CMA/STLE PUMP SEAL MASS EMISSIONS STUDY

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ABSTRACT

The Chemical Manufacturers Association and the Society of Tribologists and Lubrication Engineers conducted a study of the leakrates from pumps equipped with mechanical seals. The resulting analysis indicates that attention to maintenance issues can bring pumps into compliance with expected HON standards without major retrofits or replacement of equipment. Seal materials of construction are discussed as a means for improving performance. Mass emission rates (lb/hr) are far lower than previous EPA estimates.

INTRODUCTION

This paper is the result of a joint study by the Chemical Manufacturers Association (CMA) Equipment Leaks Work Group (ELWG) and the Society of Tribologists and Lubrication Engineers' (STLE) Seals Technical Committee (STC) Emissions Work Group. The study investigated the factors affecting leakage of air pollutants from mechanical seals in centrifugal pumps. The proper selection of seal design, wear face materials, and secondary seals are relevant factors when attempting to minimize leakage for single mechanical seals on pumps. The CMA/STLE data analysis indicates that the pumps equipped with mechanical seals, in the chemical and petrochemical plants studied, are already below maximum achievable control technology (MACT) levels specified to stay out of the quality improvement plan (QIP) requirements of the proposed National Emissions Standard for Hazardous Air Pollutants (NESHAP) or Hazardous Organic NESHAP (HON) [1].

PROPOSED NATIONAL STANDARDS FOR CONTROL OF PUMP LEAKS

A number of federal and regional regulations have been written to control volatile hazardous air pollutant (VHAP) emissions from process pumps. Pump users are advised to consult with local agencies for current standards.

On December 31, 1992, under authority of the 1990 Clean Air Act Amendments (CAAA) Title III, the United States Environmental Protection Agency (EPA) proposed regulations for the emissions of certain hazardous air pollutants from chemical manufacturing processes. This proposed HON addresses equipment leaks and is expected to be promulgated sometime early in 1994. The rule will be among the first standards promulgated by the EPA pursuant to the requirements of the CAAA. The equipment leaks standard in the HON will affect pumps, compressors, valves, flanges, pressure relief devices, and other related equipment in VHAP service.

The proposed leak standard takes the form of work practice requirements. These practices require equipment owners to Monitor and Restore Equipment Seals (MARES). The regulatory agency responsible for each program defines which seals require repair based on field monitoring results. The monitoring part of MARES is referred to as "screening" and is conducted with a portable analyzer or "sniffer." The portable analyzer generally has characteristics specified by EPA Method 21. This monitor is held 1.0 cm from a pump seal to test for VHAP concentration. If the instrument reading (i.e., screening value) exceeds a value given in the applicable regulation, the seal is leaking by definition. If the instrument reading is less than the leak definition, the seal is not leaking for regulatory purposes. Pump seal leak definitions for the HON equipment leak MACT are expected to be phased down over a three-year period to 1000 ppmv corrected screening value.

DATA COLLECTION AND ANALYSIS

Instrument reading and leakage tests were conducted by CMA and STLE participants on industrial pumps in a variety of services in chemical and petrochemical plants. All raw instrument screening test values were collected in accordance with EPA Method 21 and later corrected with appropriate response factors for the chemicals being sealed. Test methods and procedures are described in more detail in APPENDIX A. As discussed below, seal arrangements, wear faces, process fluids, secondary seals, and other variables were evaluated.

Data Analysis

Two basic categories of information from the STLE data set were analyzed. The first category involved classifying each data point as either above or below 1000 ppmv. These above-or-below 1000 ppmv classifications were used to compare pump parameters.

The second category of information involved an analysis of the estimated leakrate (lb/hr) which was calculated from the adjusted instrument reading (ppmv). The estimated leakrates were then used to compare pump parameters. See APPENDIX A for more detail.

Seal Arrangements

STLE test data on 630 single and double seals, both cartridge and noncartridge, were analyzed to determine the seal type and arrangement most likely to screen below 1000 ppmv. The seal arrangement analysis is presented in APPENDIX B. It indicates that a statistically significant difference exists between double seals and single noncartridge seals with respect to the 1000 ppmv threshold level. However, single cartridge seals were not significantly different from double seals. All subsequent analyses were done for single noncartridge seals to avoid possible anomalous results which could result from mixing seal types.

Comparison of calculated leakrates for different cartridge seal arrangements showed a small difference in emissions between double and single seals (i.e., 0.00096 lb/hr *vs* 0.0026 lb/hr, respectively), as shown in Table 1. Leakage from double seals may be attributed to the barrier fluid as opposed to process fluid.

Table 1. Average Leakrate vs Seal Arrangement, STLE Database.

	N	lb/hr average
Cartridge Double	33	0.0010
Cartridge Single	31	0.0026
Noncartridge Double	11	0.0016
Noncartridge Single	555	0.0071
Total	630	0.0064

N = number of tests in subcategory

Wear Faces

The wear face analysis is reflected in APPENDIX C. Combinations of rotating and stationary faces were compared. There are statistically significant differences among wear face materials tested. The best combination tested, demonstrating low leak performance, was a silicon carbide face against a carbon face. The calculated leakrates for the best and poorest combinations are 0.0023 lb/hr and 0.016 lb/hr, respectively. To avoid introducing anomalies due to wear face differences, the rest of the analyses were done for the two separate wear face groups (i.e., best and worst) for which enough data were available for further consideration.

Process Fluids

Process fluids were categorized into five groups (i.e., acids, aliphatics, aromatics, nitrogen containing, and oxygen containing). Statistical comparisons (APPENDIX D) of these groups showed no significant difference in defect rates. This could indicate an association between wear face material and process fluid. Therefore, a Cochran-Mantel-Haenszel [2] analysis was done to see whether process fluid or face material is more significant. The analysis indicated that wear face material had a more significant effect on defect rate.

Secondary Seals

The statistical analysis of all the secondary seal data, without distinguishing among wear faces, shows PTFE (polytetrafluoroethylene) to be highly associated with seals having instrument readings above 1000 ppmv (APPENDIX E). Comparisons within seal face categories did not show the same association. Further analysis is required to verify any relationship.

There are, however, statistically significant differences in other secondary seal materials. In nearly three-fourths of the applications, fluoroelastomers (FKM) were used as the standard seal material, which is the case in most chemical process industry related applications. Higher performance perfluoroelastomers (FFKM) tested in this study were used when FKM or fluoropolymer (PTFE) performance was not considered sufficient.

When selecting a sealing material, the performance requirements should be balanced with the material cost (total cost/benefit analysis). In demanding environments, for extended seal life and reduced downstream operating costs, a higher-cost material may be necessary. The total cost should be considered when selecting the material. This cost includes the cost of the seal, as well as downtime, maintenance, safety, environmental hazards, and other factors. As in many situations, higher front-end costs (i.e., materials costs) may produce lower downstream operating costs.

Other Variables

Pump speed, shaft size, and several properties of the fluids being pumped were analyzed. The only one of these factors that was statistically significant was the increased likelihood of having instrument readings above 1000 ppmv with increasing shaft size for the best performing wear faces. Shaft size was not significant for the poorer performing wear face materials. Further evaluation may be warranted.

MACT leakrate analysis

The way is described in APPENDIX F in which the database was used to correlate average pump leakage with the fraction of pumps with corrected screening values above 1000 ppmv. Based on these findings for the plants studied, pumps that are subject to Subpart H would have an average seal leakage of less than 0.0065 lb/hr.

DISCUSSION

The analysis shows fewer instrument readings above 1000 ppmv for cartridge seals than for noncartridge seal designs. This appears to confirm experience in industry that cartridge seals, with their preset seal setting and alignment features, are more likely to be successfully installed than noncartridge designs.

Overall tabulation of the CMA/STLE data analysis is shown in Figure 1. Only 8.3 percent of the seals inspected were above 1000 ppmv, compared to a target of less than 10 percent in the proposed Subpart H.

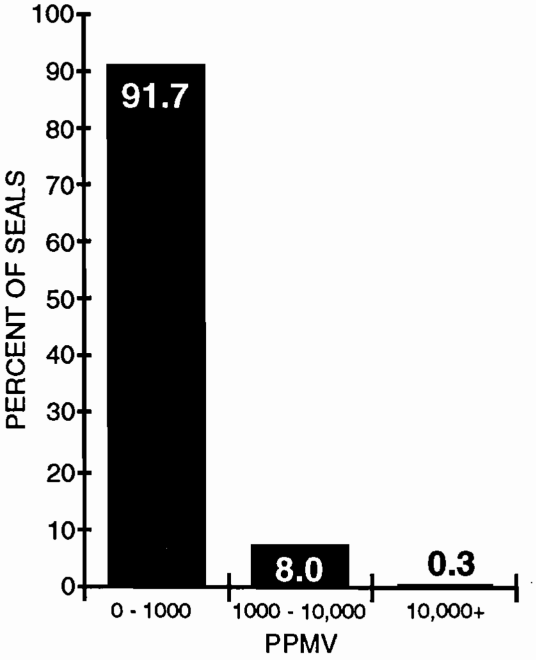

Figure 1. Corrected Concentration, STLE Database.

As the following case history indicates, this 8.3 percent may be substantially reduced. Operators of numerous plants have reported the successful implementation of MARES, a quality assurance maintenance program. Regular inspections may identify problem seals that may be brought into compliance through upgrades of seal face materials, secondary seal materials, and selection of appropriate seal designs. In effect, these reports appear to confirm the CMA/STLE statistical analysis described here, which shows that a high proportion of leaking seals and estimated emissions are associated with old seal technologies.

Case History

The following case history shows how a maintenance upgrade program can improve seal performance. In 1991, 54 pumps in a chemical plant in Texas were tested for leakage from mechanical seals, using an OVA meter in accordance with EPA Method 21. Thirty-one of the pumps tested below 100 ppmv. Only seven pumps tested above 1000 ppmv, two of which tested greater than 10,000 ppmv. After the 1991 tests, the plant instituted a program of monthly MARES and upgraded eight seals. Four seals were upgraded from PTFE secondary seals to elastomeric O-rings, three seals were upgraded from single to tandem seals, and one seal was changed from a pusher to a bellows design. In 1993, after the eight seals were upgraded as described in this paper, monthly MARES surveys indicate that all 54 pumps are operating at nondetectable screening values.

CONCLUSIONS

The CMA/STLE survey of more than 630 usable data sets for pumps in chemical and petrochemical plants indicates that:

- Single mechanical seals appear to provide a cost effective way to address the proposed HON, Subpart H, requirements.
- Actual double seal flush fluid leakrates are not much lower than single seal leakrates with good materials for faces and secondary seals (i.e., 0.0023 lb/hr *vs* 0.0011 lb/hr).
- The average process leakrate for pumps subject to HON MACT requirements may be less than 0.0065 lb/hr.
- The pumps examined in this study were found to be operating at a level below the threshold that would require the implementation of the QIP portion of the Subpart H of the HON (i.e., 8.3 percent above 1000 ppmv compared to no more than 10 percent for MACT).
- Selection of seal face and secondary seal materials should be based on cost vs benefits where upgrading materials would further improve performance.
- Emphasis on the maintenance issues related to MARES has played a key role in maintaining pumps within the proposed standard without major retrofits or replacement of equipment.
- The 1000 ppmv level associated with Phase III of the proposed HON Subpart H should be achievable when recognized and accepted maintenance procedures are followed in conjunction with a MARES program such as the one in proposed Subpart H.

GLOSSARY OF TERMS

Bagging—an actual measurement of leakrate as determined by enclosing the equipment and measuring the concentration and volume of the leak to calculate pounds lost per hour.

CAAA—U. S. Federal Clean Act Amendments of 1990.

Chi-Square Analysis—statistical technique for comparing the levels of a response between variables.

CMA—Chemical Manufactures Association.

FFKM—a perfluoroelastomer usually in the form of O-rings, used as secondary seals in end face mechanical seals.

FID—flame ionization detector.

FKM—a fluoroelastomer, used in the form of O-rings as secondary seals in end face mechanical seals.

HON—Hazardous Organic National Emission Standards For Hazardous Air Pollutants.

LDAR—leak detection and repair program as defined by proposed HON rule covering the control of equipment leaks.

MACT—Maximum Achievable Control Technology as mandated by CAAA Title III.

MARES—stands for Monitor and Restore Equipment Seals. Guided maintenance program ensure that equipment leakage is low, see LDAR.

Mass Emission Rate—leakrate in lb/hr. May be measured by bagging techniques or estimated from corrected screening value (ppmv) using EPA equation.

NESHAP—National Emission Standards for Hazardous Air Pollutants.

OVA—organic vapor analyzer.

Primary Seal—the wear faces that move relative to each other and form the flat restriction to prevent sealing fluid, usually the product being pumped, from escaping to the atmosphere.

PTFE—polytetrafluoroethylene, used in the form of a wedge, V-ring, or gasket as a secondary seal in end face mechanical seals.

QIP—Quality Improvement Program required by the proposed HON for plants with a specified fraction monitored above the defect definition. In the case of pumps, if more that 10 percent screen above 1000 ppmv (6 month rolling average), QIP is mandated. QIP requires data collection and study until the average above 1000 ppmv is reduced to below 10 percent.

Screening Concentration—a screening test that has been corrected to indicate the actual concentration of the vapor by the application of a response factor specific to the instrument used and the chemical tested.

Screening Value—a instrument reading concentration, expressed in ppmv, obtained from screening an equipment leak source. Usually expressed as equivalent ppmv of methane.

Screening—testing of chemical vapor concentration in ppmv using an approved instrument (sniffer) in accordance with EPA Method 21.

Secondary Seals—those elements of an end face mechanical seal that prevent leakage past the primary sealing elements (wear faces) and the shaft or seal chamber housing. Usually an O-ring, V-ring, wedge, bellows, or gasket.

STLE—Society of Tribologists and Lubrication Engineers.

VHAP—volatile hazardous air pollutant.

APPENDIX A

Methods and Procedures

Separate databases were compiled by STLE and CMA. These contained data from instrument readings *vs* generic materials of construction and basic arrangements of mechanical seals.

Instrument readings and leakage tests by CMA and STLE participants were conducted on industrial pumps in a variety of services in chemical and petrochemical plants. All raw instrument readings were corrected with appropriate response factors for the chemicals being sealed. Chemicals were identified by Chemical Abstract (CAS) numbers.

All the data evaluated in these two studies were accumulated using compatible protocols and procedures. Consequently, the two databases complemented each other and, when used together, greatly expanded comprehension of the subject.

The CMA mechanical seal leakrates were accumulated by CMA's Plant Organizational Software System for Emissions from Equipment (POSSEE®). This database included both corrected instrument readings (ppmv) and mass emission leakrate (lb/hr) studies.

Leakrate measurements involved enclosing the seal and analyzing the enclosed air over time. Both "blow through" (gas blown into the enclosure) and "vacuum" (gas extracted from the enclosure) bagging techniques were used. Bagging tests are the direct measurement of actual leakrates. Screening concentrations and leakrate data were the only data used from the CMA database.

The seals in the STLE database were categorized as single, double, tandem, cartridge, and noncartridge arrangements. The materials of construction of the seal faces and secondary seals were classified by generic definitions. No attempt was made in these studies to differentiate between various grades of tungsten carbide, silicon carbide, carbon, PTFE, fluoroelastomers (FKM), perfluoroelastomers (FFKM), etc. Performance differences are expected within some grades. Pump operation conditions of temperature, rpm, suction pressure, and discharge pressure were also recorded.

The STLE database was audited for data integrity to ensure that:

- each seal was in organic chemical service and concentration was known;
- an appropriate organic vapor analyzer (OVA) flame ionization detector (FID) was used for monitoring;
- proper response factors were applied;
- seal face materials were identified;
- secondary seals were identified; and
- seal arrangements were identified.

The data-integrity audit of the 2,000-plus STLE data points on instrument readings *vs* operating characteristics in the STLE database resulted in a sort-down to 630 usable data points. The loss of data was primarily due to the inability to find response factors for the fluids tested. The inability to make the response factor corrections resulted from the presence of chemicals for which response factor data were insufficient and the unavailability of information regarding barrier fluids used with dual seals. Unfortunately, so few data points (i.e., nine) were recoverable for tandem seals that this category could not be analyzed. It is important to note that entire plants or process streams were monitored and generally dropped by the same groupings when response factors were lacking. The instrument readings and mass emission leakrates are indicative of actual plant process pump leakrates with no bias for particular equipment or seal manufacturer.

Chemical and Physical Properties

Information on chemical composition in the STLE database facilitated the conversion of instrument readings to actual concentrations. This information also permitted the compilation of physical property data for the process fluids. The physical properties incorporated in the database were specific gravity (20° C), vapor pressure, viscosity, and heat capacity at operating temperature as well as heat of vaporization and boiling point. The DIPPR (Design Institute for Physical Property Research) and UPPS (Universal Physical Property System) databases were the sources of all the physical property information. Antoine coefficients were used to adjust vapor pressure for temperature and Raoult's law was used to adjust for mixtures.

Conversion of Screening Value to Concentration

With the use of Equation (A-1), all screening values in both data bases were corrected to give screening concentration.

$$\text{Response factor (RF)} = \frac{\text{concentration}}{\text{meter reading}} \qquad \text{(A-1)}$$

For each chemical compound, points relating meter reading to actual concentration were required for at least three concentrations. The points were point-to-point or spline-fit with the lowest point connected to the origin. For a given meter reading, the appropriate spline-fit curve (i.e. straight line) was used for each chemical in the process stream. Each meter reading was used to obtain the comparable concentration. The response factor (RF) for mixtures was calculated in accordance with Equation (A-2):

$$\frac{1}{RF_{\text{mixture}}} = \sum \frac{\text{Mole Fraction}_i}{RF_i} \tag{A-2}$$

Conversion of concentration to emission rate

CMA screening and bagging data were analyzed to determine the relationship between the screening concentration and the emission rate. As shown in Figure 2, the resulting Equation (A-3), including scale bias correction factor, is:

$$\text{Emission Rate (lb/hr)} = 6.138 \times 10^{-5}\ (\text{ppmv})^{0.733} \tag{A-3}$$

This relationship was not significantly different from a comparable formula, recently developed by EPA, Equation (A-4):

$$\text{Emission Rate (lb/hr)} = 4.18 \times 10^{-5}\ (\text{ppmv})^{0.824} \tag{A-4}$$

When there is no significant difference, the EPA protocol allows for combining the data or using the EPA equation. The latter option was selected for convenience. EPA default constants for pumps with screening values below the limit of detection (i.e., screening value = 0) and for those with screening values above 10,000 were also used. These are 1.65 × 10^{-5} lb/hr and 0.5346 lb/hr, respectively.

Seal Arrangement	Total	Below 1000 ppmv	Leakers Above 1000 ppmv	Leakers Percent
Cartridge Double	33	33	0	0
Cartridge Single	31	30	1	3
Noncartridge Double	11	10	1	9
Noncartridge Single	555	507	48	9
Total	630	580	50	8

Chi-Square = 4.192 with 3 DF, no significant difference
Analysis of variance: 98.7 percent level of significance

```
 Level        N     Mean    Ind. 95 percent CI's for Log Leak
                            Rate Based on Pooled Std. Dev.

Cart Dbl      33  -3.5739                 <-------------->
Cart Sgl      31  -3.1611                       <------------->
Noncart Dbl   11  -3.8116     <--------------------->
Noncart Sgl  555  -3.1954                           <->
                            --------|------------|------------|-------
                                  -4.00        -3.50        -3.00
Pooled standard deviation = 0.8782
```

Wear Face Materials	Total	Below 1000 ppmv	Leakers Above 1000 ppmv	Leakers Percent
Silicon Carbide	361	345	16	4
Ceramic	2	2	0	0
Tungsten Carbide	135	115	20	15
Nickel Alloys	53	41	12	21
Total	551	503	48	9

Chi-Square=35.429 with 4 DF,99.5 percent level of sign.
Analysis of variance: 99.99 percent level of significance

```
 Level      N     Mean     Indivi. 95 percent CI's for Mean
                             Based on Pooled Std. Dev

SC        361   -3.2086           <->
Ceramic     2   -4.7520    <---------->
TC        135   -3.3042          <->
Stellite   52   -2.8069              <->
Niresist    1   -1.3526                 <---------------->
                           ------|---------------|---------------|---
                               -4.0            -2.0            0.0
```

Pooled standard deviation = 0.8856

Summary Wear Face Materials	N	lb/hr average
Best Performing	363	0.0023
Poorest Performing	188	0.0163

Using Only Best Wear Face Materials

Product	Total	Below 1000 ppmv	Leakers Above 1000 ppmv	Leakers Percent
Acids	4	4	0	0
Alipathics	338	323	15	4
Aromatics	9	8	1	11
Oxides	4	4	0	0
Total	355	339	16	4

Chi-Square = 1.293 with 3 DF, no significant difference

Using Only Poorest Wear Face Materials

Product	Total	Below 1000 ppmv	Leakers Above 1000 ppmv	Leakers Percent
Acids	48	37	11	23
Alipathics	48	39	9	19
Aromatics	39	31	8	20
Nitriles	23	23	0	0
Oxides	20	19	1	5
Total	178	149	29	16

Chi-Square = 8.613 with 4 DF, no significant difference

Using Only Best Wear Face Materials

Sec. Seal Matl.	Total	Below 1000 ppmv	Leakers Above 1000 ppmv	Leakers Percent
FFKM	2	2	0	0
PTFE	10	10	0	0
FKM	355	339	16	4
Total	367	351	16	4

Chi-Square = 0.565 with 2 DF, no significant difference
Analysis of variance: 97.3 percent level of significance

```
Level     N       Mean      Individual 95 percent CI's for Mean
                                Based on Pooled Std. Dev.

FFKM      2     -2.7251           <------------------------------>
PTFE     10     -3.7107   <----------->
FKM     355     -3.2043              <->
                          ----------|------------|------------|--------
                                 -3.50        -2.80        -2.10
Pooled standard deviation = 0.6398
```

Using Only Poorest Wear Face Materials

Sec. Seal Matl.	Total	Below 1000 ppmv	Leakers Above 1000 ppmv	Leakers Percent
Buna N	7	4	3	43
EPR	3	2	1	33
FFKM	19	18	1	5
Neoprene	18	18	0	0
PTFE	95	75	20	21
FKM	46	39	7	15
Total	188	156	32	17

Chi-Square = 10.625 with 5 DF, no sign.diff. at 95 percent conf.
Analysis of variance: 99.99 percent level of significance

```
 Level      N      Mean     Individual 95 percent CI's for Mean
                               Based on Pooled Std. Dev.

Buna N      7    -2.155                 <----------->
EPR         3    -1.812                  <----------------->
FFKM       19    -4.448     <------>
Neoprene   18    -3.906        <------>
PTFE       95    -2.938              <->
FKM        46    -3.019             <-->
                            ----|----------|-----------|----------|---
                              -4.5       -3.0        -1.5         0
Pooled standard deviation = 1.144
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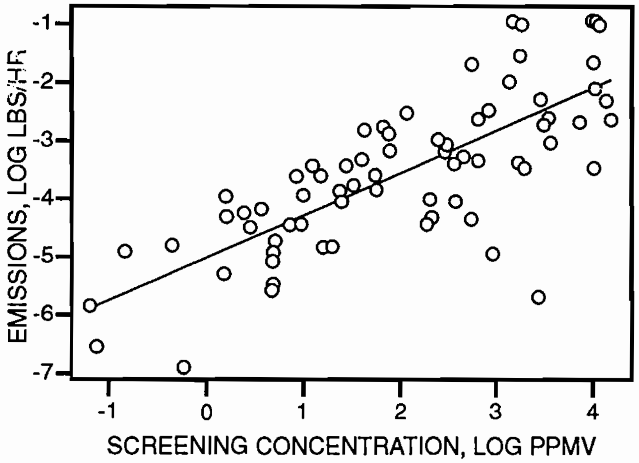

Figure 2. Fitted Line of Log Emissions Vs *Screening Concentrations, CMA Data Base.*

APPENDIX F

MACT Pump Emission Rate

For valves, a strong relationship has been reported between the average leakrate and the fraction screened above a defect definition. A similar relationship should exist for pumps. To test this hypothesis, it was necessary to divide the pump data into individual processes. Since the individual processes were not identified, a random number approach was used to break the database into segments of about 50 pump "processes."

The groupings obtained were averaged to give the percent screened above 1000 ppmv and the average log of the leakrates (lb/hr). These values were graphed in Figure 3.

The relationship shown in Figure 3 provides a simplified way to predict leakrate based on the fraction of pumps with screening values above 1000 ppmv. It also gives a way to predict the maximum leakrate for pumps that fall under MACT requirements.

The average leakrate of pumps in a process is:

Ave. Leak, lb/hr = $0.0042 \times 10^{1.932L}$

Where

L = fraction of corrected screening values above 1000 ppmv.

The average leakrate of pumps in a process with 10 percent of the pumps with corrected screening values above 1000 ppmv = 0.0065 lb/hr.

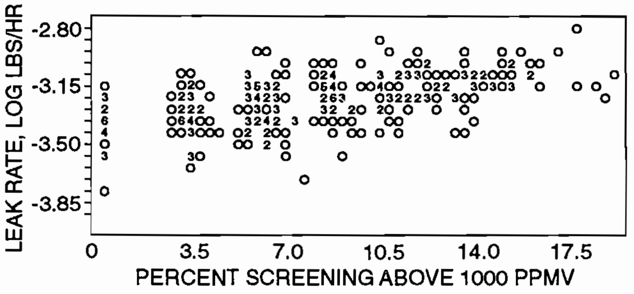

Figure 3. Plot of log Leakrate Vs *Percent Screening Concentrations above 1000 ppmv.*

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