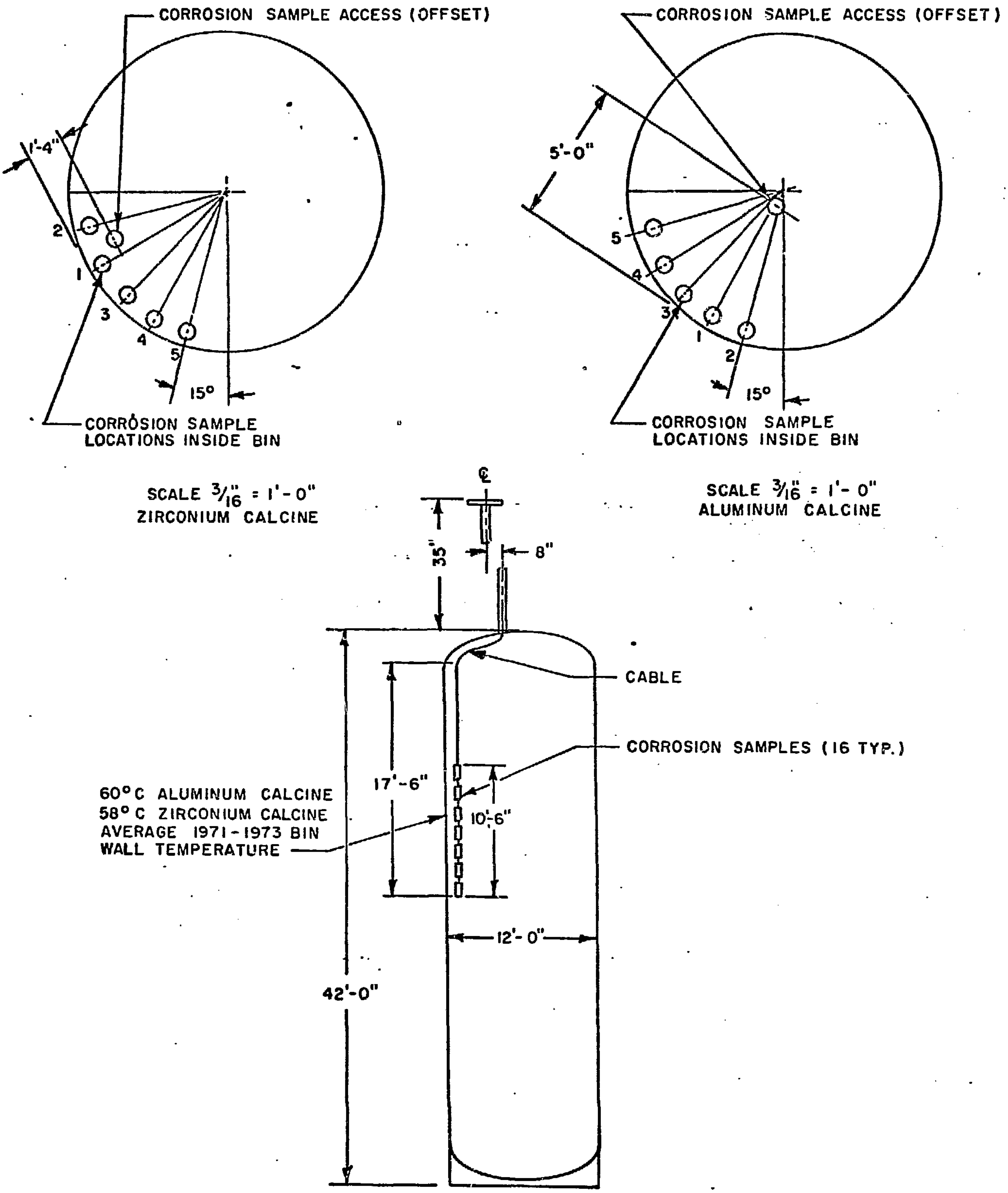
FIRST CLACINE SOLIDS STORAGE BIN

FIGURE 1



SECOND CALCINE
SOLIDS STORAGE BINS

FIGURE 2



CORROSION COUPON LOCATIONS IN THE SECOND CALCINE SOLIDS STORAGE BINS

FIGURE 3

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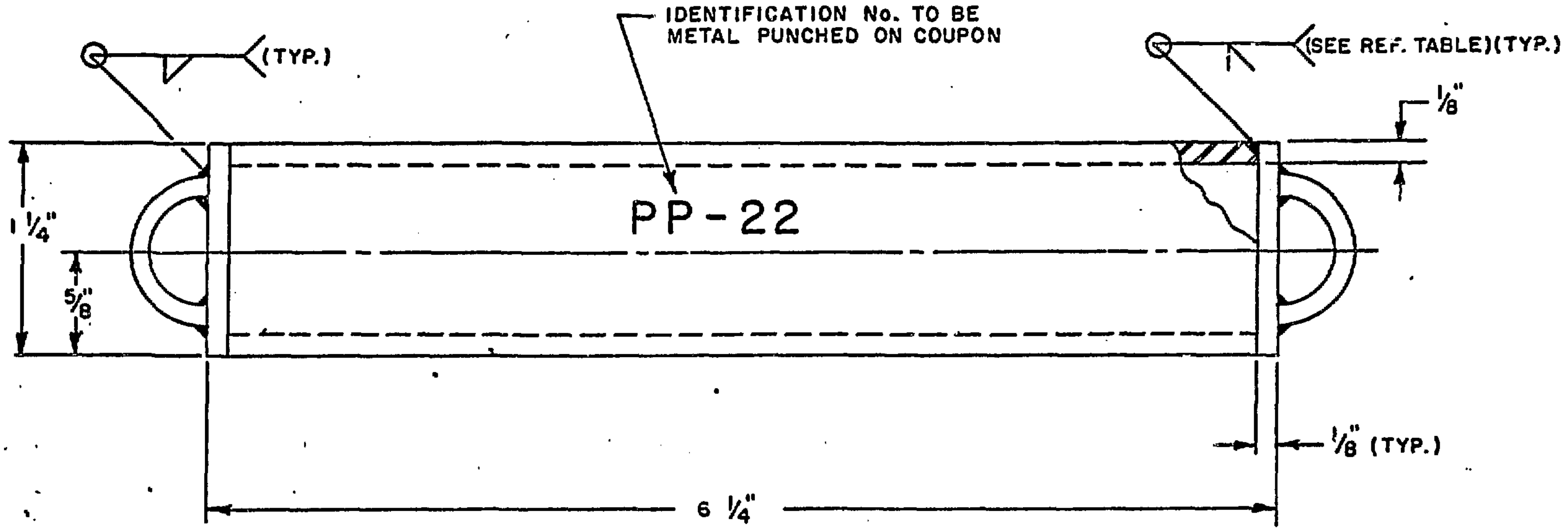

WELDED CYLINDER TEST COUPON

FIGURE 4

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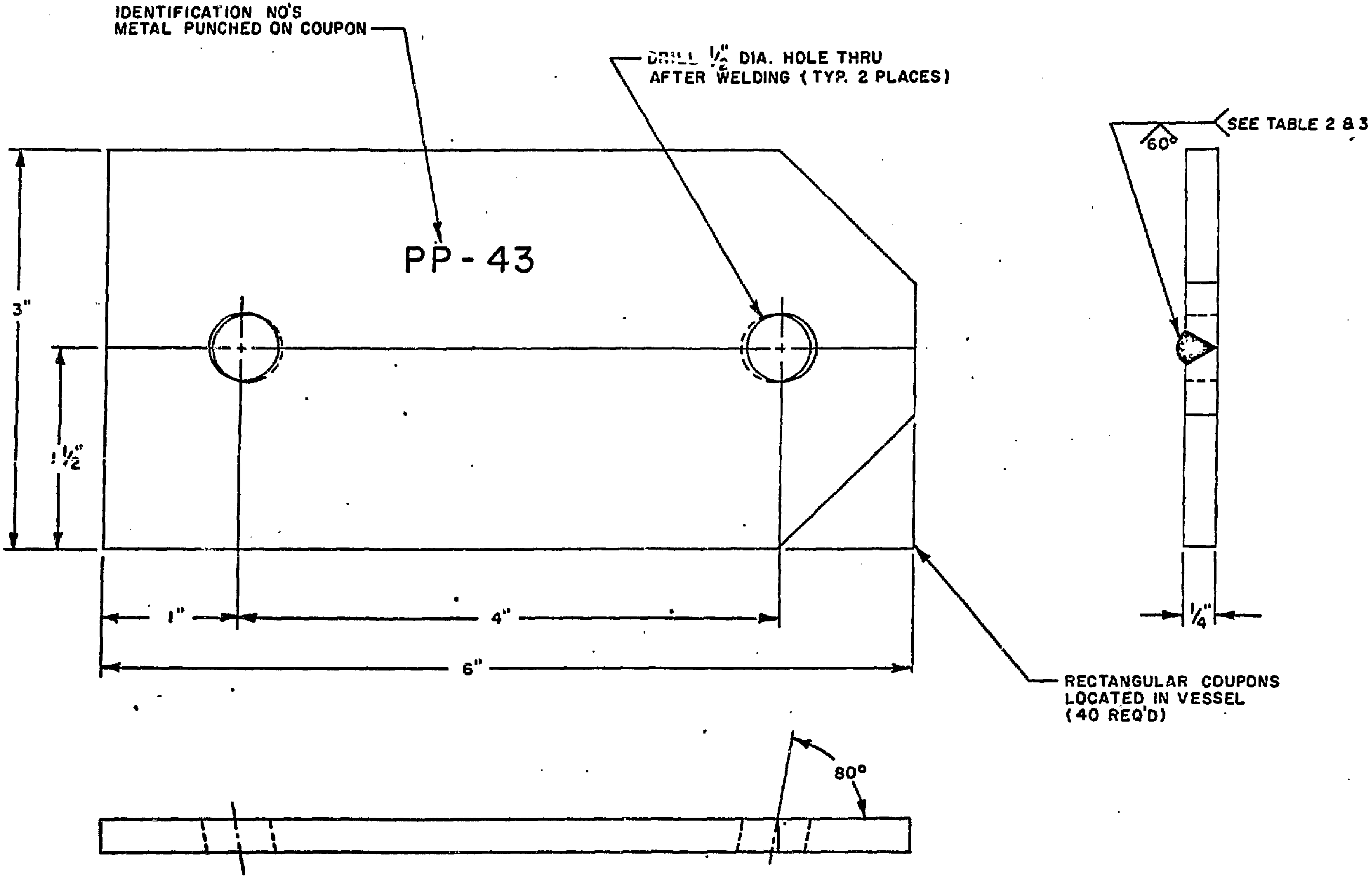

WELDED PLATE TEST COUPON

FIGURE 5

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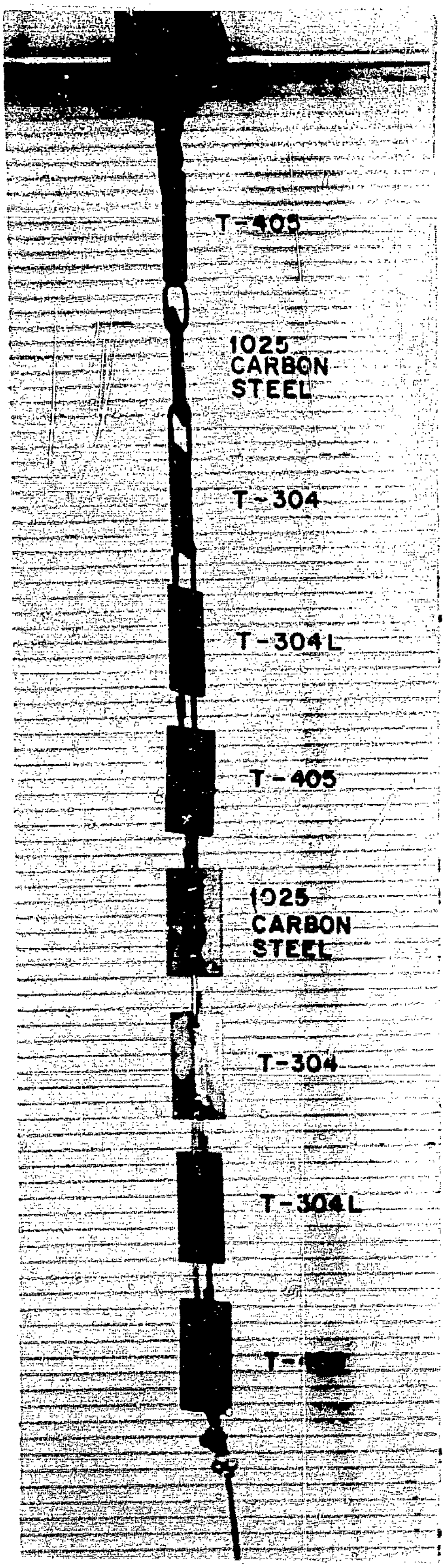
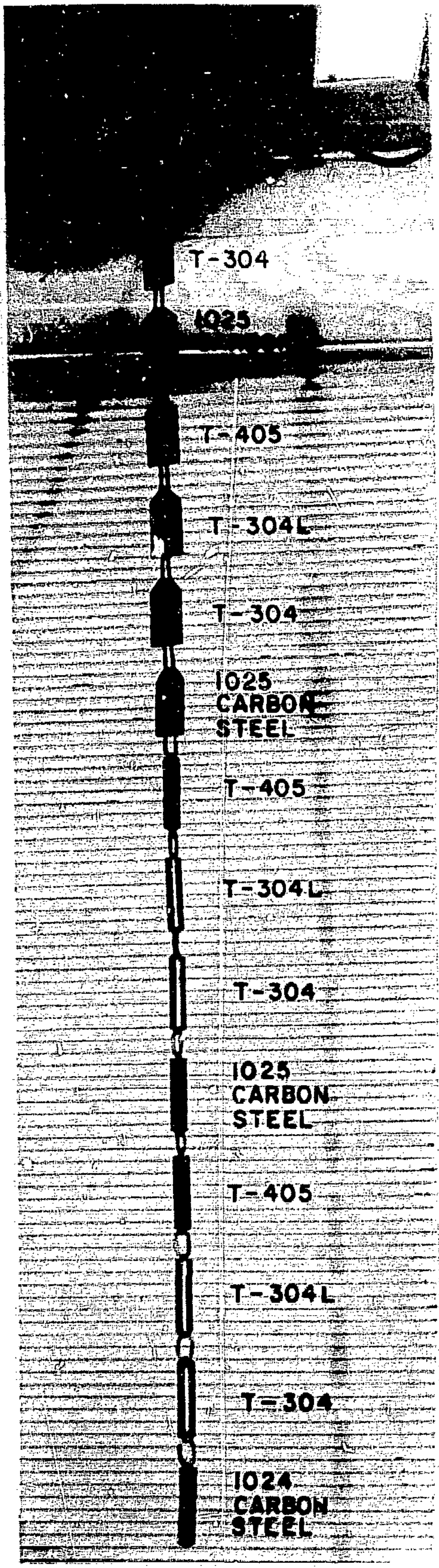


WELDED PLATE TEST COUPONS

(Exposure: Aluminum Calcine, 6 Years)

FIGURE 6



WELDED PLATE AND CYLINDER TEST COUPONS

(Exposure: Zirconium Calcine, 2 Years)

FIGURE 7