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HYDROGEN FLUORIDE CYLINDER FAILURE

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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE GASEOUS DIFFUSION PLANT

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HYDROGEN FLUORIDE CYLINDER FAILURE

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ABSTRACT

An anhydrous hydrogen fluoride cylinder released its contents in an explosive manner. The valve cap, valve, and valve boss assembly separated from the cylinder in the heat-affected zone of the boss-to-cylinder weld. Internal hydrogen pressure and a preexisting crack in the cylinder were evident factors in the failure. Eight adjacent cylinders stored under similar conditions were considered potential hazards, and precautions were taken to minimize the risk from these cylinders.

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CONTENTS

	<u>Page</u>
INTRODUCTION	7
SUMMARY	7
CYLINDER FAILURE	7
POTENTIAL HAZARD OF ADJACENT CYLINDERS	8
Evaluation of Remaining Cylinders	8
RESIDUE IN FAILED CYLINDER	9
METALLURGICAL EVALUATION	10
INDUSTRY EXPERIENCE	17
RECOMMENDATIONS	18
ACKNOWLEDGEMENTS	18
REFERENCE	19

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HYDROGEN FLUORIDE CYLINDER FAILURE

INTRODUCTION

A vendor-owned anhydrous hydrogen fluoride (HF) cylinder, having a 200-lb capacity failed in an explosive manner. The cylinder had been fabricated in accordance with DOT Specification¹ No. 4BA240. The original test date stamped on the cylinder was October 1955; no retests were evident. Records indicate that the cylinder was received at the Paducah Gaseous Diffusion Plant, Paducah, Kentucky, on July 27, 1962, and that it was transferred to the Oak Ridge Gaseous Diffusion Plant on April 4, 1964. The cylinder was then stored on a sheltered cylinder dock until the time of its failure, which occurred at 7 p.m. on June 5, 1969.

SUMMARY

The anhydrous HF cylinder failed by releasing its contents in an unusual manner. The valve boss blew out of the cylinder head with explosive force. Based upon pressure readings and analyses of gases in several other HF cylinders, it is probable that this cylinder contained hydrogen at a pressure well in excess of 100 psig. The valve showed evidence of leakage and corrosion. Metallurgical examination of the failed cylinder indicated that there was a preexisting external crack in the heat-affected zone of the weld, which attached the valve boss to the cylinder head with only a small cross-sectional area of sound metal remaining. The shear strength of the remaining metal was apparently exceeded by the force applied by the hydrogen pressure, thereby resulting in the failure.

CYLINDER FAILURE

The failure was explosive in nature. The valve cap, valve, and valve boss assembly separated from the cylinder in the heat-affected zone of the boss-to-cylinder weld. The assembly was blown through the Transite roof 20 ft above the cylinder storage dock. There was no swelling or distortion of the cylinder as would be expected in a normal overpressure failure. The ambient temperature at the time of failure was about 70°F. The HF vaporized vigorously for about 5 min, after which it steadied down to more normal vaporization. The wind carried the vapors away from all buildings and personnel.

The cylinder and adjacent areas were washed down with a fire hose. The cylinder was then taken to a suitable venting area where the remaining vapors were exhausted through a vent stack.

POTENTIAL HAZARD OF ADJACENT CYLINDERS

Eight adjacent cylinders in the storage area were considered potential hazards, and precautions were taken to minimize the risk from these cylinders. A wooden containment was built around the sides of the cylinders, and they were packed with dry ice to the level of the valve boss on Friday evening, June 6. The cylinders were covered with a tarpaulin and occasionally replenished with dry ice until Monday, June 9.

EVALUATION OF REMAINING CYLINDERS

On Monday, June 9, the pressure of each cylinder, at dry ice temperature, was measured; a sample of noncondensable gas from each cylinder was taken for analysis by scanning mass spectrometry. The results of these pressure measurements and analyses are shown in table 1.

Table 1

PRESSURE AND NONCONDENSABLE GAS COMPOSITION
OF HYDROFLUORIC ACID CYLINDERS

Cylinder No.	Pressure, psig (at -78°C)	Gas Composition, mole %			
		Hydrogen	Nitrogen	Oxygen	Argon
1	31.0	89.6	10.0	0.1	0.3
2	48.5	97.4	2.1	0.3	0.2
3	35.5	96.8	2.8	0.2	0.2
4	37.0	95.7	3.6	0.5	0.2
5	65.0	99.1	0.6	0.2	0.1
6	21.0	96.5	3.3	0.1	0.1
7	34.0	96.9	2.9	0.1	0.1
8	39.5	95.5	3.7	0.6	0.2

The results indicated a large buildup of hydrogen in the cylinders, due to the reaction of hydrogen fluoride with the cylinder walls.

While the cylinders were still packed in dry ice, the pressure of each cylinder was reduced to atmospheric by venting. Cylinder 1 was removed to a safe venting area; the cylinder and contents were permitted to warm up to ambient temperature to determine whether the dry ice had condensed any material which would cause excessive pressure on warming. A pressure measurement at that point showed 37.5 psig and an analysis of a vapor sample indicated 57% hydrogen and 43% nitrogen in the noncondensable phase.

Since the dry ice level in the containment area had, meanwhile, been lowered significantly due to vaporization, the pressures of two of the eight cylinders were measured again and found to be approximately 20 psig. As a precautionary measure, each cylinder was again vented to atmospheric pressure and then transferred by an evaporation-condensation process to existing bulk storage facilities.

RESIDUE IN FAILED CYLINDER

A large amount of dark-brown solid and some residual liquid remained in the failed cylinder after the venting was complete. Eleven milliliters of the liquid was evaporated to provide 0.566 g of solid for analysis. Qualitative spectrochemical analyses were performed on the dark-brown solid and on the solid remaining from evaporation of the liquid. The results are presented in table 2.

Table 2

SPECTROCHEMICAL ANALYSIS OF RESIDUES FROM CYLINDER

Results in %

<u>Element</u>	<u>Dark-Brown Solid</u>	<u>Solid from Liquid Evaporation</u>
Al	0.03	0.2
Co	0.05	0.05
Cr	0.1	0.2
Cu	0.05	0.05
Fe	Strong	Strong
Mg	0.01	0.01
Mn	0.5	0.05
Mo	NF	0.1
Ni	0.1	0.2
Si	0.03	NF
Sn	0.3	2
Ti	NF	0.03

NF - Indicates element was sought but not found.

X-ray analysis identified the solid material as ferrous fluoride (FeF_2).

METALLURGICAL EVALUATION

The failed cylinder is shown after venting and rinsing, in figure 1. The valve and valve boss which separated from the cylinder are seen in figure 2. The valve showed evidence of leakage and corrosion above the seat. The underside of the valve boss and the interior of the cylinder were coated with a dark, dense, adherent layer identified by X-ray diffraction as ferrous fluoride, FeF_2 . The layer was about 0.015-in. thick at the top of the cylinder; a large volume of similar loose material was found at the bottom of the cylinder when it was emptied. A black, coarsely crystalline material was found on the portion of the aluminum bronze valve exposed to the cylinder contents. This material was identified, also by X-ray diffraction, as copper sulfide, Cu_2S .

The fracture was found to have occurred at the toe of the weld attaching the valve boss to the cylinder. Low-magnification examination (figure 3) showed the fracture to be of a brittle nature over most of its area; the inner 0.010 to 0.015 in., for most of the fracture circumference, however, had the appearance of a shear lip. Metallographic sections through the fracture zone are shown at several magnifications in figures 4, 5, and 6. The cross sections verified the division of the fracture into brittle and ductile zones.

The cylinder steel had a fine-grained structure (figure 7) and was of a composition specified as acceptable in DOT Specification 4BA240, under which the cylinder was manufactured. Mechanical properties of steel samples taken from the cylinder wall were marginally lower than specification requirements, but since the wall may have been thinned by 10 or 15% by corrosion (figure 4), it cannot be concluded that the properties of the full wall section were not within these requirements at the time the cylinder was fabricated. The chemical composition of the steel from the failed cylinder is shown in table 3. The mechanical properties of the failed cylinder and average values from two intact cylinders are shown in table 4.

The ductility and impact properties of the cylinder steel suggest that a sudden fracture propagated through the cylinder wall would be fully ductile. Impact tests on samples in both longitudinal and transverse directions showed no evidence of brittle behavior. The fact that the observed fracture was not ductile over most of its extent indicates that this portion of the fracture existed before the catastrophic separation occurred. A mechanism for initiation and propagation of such a crack could not be established, and examination of two intact cylinders with similar histories failed to show any evidence of cracking in the valve boss (figure 8) or the adjacent weld area.

The ductile portion of the failure around the entire base of the valve boss covered a total area of approximately 0.1 sq in., enough to support a total shear load of only 2000 to 4000 lb. This would correspond to an internal pressure in the cylinder of only 150 to 300 psi.

1004

Figure 1

HF CYLINDER AFTER PURGING

Damaged paint is due to contact with HF vapors over a 4-day period following the failure.

1002

1003

Figure 2
VALVE BOSS AND WELD AREA
Viewed from Above and Below

A3220

15X

Figure 3
FRACTURE SURFACE

The fracture propagated through the cylinder wall material at the edge of the weld. The outer portion was apparently non-ductile, while the inner portion, from 0.010 to 0.015 inch in width, had the appearance of a shear lip.

A3221

8X

Figure 4

SECTION THROUGH FAILURE, SHOWING VALVE BOSS AND CYLINDER TOP

9668

50X

Figure 5
SECTION THROUGH FAILURE

9669

150X

Figure 6
DETAIL OF SHEAR LIP

9670

250X

Figure 7

GENERAL MICROSTRUCTURE OF CYLINDER WALL

9671

250X

Figure 8

GENERAL MICROSTRUCTURE OF VALVE BOSS

Table 3

CHEMICAL COMPOSITION OF
STEEL FROM FAILED CYLINDER

Values in %

Carbon	0.15	Molybdenum	< 0.1
Manganese	1.00	Nickel	< 0.1
Silicon	0.2	Copper	0.3
Chromium	0.05	Aluminum	Trace

Table 4

MECHANICAL PROPERTIES OF CYLINDER STEELS

Specimen Source	Ultimate Tensile Strength, psi	Yield Strength, psi	% Elongation, 2-in. Gage Length	Grain Size	Impact Strength, ft-lb
Failed Cylinder	75,000	44,000	26	7	27.5* 60.9**
Intact Cylinders (Average of 2)	59,500	37,000	26	--	--

*Longitudinal Direction, extrapolated to 10-mm thickness.

**Circumferential Direction, extrapolated to 10-mm thickness.

It must be concluded on the basis of the observed evidence that the failure occurred when the small remaining wall thickness under the pre-existing crack could no longer withstand the hydrogen pressure in the cylinder.

INDUSTRY EXPERIENCE

The incident was discussed with the vendor of the cylinder and with three other major HF manufacturers and distributors. None had ever experienced or heard of failures of this type and each considered it unique to the HF industry.

The vendor reported that they had experienced only a few weld and valve leaks in their 25 yr of experience. For the past several years, they have had a practice of keeping HF cylinders for 12 days after filling them, to make sure that there were no leakage or other problems prior to shipment.

One HF manufacturer stated they are aware that pressures sometimes accumulate in HF cylinders (above expected HF vapor pressures), but they had never analyzed the gas or determined the cause for such accumulations. This manufacturer had stored two HF cylinders in an open field for a period of 4 yr in order to observe cylinder pressures. During this period, the highest pressure recorded was 20 psig. Another HF manufacturer had experienced hydrogen accumulations in cylinders which had been in storage for about 2 yr; however, the pressures were not measured.

All of the manufacturers felt that hydrogen accumulations were possible because of HF reaction with the steel material of the cylinder. Each theorized that over long periods of time, thermal expansion and contraction of the cylinder would cause breaks in the passivated coatings, exposing small additional areas of bare metal to the reaction process. They also stated that over long periods of time, pressures of considerable force would be conceivable.

All of the manufacturers expressed concern over the long storage period of the failed cylinder. They stated that normal retention of HF cylinders is from 6 mo to 1 yr, but admitted that some are out for longer periods and some may never get returned to them. They expect valve leakage, corrosion, and other deterioration to develop over long storage periods, but they inspect all cylinders before filling them and fill only those that are in good condition. It appears to be a general practice with the HF vendors to retest the cylinders prior to filling them if it has been at least 4 yr since the last test. (DOT Regulations prohibit refilling beyond a 5-yr retest schedule.)

RECOMMENDATIONS

In view of the potential seriousness of HF cylinder failures and the findings associated with this incident, it is evident that additional precautions are required to protect against the potential hazard of hydrogen in HF cylinders. The recommended additional precautions are as follows:

1. Only the required amount of HF should be stocked, and all cylinders which are no longer needed should be returned promptly.
2. Users should periodically examine HF cylinders in their possession for signs of valve or other leakage, external deterioration, or other objectionable conditions. If the hydrostatic test date (stamped on the cylinder) is older than 5 yr, the cylinder should be used with caution or returned to the vendor.
3. Users should recognize that HF cylinders which have been stored for appreciable lengths of time may contain hydrogen. Such cylinders should be safely vented prior to using the HF or extending their storage periods. They should also be vented before returning them to the vendor if unvented storage has been prolonged.
4. The previously acceptable practice of using air pressure to transfer HF from cylinders should be discontinued to avoid the possibility of generating explosive or ignitable mixtures with hydrogen. If pressure transfer (above the vapor pressure of the HF) is needed, nitrogen or other inert gases should be used, but with due regard to maximum permissible cylinder pressures and only after good condition of the cylinder has been assured.

It is further recommended that the Manufacturing Chemists' Association be informed of this cylinder failure incident and the results of the investigation. Via their committee, which is concerned with Data Sheet SD-25, *Properties and Essential Information for Safe Handling and Use of Hydrofluoric Acid (Anhydrous and Aqueous)*, appropriate action can be taken to acquaint the industry with the need for precautions concerning the possibility of hydrogen accumulation in anhydrous HF cylinders.

ACKNOWLEDGEMENTS

The unusual nature of the described failure and the uncertainty of the cause demanded prompt and deliberate attention to the safe handling of the remaining cylinders, to the safe evaluation of the hazards, and to the determination of the reason for failure. These objectives were accomplished with minimum risk to personnel safety by the coordinated effort of a large number of plant organizations.

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REFERENCE

1. *Department of Transportation Regulations*. Issued August 5, 1966, by T. C. George, Agent, 63 Vesey St., New York, New York 10007.