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LARGE-SCALE RELEASE TESTING OF A MODIFIED HF ALKYLATION CATALYST

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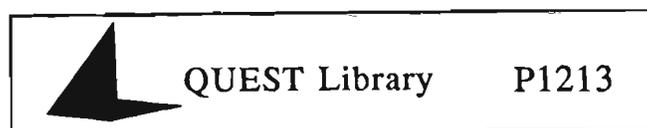
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Abstract

A large-scale experimental program was conducted to evaluate the aerosol-suppression capabilities of a modified hydrogen fluoride (MHF) alkylation catalyst. In this program, approximately 150 to 500 pounds of MHF were released per test through a circular orifice into a specially designed flow chamber. The amount of airborne HF and the amount of HF falling downward into collection pans to form a liquid pool (rainout) were measured. Tests were conducted for a range of MHF compositions, temperatures, pressures and orifice sizes. Results of the testing demonstrated that the properties of a HF alkylation catalyst could be modified to promote rainout of HF to the ground, significantly reducing the amount of HF traveling downwind from an accidental release compared to the existing HF alkylation catalyst.

INTRODUCTION

Hydrogen fluoride (HF) is widely used in petroleum refining as a catalyst in the alkylation process [1]. Product from alkylation is a key blending component in the production of reformulated gasoline which can meet new federal fuel specifications since alkylate contains virtually no aromatics or olefins and has a high octane value.

Recently, there has been growing concern over the safety of processes which use HF. This concern evolved after a series of large-scale tests conducted by Amoco [2] in Frenchman Flats, Nevada demonstrated that releases of superheated HF liquid at near 100° F and 100 psig resulted in the formation of an airborne cloud consisting of HF vapor and entrained aerosol. Upon release, the liquid HF stream quickly disintegrated into small droplets by flash atomization and the droplets vaporized. Nearly all of the HF became airborne and interacted with humidity in the air to form a visible cloud which persisted for several hundred meters downwind. To address concerns pertaining to HF safety, industry proactively embarked on a series of research programs in 1988 [3] to identify means to minimize the consequences of accidental releases of HF and to predict how an HF cloud disperses in the atmosphere. Many of the findings of these research programs have since been implemented at facilities which handle HF.

Nevertheless, regulatory agencies have recently initiated their own studies to evaluate HF and have even begun to regulate its use. The Clean Air Act Amendments of 1990 require the Environmental Protection Agency to conduct a study of the potential hazards of HF and its use and make recommendations to Congress for the reduction of the hazards, if appropriate. In April 1991, the South Coast Air Quality Management District (SCAQMD) in California enacted Rule 1410 which phases out the use of conventional HF alkylation at refineries in the Los Angeles area.

To enhance the safety of the HF alkylation process and to permit its continued use in the Los Angeles area, Mobil and Phillips Petroleum are currently developing a modified HF (MHF) catalyst which significantly reduces the amount of HF that can become airborne, compared to existing HF catalyst, if accidentally released from an alkylation unit. The MHF is derived by mixing adequate quantities of an additive with the HF to reduce the vapor pressure sufficiently to suppress the flash atomization process. This is done while maintaining the required catalytic activity for the alkylation process. Therefore, a pressurized release of MHF is much more likely to result in the HF falling to the ground as a liquid pool, instead of becoming immediately airborne. Scoping experiments conducted by Mobil in a small-scale release apparatus showed that the additive indeed reduced the aerosol forming tendency of HF.

Large-scale release studies have primarily focused on single-component, super-heated liquids. The earliest efforts predicted the airborne fraction from a release from simple flash calculations, assuming that the remaining liquid fraction would all fall to the ground and form a pool. However, large-scale release testing with superheated HF [2,3], monomethylamine [4] and chlorine, monomethylamine and cyclohexane [5] have shown that a significant portion of unflashed liquid may become airborne as entrained liquid aerosol droplets. Models such as those of Papadourakis et al. [6] have been developed to study the dynamics in flashing jets. Such efforts have shown that jet expansion due to superheat, air entrainment into the jet, and droplet evaporation in the jet are important in determining the airborne fraction of the released material. However, releases of subcooled, but volatile fluid mixtures, such as MHF mixtures,

have not been studied on a large scale. These liquid jets, in contrast to the superheated sprays, do not disintegrate by flash atomization and are thus expected to result in smaller airborne mass fractions.

The objective of this study was to experimentally measure the amount of airborne MHF under a variety of release conditions. The field experiments consisted of large-scale, pressurized releases of MHF mixtures for a variety of release conditions to simulate the accidental release of the material from an alkylation unit retrofitted with this MHF catalyst. These experiments were conducted by Mobil and Phillips Petroleum in a specially designed apparatus constructed at a test site near Norman, OK operated by Quest Consultants.

EXPERIMENTAL APPARATUS AND METHODS

The equipment for the release tests is described in detail by Schatz, et al. [7]. In summary, the apparatus consisted of a 300 gallon release tank, connecting piping, an orifice plate, and a large flow chamber with approximate dimensions of 15 ft by 16 ft by 128 ft. Figures 1 and 2 show a schematic of this apparatus. The orifice plate contained holes ranging from 1/8-inch to 1-inch in diameter to simulate leaks of various sizes. Eight collection pans, each of dimensions 10 ft by 15 ft, were located in the enclosure downstream of the orifice plate to capture the liquid falling downward from the releases. Two water spray scrubbers and blowers for air circulation were located within the enclosure. Other equipment at the facility included a 1000 gallon tank for collecting liquid from the capture pans, several inventory tanks for containing and mixing additive and HF, a liquid nitrogen system for pressurization of the release tank, and other miscellaneous control systems. Several thermocouples and a pressure transducer were located in the enclosure to measure temperature and pressure.

Release experiments were conducted by mixing weighed quantities of HF and additive in the release tank to simulate a MHF alkylation catalyst. The release tank was then pressurized and the mixture was released into the enclosure through a selected orifice in the orifice plate to simulate a leak. The liquid falling out of the release stream (rainout) was collected in the capture pans and drained to the collection tank. Airborne MHF was carried by the air flow toward the rear of the enclosure and was captured by the water spray scrubbing system. Both the release tank and collection tank were supported on load cells so that the weights of the released material and captured material could be determined. The load cell calibrations were performed to record weights to within 0.03% of full scale.

An on-site analytical lab was utilized to conduct compositional analysis. The released and captured MHF were sampled and analyzed for HF and additive. The captured MHF was additionally analyzed for water pick-up from atmospheric water vapor. The HF concentration was determined by neutralization and subsequent back-titration with caustic [8]. The water concentrations of the captured MHF were determined using Karl-Fischer titration [8]. All compositional analyses were replicated to ensure sufficient accuracy, and the replicated analyses were averaged. In order to close material balances, the water from the water spray scrubbing system sumps was also analyzed for HF and additive contents at the beginning and end of every test.

Prior to testing, extensive shakedown of the test apparatus was performed. Fifteen shakedown tests were conducted with the flow chamber completely sealed and with blowers positioned in

the enclosure to recirculate air flow over the capture pans, through the water spray scrubbing system, under the capture pans, and back to the orifice (see Figure 1). The shakedown tests were conducted to screen the effectiveness of the MHF catalyst in reducing airborne HF, and to evaluate efficiency of the water spray scrubbing system to determine if the enclosure could be operated in an open-flow mode within acceptable environmental constraints.

The apparatus was then modified to simulate full-scale accidental releases. The rear of the enclosure was opened and blowers were positioned at the rear to allow a single-pass of ambient air flow from the release orifice, over the capture pans, through the scrubbers and out the end of the enclosure (see Figure 2).

Three MHF compositions were selected to span a range of MHF vapor pressures. Composition 1 had the lowest vapor pressure while Composition 3 had the highest vapor pressure. Composition 2 had a vapor pressure between these.

The pressures and temperatures were selected to represent a range of conditions for an HF alkylation unit. Release pressures ranged from 50 psig to 140 psig while release temperatures ranged from 55° F to 110° F.

Orifice sizes were varied to simulate several size leaks. The diameters of the orifices used in this study were 1/8-, 1/4-, 1/2-, and 3/4-inch.

In addition to the MHF tests, two other proprietary mitigation technologies were evaluated for their ability to reduce airborne HF. These technologies were tested in combination with the MHF catalyst.

RESULTS AND DISCUSSION

In general, the test results indicate that pressurized releases of the subcooled MHF catalyst resulted in significantly less airborne HF than equivalent anhydrous HF releases. Under similar conditions, anhydrous HF releases are assumed to result in 100% airborne HF, based on the testing conducted by Amoco in Nevada in 1986 [2]. To quantify the effectiveness of the modified catalyst in reducing airborne HF, a total airborne HF reduction percentage, relative to anhydrous HF, was calculated for each test. The total airborne HF reduction for the MHF incorporates the reduced amount of airborne HF due to the liquid rainout of HF, as well as the HF reduction due to the diluent effect of the additive in the MHF mixture. This total airborne HF reduction is defined as

$$\text{Percent Airborne HF reduction} = 100 [1 - w_{\text{HF}} (1 - c_{\text{HF}})]$$

where w_{HF} is the weight fraction of HF in the release mix and c_{HF} is the fraction of released HF that is collected as liquid rainout.

Total airborne HF reductions for all tests ranged from 62.8% to nearly 100%, depending on release conditions. A detailed description of the test conditions, airborne HF reduction, and material balance closures is given in Table 1. During the tests, the average material balance closures for HF and additive were 96% and 101%, respectively.

The following summarizes the key effects identified from the test program.

EFFECT OF HF VAPOR PRESSURE

A higher HF vapor pressure of the release mixture generally results in a lower HF airborne reduction. HF vapor pressure is the primary driving force for HF evaporation from the drops of the atomized jet. The HF vapor pressure can be altered in two ways - by varying the temperature or by modifying the HF concentration in the MHF mixture. In the former case, the change in airborne HF reduction is due solely to the change in HF rainout (the composition of the MHF remains constant, and therefore there is no additional diluent effect from the additive). If the vapor pressure is reduced by diluting the HF fraction with more additive, both the increased rainout and the dilution contribute to airborne HF reduction.

Figure 3 shows airborne HF reduction versus vapor pressure for a 1/4-inch release of three compositions of MHF at release pressure and temperature of 140 psig and 90 °F, respectively. In this plot, compositional contributions to vapor pressure are represented. The left-most point shows the case for a 100% additive composition, and the right-most point represents anhydrous HF with a flashing mechanism for aerosol formation resulting in no liquid capture based on the Amoco HF tests. For the range of vapor pressures for the three MHF compositions, the airborne HF reduction decreases with increasing vapor pressure.

EFFECTS OF ORIFICE SIZE AND PRESSURE

Releases through larger orifices resulted in greater airborne HF reductions as shown in Figure 4 for Composition 2 at 50 psig and 90 °F. This effect may be due to two reasons. Firstly, the lower surface to volume ratio of liquid through larger orifices contributes to lesser mechanical shearing with air and thus less atomization per unit volume than that at smaller orifices. This results in either larger or fewer drops for larger orifices and hence less droplet surface area and less HF evaporation. Secondly, the mass ratio of the entrained air to released liquid varies inversely as the orifice diameter [9]. Thus a larger orifice has a lower ratio of entrained air to released liquid, resulting in lower HF evaporation rates from the release stream.

The airborne HF reductions are also sensitive to release pressure as shown in Figure 5 for Compositions 2 and 3. Tests at lower pressure (50 psig) resulted in larger HF rainouts and airborne HF reductions than tests conducted at higher pressures (140 psig). Low pressure releases do not create as much mechanical shearing in the released liquid. This results in lower jet atomization (bigger and fewer droplets) thus contributing to a higher liquid rainout. The Weber number criterion [6] supports this. The critical Weber number is given by

$$We_{cr} = \frac{\rho_{air} u^2 d_{max}}{\sigma}$$

where u is the droplet velocity, d_{max} is the maximum stable droplet size diameter, ρ_{air} is the density of air and σ is the surface tension. The critical Weber number is believed to be between 10 and 20 [10,11]. Since the velocity is proportional to the square root of the release pressure, the Weber number criterion predicts the maximum drop size to vary inversely as the pressure. While this strong pressure dependence has not been quantitatively tested in large releases, the qualitative trends of the criterion may be correct.

EFFECT OF RELEASE TEMPERATURE

The temperature of the release mixture did not have a simple effect on rainout. Figure 6 illustrates this effect for two cases: (i) at fixed composition and (ii) at different compositions. In the first case, lowering the release mixture temperature from 90°F to 55°F, lowers the vapor pressure of a Composition 1 mixture. The reduction of vapor pressure by more than half increases the airborne HF reduction only slightly, possibly due to rapid heat transfer to the droplets from the surroundings. On the other hand, Composition 2 at 110°F yields a higher airborne HF reduction than Composition 3 at 78°F although the vapor pressure of the latter is less than that of the former. This could be primarily due to increased HF vapor phase polymerization in the lower temperature case resulting in a greater mass flux of HF from the drops.

PREFERENTIAL ADDITIVE RAINOUT

Figure 7 shows the airborne HF reductions and additive captures for a 1/4-inch orifice at 140 psig and the three MHF compositions. The additive captures are between 89 and 94% and relatively insensitive to the release mix vapor pressure whereas the airborne HF reductions decrease with increasing vapor pressure. This clearly reveals that HF evaporation from droplets is the primary contributor to airborne HF rather than carryover of any significant fraction by the mass of the droplets themselves. This is corroborated by the 98% capture for the pure additive release, where mechanical shear atomization is the primary mechanisms of droplet formation.

ENHANCED HF CAPTURE

Two proprietary technologies were evaluated for their ability to improve the airborne HF reduction for the MHF catalyst. These technologies were tested in combination with the MHF to evaluate the overall airborne HF reduction potential. Results are shown in Table 2. For Composition 3 released through a 0.25-inch orifice and at a pressure of 140 psig, the airborne HF reduction with additional mitigation from Technology 1 was approximately 67%, whereas the base case without the addition of Technology 1 was about 63%. A Composition 2 release from a 0.5-inch orifice at 50 psig yielded an HF reduction, with the addition of Technology 1 of approximately 91%, whereas without Technology 1, an identical test gave an HF reduction of about 87%. These tests thus show that the addition of Technology 1 with MHF improved results by about 4%. The experimental uncertainty is expected to be much smaller than this. For example, two almost identical tests (#30 and #34) yielded HF reductions differing only by 0.6%.

Tests with a second proprietary mitigation technology are also shown in Table 2. For the two compositions that were tested, the addition of proprietary Technology 2 significantly improved the airborne HF reductions for MHF. For Composition 2, the HF reductions improved from near 85% to 98% and greater. For Composition 3, Technology 2 with MHF resulted in an improvement of the HF reduction from 68% to 94%.

FLOW CHAMBER MEASUREMENTS DURING TESTING

Figure 8 depicts important variables during the course of a typical test. The release stream temperature measured by a thermocouple five feet in front of the orifice drops sharply as soon as the test commences. This is due to the cooling associated with HF evaporation from the liquid. The liquid collected as rainout is also substantially cooler (drain temperature in figure) than the released liquid (orifice temperature). The temperature of the vapor and aerosol approximately 65 feet downstream of the release orifice (grid temperature in figure) shows an increase probably due to the vapor phase chemistry. The pressure within the chamber varies slightly during the test by less than plus or minus 0.05 inches of water.

SUMMARY AND CONCLUSIONS

Large scale release studies with different HF/additive mixtures and several release conditions (orifice sizes between 1/8-inch and 3/4-inch, release pressures between 50-140 psig and release temperatures between 55-110 °F) have shown that a MHF composition is effective in reducing airborne HF for a simulated accidental release from an alkylation unit. Quantitative risk assessment studies would need to be performed to assess the risk reduction magnitude for a particular site.

Salient results of this study are:

- The additive significantly reduces the amount of airborne HF resulting from simulated release scenarios. The total airborne HF reduction (pure HF = 100% airborne) , which includes the effect of dilution of the released stream with additive, is in the range 63-90%.
- Proprietary mitigation technologies in combination with MHF improve the airborne HF reductions. For proprietary Technology 1, improvements in airborne HF reduction were about 4% for Compositions 2 & 3. For proprietary Technology 2, airborne HF reductions increased from 85% to 98+% for Composition 2 and from 68% to 94% for Composition 3.
- The airborne HF reduction is improved by raising the additive concentration (lowering vapor pressure) in the release mixture, increasing the orifice size (0.125-0.75 inches) and reducing the release pressure (140-50 psig). The preferential rainout of almost all the additive reveals that HF evaporation (from the release jet and droplets) is the primary cause for airborne HF, rather than the carryover of any significant mass by the droplets formed due to mechanical jet-atomization.
- The release mixture temperature has a complex influence on rainout.

ACKNOWLEDGEMENTS

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Table 1 : Test Summary

Test No.	Release Composition	P (psig)	T (F)	Orifice (inch.)	Ambient T (F)	Rel. hum.	% Airborne HF reduction	HF MB Closure %	Additive MB Closure %
16	Composition 1	50	90	0.125	80.8	80	92.1	93.7	85.9
17	Composition 1	140	90	0.25	84.0	83	92.0	96.7	95.4
18	Composition 1	140	55	0.25	85.2	65	93.0	98.0	99.7
19	Composition 2	50	90	0.125	86.0	66	77.5	88.7	104.8
20	Composition 2	50	90	0.25	92.1	60	85.6	93.4	88.3
21	Composition 2	140	90	0.25	87.5	68	79.7	101.4	95.2
22	Composition 2	50	90	0.5	94.9	56	87.0	97.6	94.8
23+	Composition 2	50	90	0.5	91.0	57	90.8	-	-
24	Composition 3	50	90	0.25	82.4	46	72.3	96.3	101.0
25	Composition 3	140	90	0.25	76.5	57	62.8	95.9	101.9
26+	Composition 3	140	80	0.25	88.8	44	66.8	104.5	108.9
27+	Composition 3	50	77	0.125	86.7	53	73.6	98.9	157.9
28	Composition 3	140	78	0.5	84.1	59	67.8	96.8	117.2
29	Composition 3	100	88	0.25	89.0	48	65.2	98.3	101.4
30	Composition 2	140	110	0.5	86.0	52	82.0	93.8	94.2
31	Composition 2	100	110	0.5	89.6	42	84.5	88.3	107.6
32	Composition 2	50	90	0.75	92.0	39	89.8	97.8	105.3
33	Composition 3	140	93	0.5	80.7	69	68.0	101.0	91.7
34	Composition 2	140	108	0.5	83.8	73	81.4	104.5	90.5
35 *	Composition 2	50	90	0.25	88.4	58	99+	101.2	82.6
36 *	Composition 2	140	110	0.75	81.0	70	98.3	105.6	99.3
37 *	Composition 3	140	90	0.75	87.5	59	94.1	101.5	107.5
38 *	Composition 3	140	90	0.75	83.2	67	89.5	100.7	106.0

+ Tests with proprietary mitigation technology 1

* Tests with proprietary mitigation technology 2

Note :- Tests 1 - 15 are shakedown tests

Table 2

Effect of Proprietary Mitigation Technology
on Airborne HF Reduction

Mitigation Technology 1

<u>Orifice (in.)</u>	<u>Press. (psig.)</u>	<u>Temp. (°F)</u>	<u>Composition Number</u>	<u>HF Reduct. (%)</u>	<u>Proprietary Technology Active</u>
0.5	50	90	2	87.0	No
0.5	50	90	2	90.8	Yes
0.25	140	90	3	62.8	No
0.25	140	80	3	66.8	Yes

Mitigation Technology 2

0.25	50	90	2	85.6	No
0.25	50	90	2	99+	Yes
0.5	140	108	2	81.4	No
0.75	140	110	2	98.3	Yes
0.5	140	78	3	67.8	No
0.75	140	90	3	94.1	Yes

Figure 1

Modified HF Release Tests

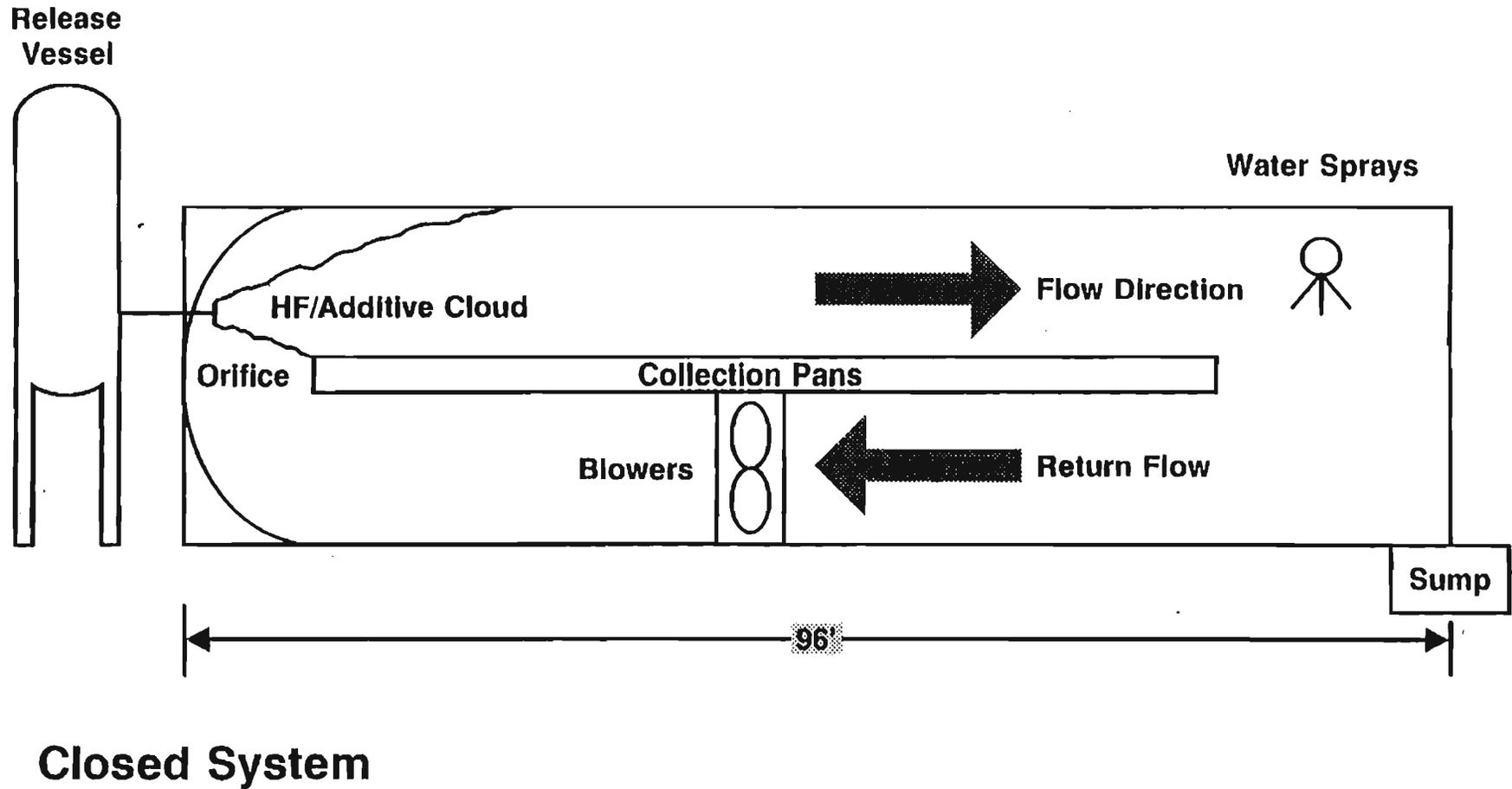


Figure 2

Modified HF Release Tests

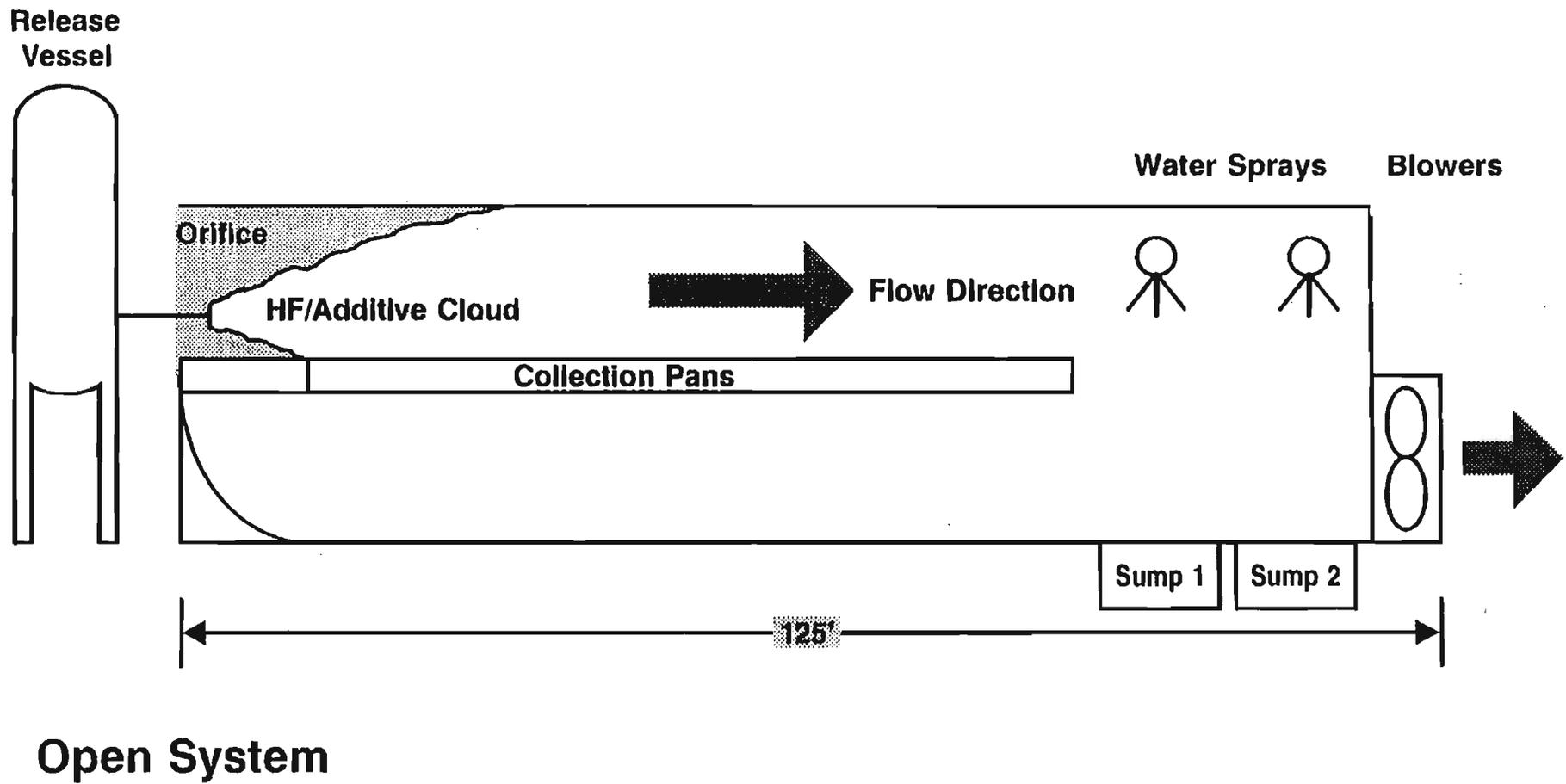


Figure 3

Effect of Vapor Pressure on Airborne HF Reduction

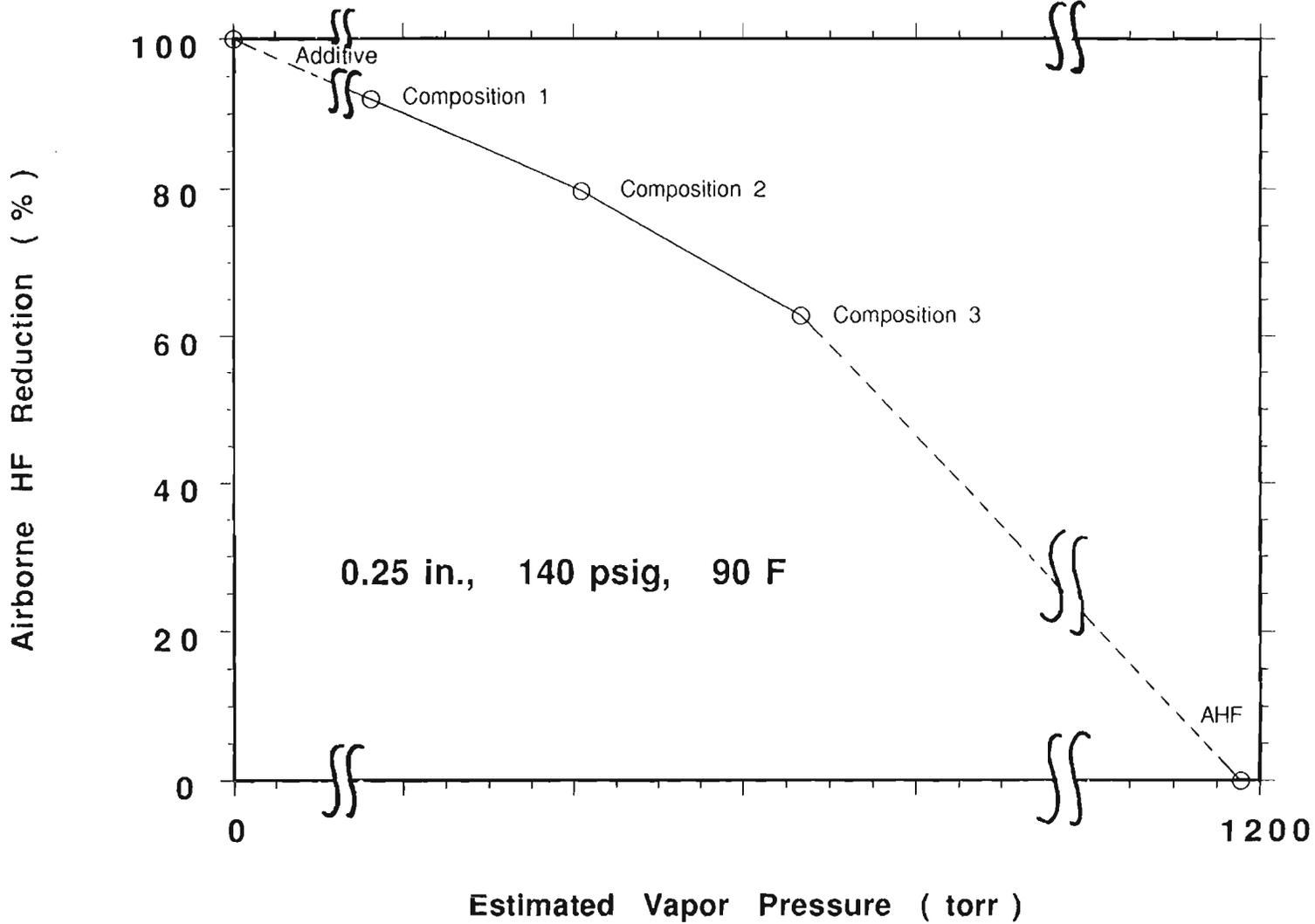


Figure 4

Effect of Orifice Size on Airborne HF Reduction

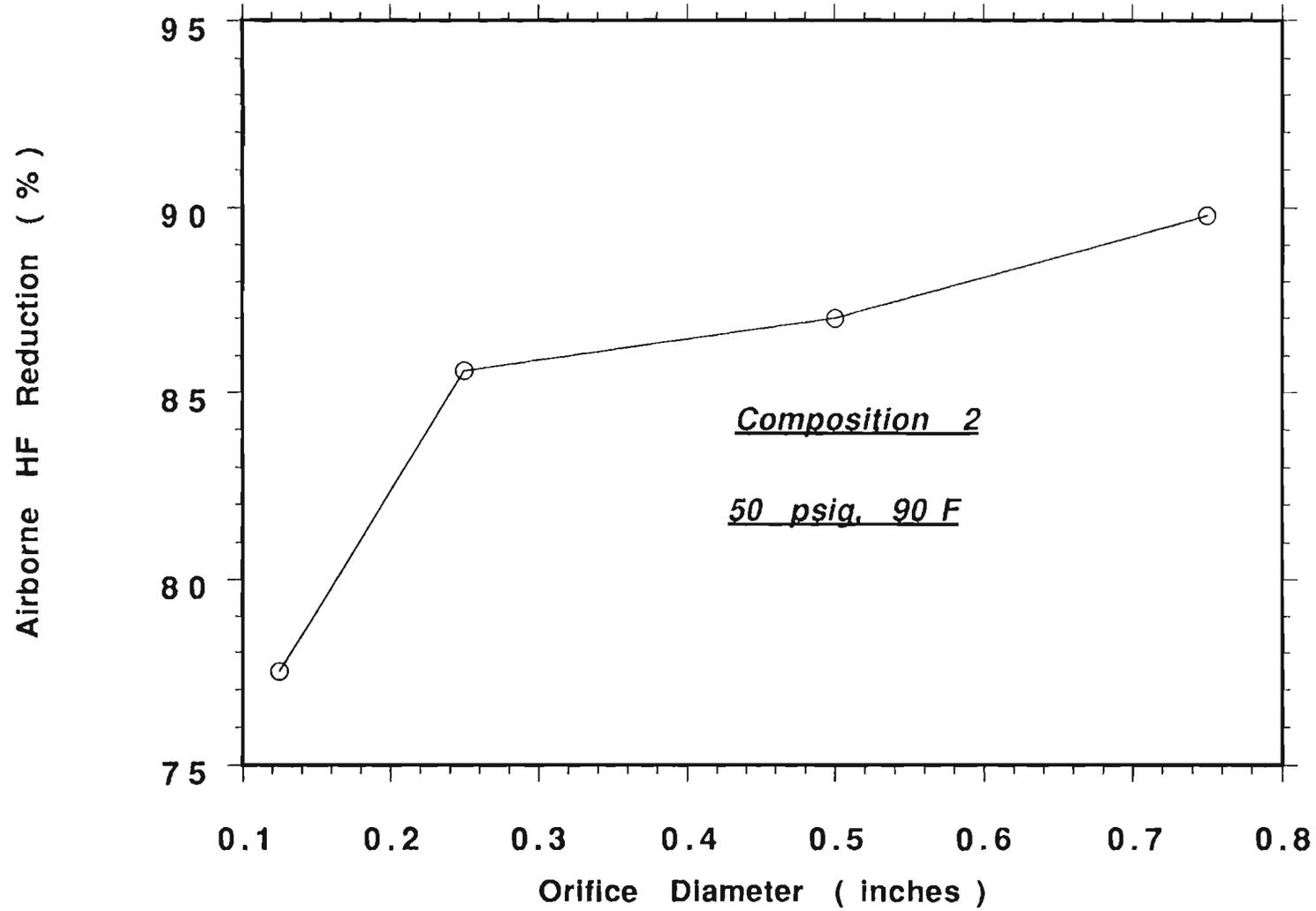


Figure 5

Effect of Release Pressure on Airborne HF Reduction

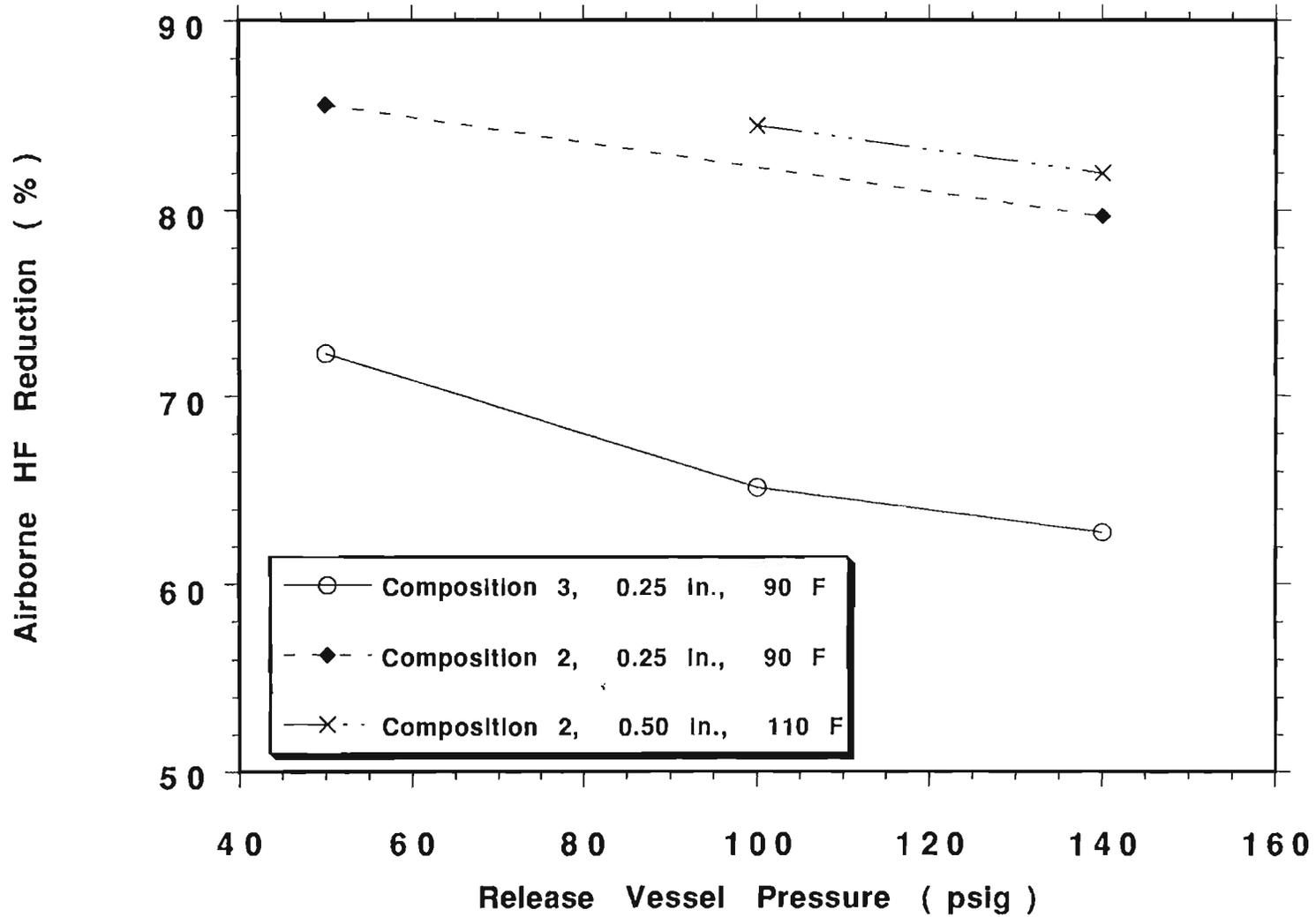


Figure 6

Effect of Release Temperature on Airborne HF Reduction

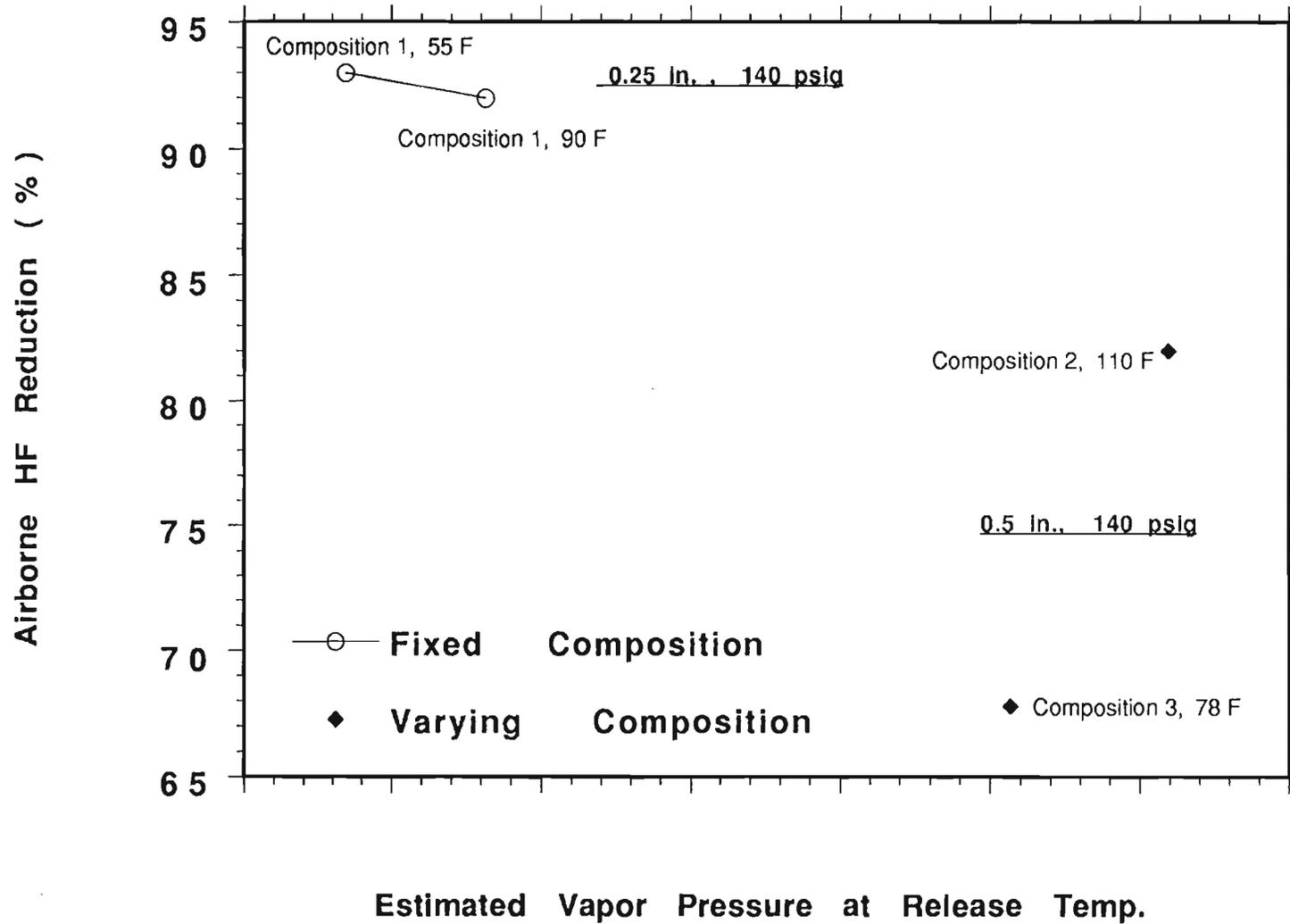


Figure 7

Preferential Rainout of Additive

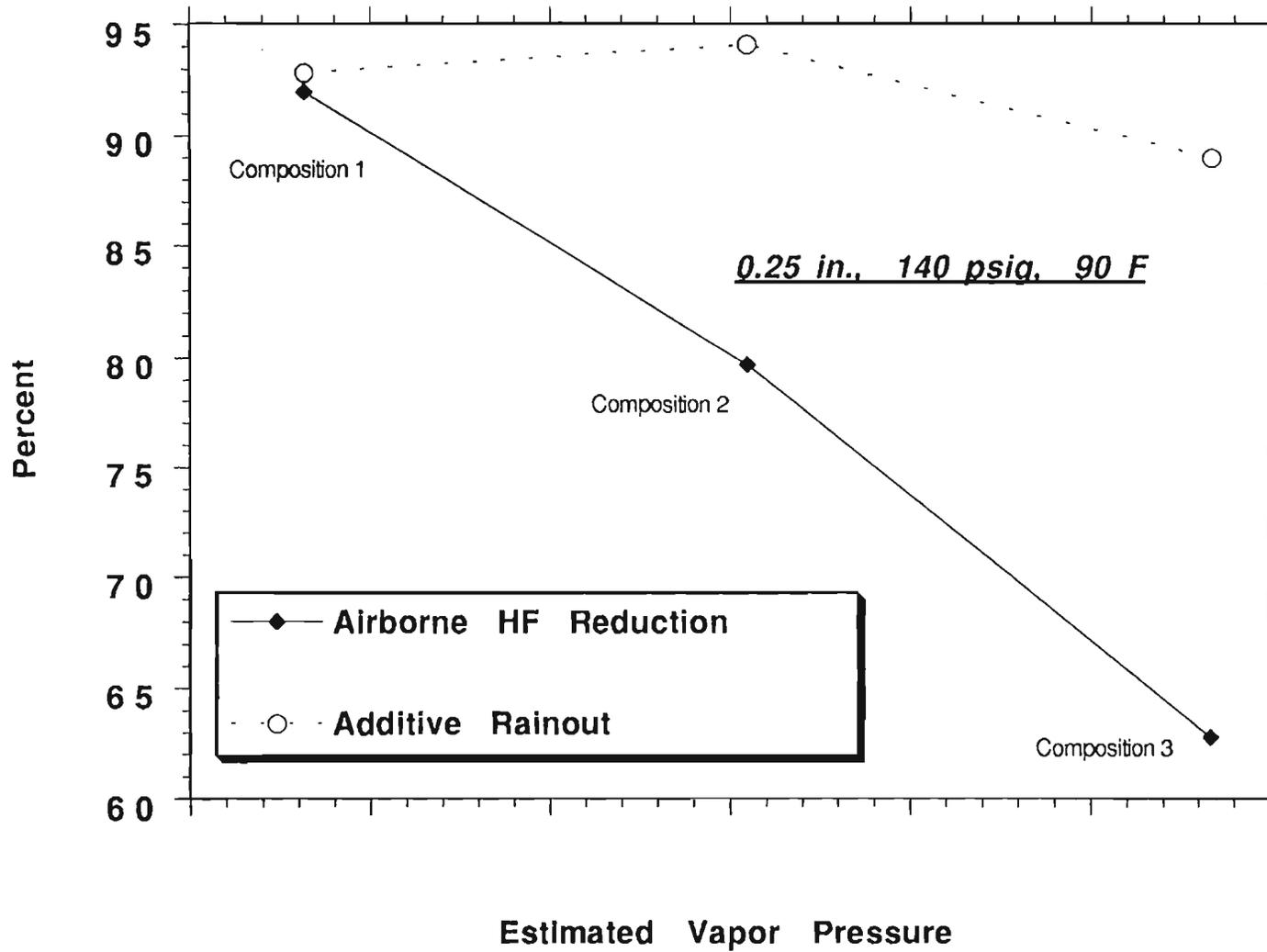


Figure 8

Catalyst 2, 0.5 inch orifice, 50 psig, 90 F

