Section 313, Emergency Planning
and Community Right-to-Know Act

Estimating Releases for Mineral Acid Discharges Using pH Measurements

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U.S. Environmental Protection Agency
Office of Toxic Substances
Economics and Technology Division

6-12-91

ESTIMATING RELEASES FOR MINERAL ACID DISCHARGES USING pH MEASUREMENTS

The mineral acids currently listed on the section 313 toxic chemical list are commonly used throughout the manufacturing sector as product ingredients, reactants, and chemical processing aids. Currently, inorganic bases are not listed on the section 313 toxic chemical list and, as a result, this directive focuses on mineral acids. The guidance in this directive applies only to these mineral acids listed below:

	Name	CAS Number	Formula
•	Sulfuric Acid	7664-93-9	H_2SO_4
•	Nitric Acid	7697-37-2	HNO_3
•	Hydrochloric Acid	7647-01-0	HCl
•	Phosphoric Acid	7664-38-2	H_3PO_4
•	Hydrofluoric Acid	7664-39-3	HF

These mineral acids may be present in aqueous waste streams that are sent to on-site neutralization or are discharged to a POTW or other offsite treatment facility. On-site acid neutralization and its efficiency must be reported in Part III, section 7 of Form R (Waste Treatment and Efficiency Section). For purposes of reporting on Form R, EPA considers a waste mineral acid at a pH 6 or higher to be effectively neutralized. That is, the treatment efficiency of the neutralization can be considered 100% and water discharges to streams or POTWs can be reported as zero. It is important to note that this interpretation applies only to mineral acids, not other Section 313 chemicals. If the treatment efficiency is not equal to 100 percent (pH is less than 6), the amount of the listed mineral acid remaining in the waste stream which is released to the environment on-site must be reported in Part III section 5 of Form R. If the waste stream is sent off-site for further treatment, the amount of mineral acid remaining in the waste stream must be reported in Part III section 6.

1. Estimating Mineral Acid Release

In the case of a listed mineral acid, the pH of the waste stream can be used to calculate the amount of acid in a waste stream and the efficiency of the neutralization. The pH is a commonly available measure of the acidity or alkalinity of a waste stream and can be obtained using a pH meter or pH sensitive paper. The pH scale itself varies from 0 to 14.

The total mineral acid concentration (ionized and unionized) in pounds/gallon can be derived by using the pH value of the solution, the molecular weight and ionization constant of the acid, and appropriate conversion factors. The total acid concentration for each mineral acid for different pH values is listed in Table 1. The derivation of this table is discussed in a separate addendum to this directive, Estimating Releases for Mineral Acid Discharges Using pH Measurements - Addendum, and is available from the EPCRA Hotline, USEPA, 401 M Street, SW (OS-120), Washington, DC 20460; telephone (800) 535-0202 or (703) 920-9877.

The approach outlined in this directive can only be used for one mineral acid in a solution. Also, release estimates for a listed mineral acid(s) based solely on pH calculations provide only a rough estimate. The estimates can be made for a wastestream with a steady pH below 6 or for one whose pH temporarily drops to below pH 6. Facilities should use their best engineering judgement and knowledge of the solution to evaluate the reasonableness of the estimate.

TABLE 1
MINERAL ACID CONCENTRATION VS pH VALUE

Concentration in lbs/gallon

pH		H_2SO_4	HNO_3	HCl	H_3PO_4	HF
0		0.8200000	0.5200000	0.3000000	**********	**********
0.2		0.5200000	0.3300000	0.1900000	**********	**********
0.4		0.3300000	0.2100000	0.1200000	**********	**********
0.6		0.2100000	0.1300000	0.0760000	7.0700000	**********
0.8		0.1300000	0.0830000	0.0480000	2.8600000	**********
1		0.0820000	0.0520000	0.0300000	1.1700000	4.8000000
1.2		0.0520000	0.0330000	0.0190000	0.4800000	1.9100000
1.4		0.0330000	0.0210000	0.0120000	0.2000000	0.7600000
1.6		0.0210000	0.0130000	0.0076000	0.0890000	0.3000000
1.8		0.0130000	0.0083000	0.0048000	0.0400000	0.1200000
2		0.0082000	0.0052000	0.0030000	0.0190000	0.0490000
2.2		0.0052000	0.0033000	0.0019000	0.0095000	0.0200000
2.4		0.0033000	0.0021000	0.0012000	0.0050000	0.0082000
2.6		0.0021000	0.0013000	0.0007600	0.0027000	0.0034000
2.8		0.0013000	0.0008300	0.0004800	0.0016000	0.0015000
3		0.0008200	0.0005200	0.0003000	0.0009200	0.0006400
3.2		0.0005200	0.0003300	0.0001900	0.0005600	0.0002900
3.4		0.0003300	0.0002100	0.0001200	0.0003400	0.0001400
3.6		0.0002100	0.0001300	0.0000760	0.0002100	0.0000720
3.8		0.0001300	0.0000830	0.0000480	0.0001300	0.0000380
4		0.0000820	0.0000520	0.0000300	0.0000830	0.0000214
4.2		0.0000520	0.0000330	0.0000190	0.0000520	0.0000120
4.4		0.0000330	0.0000210	0.0000120	0.0000330	0.0000074
4.6		0.0000210	0.0000130	0.0000076	0.0000210	0.0000045
4.8		0.0000130	0.0000083	0.0000048	0.0000130	0.0000028
5		0.0000082	0.0000052	0.0000030	0.0000082	0.0000017
5.2		0.0000052	0.0000033	0.0000019	0.0000052	0.0000011
5.4		0.0000033	0.0000021	0.0000012	0.0000033	0.0000007
5.6		0.0000021	0.0000013	0.0000008	0.0000021	0.0000004
5.8		0.0000013	0.0000008	0.0000005	0.0000013	0.0000003
6		0.0000008	0.0000005	0.0000003	0.0000008	0.0000002

********* denotes a pH value not possible for this acid because of incomplete ionization.

Example 1: In a calendar year, a facility transfers 1.3 million gallons of a solution containing hydrofluoric acid (HF), at pH 4, to a POTW. Using Table 1, a pH of 4 corresponds to a concentration of 0.000021 lbs HF/gallon of solution. The weight of HF transferred can be estimated using the equation:

Transfer of HCl = (concentration of HF) x (effluent flow rate)

Substituting the values into the above equation yields:

$$\text{Transfer of HCL} = 0.000021\ \frac{\text{lbs}}{\text{gal}}\ \text{HF} \times 1{,}300{,}000\ \frac{\text{gal solution}}{\text{yr}}$$

$$= 27\ \text{lbs/yr}$$

Example 2: A facility had an episodic release of hydrochloric acid (HCl) in which the waste stream was temporarily below pH 6. During the episode, the waste water (pH 1.6) was discharged to a river for 10 minutes at a rate of 106 gallons per minute. Using Table 1, a pH of 1.6 for HCl represents a concentration of 0.0076 lbs HCl/gallon of solution. The amount of the HCl released can be estimated using the following equation:

Release of HCl = (concentration of HCl) x (effluent flowrate)

Substituting the values in the above equation:

$$\text{Release of HCl} = 0.0076\ \frac{\text{lbs}}{\text{gal}} \times 106\ \frac{\text{gal}}{\text{min}} \times 10\ \text{min}$$

$$= 8\ \text{lbs/yr}$$

2. Estimate Treatment Efficiencies for Acid Neutralization

Mineral acid solutions that are neutralized to a pH of 6 or above have a treatment efficiency of 100 percent. If a mineral acid is neutralized to a pH is less than 6, then the reportable treatment efficiency is somewhere between 0 and 100 percent. It is possible to estimate the neutralization treatment efficiency using the mineral acid concentration values directly from Table 1 in the equation below. The concentrations correspond with the pH values before and after treatment.

$$\text{Treatment Efficiency} = \frac{(I-E)}{I} \times 100$$

where I = acid concentration before treatment
E = acid concentration after treatment

Example 3: An H_3PO_4 acid wastestream of pH 2.4 is neutraliaed to pH 4.6. Using Table 1, the initial acid concentration is 0.005 mol/liter and the final concentration is 0.000021 mol/liter. Substituting these values into the equation for treatment efficiency:

$$\text{Treatment Efficiency} = \frac{0.005 - 0.000021}{0.005} \times 100$$

$$= 99.6\ \text{percent}$$

For strong acids only (H_2SO_4, HNO_3, and HCl), the net difference in pH can be used more easily to estimate the efficiency by utilizing Table 2, since pH is directly proportional to the acid concentration For example, a pH change (before pH -after pH) of one unit results in a treatment efficiency of 90 percent, whether the pH change is from pH 1 to pH 2 or from pH 4 to pH 5.

The following table summarizes treatment efficiencies for various pH changes. Some pH changes result in the same treatment efficiency values in the table due to rounding to one decimal place. The pH change is the difference between the initial pH and the pH after neutralization treatment.

TABLE 2: Treatment Efficiencies for Various pH Unit Changes for Sulfuric, Nitric, or Hydrochloric Acid

pH Unit Change	Treatment Efficiency (%)	pH Unit Change	Treatment Efficiency (%)
1.0	90.0	2.0	99.0
1.1	92.1	2.1	99.2
1.2	93.7	2.2	99.4
1.3	95.0	2.3	99.5
1.4	96.0	2.4	99.6
1.5	96.8	2.5	99.7
1.6	97.5	2.6	99.8
1.7	98.0	2.7	99.8
1.8	98.4	2.8	99.8
1.9	98.7	2.9	99.9
		3.0	99.9

Example 4: If a HNO_3 wastestream of pH 2 is treated to pH 4, the pH change is 2 units. Using Table 2 above, the treatment efficiency is given as 99.0 percent.

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ADDENDUM

Introduction

This addendum explains the derivation of tables in Estimating Releases for Mineral Acid Discharges Using pH Measurements. In that document, Table 1 shows the acid concentration in lbs/gallon derived from pH values for the mineral acids listed below. Also, the derivation of Table 2, which relates neutraliztion treatment efficiency to the change in pH for neutralization of strong mineral acids, is given.

Section 313 Mineral Acids

	Name	CAS Number	Formula	Molecular Weight
•	Sulfuric Acid	7664-93-9	H_2SO_4	98.08
•	Nitric Acid	7697-37-2	HNO_3	63.01
•	Hydrochloric Acid	7647-01-0	HCl	36.46
•	Phosphoric Acid	7664-38-2	H_3PO_4	98.00
•	Hydrofluoric Acid	7664-39-3	HF	20.01

Relationship between pH and hydrogen ion concentration

The pH or hydrogen ion activity is a measure of the acidity or alkalinity of a solution. The pH is determined by the hydrogen ion concentration $[H^+]$ when an acid or alkaline solution dissociates into its charged ionic parts. Acids such as hydrochloric acid dissociate as follows:

$$[HCl] \longleftrightarrow [H^+] + [Cl^-]$$

The equation indicates that an equilibrium exists between the hydrochloric acid and the hydrogen and chloride ions, although the equilibrium lays far to the right. The pH is a logarithmic measure of the hydrogen ion concentration:

$$pH = -\log_{10}[H^+]$$

which can be rearranged for $[H^+]$ to yield:

$$[H^+] = 10^{-pH} = 1 \times 10^{-pH}$$

where $[H^+]$ = concentration of hydrogen ions in moles per liter.

The following table summarizes $[H^+]$ values in moles/liter corresponding to various pH values:

TABLE A1: $[H^+]$ Values Corresponding to Various pH Values in Moles/Liter

pH	$[H^+]$	pH	$[H^+]$	pH	$[H^+]$
0	1.0	1.0	0.1	2.0	0.01
0.1	0.79	1.1	0.079	2.1	0.0079
0.2	0.63	1.2	0.063	2.2	0.0063
0.3	0.50	1.3	0.050	2.3	0.0050
0.4	0.40	1.4	0.040	2.4	0.0040
0.5	0.32	1.5	0.032	2.5	0.0032
0.6	0.25	1.6	0.025	2.6	0.0025
0.7	0.20	1.7	0.020	2.7	0.0020
0.8	0.16	1.8	0.016	2.8	0.0016
0.9	0.12	1.9	0.012	2.9	0.0012
pH	**$[H^+]$**	**pH**	**$[H^+]$**	**pH**	**$[H^+]$**
3.0	0.001	4.0	0.0001	5.0	0.00001
3.1	0.00079	4.1	0.000079	5.1	0.0000079
3.2	0.00063	4.2	0.000063	5.2	0.0000063
3.3	0.00050	4.3	0.000050	5.3	0.0000050
3.4	0.00040	4.4	0.000040	5.4	0.0000040
3.5	0.00032	4.5	0.000032	5.5	0.0000032
3.6	0.00025	4.6	0.000025	5.6	0.0000025
3.7	0.00020	4.7	0.000020	5.7	0.0000020
3.8	0.00016	4.8	0.000016	5.8	0.0000016
3.9	0.00012	4.9	0.000012	5.9	0.0000012

Strong acid dissociation

Strong acids such as hydrochloric, sulfuric, and nitric acid dissociate almost completely thus the total molar concentration of the acid is equal to the $[H^+]$ concentration. Since every mole of $[H^+]$ represents a mole of acid, one can just multiply the hydrogen ion concentration (moles/liter) by the molecular weight of the acid (gram/mole) to get the acid concentration. To convert the acid concentration from gram/liter to lbs/gallon, additional conversion factors are used. Thus the values of acid concentration (lbs/gal) in Table 1 for H_2SO_4, HNO_3 and HCl were obtained from the following equation.

$$\text{Acid concentration } \frac{\text{lbs}}{\text{gal}} = \frac{10^{-pH}\text{ mol}}{\text{L}} \times \frac{M\text{ g}}{\text{mol}} \times \frac{\text{lbs}}{454\text{g}} \times \frac{3.78\text{ L}}{\text{gal}}$$

where M = molecular weight of the acid.

Using $[H^+]$ values directly from Table A1 yields equation A1:

Equation A1:

$$\text{Acid concentration } \frac{\text{lbs}}{\text{gal}} = \frac{H^+\text{ mol}}{\text{L}} \times \frac{M\text{ g}}{\text{mol}} \times \frac{\text{lbs}}{454\text{g}} \times \frac{3.78\text{ L}}{\text{gal}}$$

Example A1: A solution contains hydrochloric acid (HCl), a listed section 313 toxic chemical at pH 3. The concentration of $[H^+]$ of 0.001 mole/liter is obtained from Table A1. Using Equation A1, the acid concentration in lbs/gallon is estimated.

$$\text{HCl concentration } \frac{\text{lbs}}{\text{gal}} = \frac{0.001\text{ mol}}{\text{L}} \times \frac{36.46\text{ g}}{\text{mol}} \times \frac{\text{lbs}}{454\text{g}} \times \frac{3.78\text{ L}}{\text{gal}}$$

$$= 0.003\text{ lbs HCl/gallon solution}$$

Weak acid dissociation

Weak acids, such as phosphoric and hydrofluoric acid, do not dissociate completely and an equilibrium is reached in which the concentration of the undissociated acid is much greater than zero. As a result, the total acid molar concentration must be calculated as the sum of the undissociated and the dissociated acid. Because every mole of hydrogen ion represents one mole of dissociated acid, the hydrogen ion concentration is used as a measure of the dissociated acid concentration. By substituting the hydrogen ion concentration for the dissociated acid concentration, the total acid molar concentration is given by Equation A2:

Equation A2:

$$\text{Total acid molar concentration} = \text{Concentration of undissociated acid} + \text{Hydrogen ion concentration}$$

Hydrofluoric acid

For hydrofluoric acid, the dissociation is expressed as:

$$\text{HF} \longleftrightarrow \text{H}^+ + \text{F}^-$$

The total acid molar concentration for hydrofluoric acid is given by Equation A3:

Equation A3:

$$\text{Total hydrofluoric acid molar concentration} = [\text{HF}] + [\text{H}^+]$$

In order to determine the concentration of undissociated acid, [HF], the equilibrium constant, which represents the degree of dissociation of the acid, must be used. The equilibrium constant, K_a, for HF is given by Equation A4:

Eqaution A4:

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

Since every mole of dissociated hydrogen ion produces one mole of fluoride ion, then $[\text{H}^+] = [\text{F}^-]$. The K_a for hydrofluoric acid is 3.5×10^{-4} (CRC). Substituting these values into Equation A4 yields:

$$3.5 \times 10^{-4} = \frac{[\text{H}^+]^2}{[\text{HF}]}$$

Solving for [HF], the equation becomes:

$$[\text{HF}] = \frac{[\text{H}^+]^2}{3.5 \times 10^{-4}}$$

This value for [HF] can be substituted into Equation A3 and, therefore, the total acid molar concentration for hydrofluoric acid is given by Equation A5:

Equation A5:

$$\text{Total hydrofluoric acid molar concentration } \frac{\text{mol}}{\text{L}} = \frac{[\text{H}^+]^2}{3.5 \times 10^{-4}} + [\text{H}^+]$$

The $[\text{H}^+]$ concentration for a given pH can be found using Table A, the total acid molar concentration calculated and then converted into lbs/gallon using the similar approach as for the strong acids by equation A6:

Equation A6:

$$\text{Total Acid Concentration } \frac{\text{lbs}}{\text{gal}} = \frac{\text{Acid Conc. mol}}{\text{L}} \times \frac{\text{M g}}{\text{mol}} \times \frac{\text{lbs}}{\text{454g}} \times \frac{\text{3.78 L}}{\text{gal}}$$

where M = acid molecular weight

See the summary equations on page A7.

Example A2: A solution of hydrofluoric acid has a pH of 5. Using Table A1, the value of $[H^+]$ is 0.00001 moles/liter. For HF, use equation A5 to calculate the total acid molar concentraton (moles/liter).

$$\text{Total hydrofluoric acid molar concentration} = \frac{[H^+]^2}{3.5 \times 10^{-4}} + [H^+]$$

$$= \frac{(0.00001)^2}{0.00035} + 0.00001$$

$$= 0.00001 \text{ moles HF/liter solution}$$

Now use equation A6 to convert the concentration into lbs/gallon. The molecular weight of HF is 20.01.

$$\text{Total HF Acid Conc.} \frac{\text{lbs}}{\text{gal}} = \frac{\text{Acid Conc. mol}}{\text{L}} \times \frac{\text{M g}}{\text{mol}} \times \frac{\text{lbs}}{454\text{g}} \times \frac{3.78 \text{ L}}{\text{gal}}$$

$$= \frac{0.00001 \text{ mol}}{\text{L}} \times \frac{20.01 \text{ g}}{\text{mol}} \times \frac{\text{lbs}}{454\text{g}} \times \frac{3.78 \text{ L}}{\text{gal}}$$

$$= 1.7\text{x}10^{-6} \text{ or } 0.0000017 \frac{\text{lbs HF}}{\text{gal solution}}$$

Because hydrofluoric acid is a weak acid and does not dissociate completely, there exists a lower pH limit, denoted by ***** in Table 1. This limit can be estimated by using a theorectical maximum acid concentration, equation A5 and $\text{pH} = -\log_{10}[H^+]$. For HF, the maximum possible concentration approaches 100% since the acid is infinitely soluble in water. At 100% concentration, the density of HF is 0.9576 g/ml at 25°C (Kirk-Othmer). Therefore the concentration of HF in mol/L can be calculated as follows:

$$\frac{0.9576 \text{ g}}{\text{ml}} \times \frac{1000 \text{ ml}}{\text{L}} \times \frac{\text{mole HF}}{20.01 \text{ g}} = \frac{47.86 \text{ mol}}{\text{L}} = \text{Total HF concentration}$$

Eqaution A5 can be rearranged to give equation A6:

Equation A5: $$\text{Total hydrofluoric acid molar concentration } \frac{\text{mol}}{\text{L}} = \frac{[H^+]^2}{3.5 \times 10^{-4}} + [H^+]$$

Equation A6: $$[H^+]^2 + (3.5\text{x}10^{-4})[H^+] - (3.5\text{x}10^{-4})(\text{Total HF conc.}) = 0$$

Substituting Total HF concentration = 47.86 mol/L gives:

$$[H^+]^2 + (3.5\text{x}10^{-4})[H^+] - (1.68\text{x}10^{-2}) = 0$$

where $[H^+]$ is equal to 0.13 moles/L. Therefore:

$$\text{pH} = -\log_{10} [H^+] = -\log_{10} (0.13) = 0.88$$

Therefore, a pH of 0.88 is the theorectical lowest pH that can be measured for a HF solution.

Phosphoric Acid

Three dissociations exist for phosphoric acid:

(1) $H_3PO_4 \longleftrightarrow H^+ + H_2PO_4^-$
(2) $H_2PO_4^- \longleftrightarrow H^+ + HPO_4^{2-}$
(3) $HPO_4^{2-} \longleftrightarrow H^+ + PO_4^{3-}$

The second and third dissociations are very small and are considered to be negligible compared to the first dissociation of phosphoric acid. Because their contribution to the hydrogen ion concentration is expected to be too small to affect the results, only the first dissociation of phosphoric acid will be considered when calculating the total acid molar concentration. Thus for phosphoric acid, the total acid molar concentration is given by Equation A8.

Equation A8: $$\text{Total phosphoric acid molar concentration} = [H_3PO_4] + [H^+]$$

For the first dissociation of phosphoric acid, the equilibrium constant, K_a, is given by Equation A9.

Equation A9: $$K_a = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$$

where $K_a = 7.5 \times 10^{-3}$ (CRC) and
$[H_2PO_4^-] = [H^+]$

Substituting these values into Equation A9 yields:

$$7.5 \times 10^{-3} = \frac{[H^+]^2}{[H_3PO_4]}$$

Solving for $[H_3PO_4]$, Equation A9 becomes:

$$[H_3PO_4] = \frac{[H^+]^2}{7.5 \times 10^{-3}}$$

This value for $[H_3PO_4]$ can be substituted into Equation A8 and, therefore, the total phosphoric acid molar concentration is given by Equation A10.

Equation A10: $$\text{Total phosphoric acid molar concentration } \frac{\text{mol}}{\text{L}} = \frac{[H^+]^2}{7.5 \times 10^{-3}} + [H^+]$$

Similarly, as was done for hydrofluoric acid, the values of $[H^+]$ can be obtained from Table A1 and then the resulting phosphoric acid molar concentration can be converted to pounds per gallon by using Equation A6. See the summary equations on page A7.

Because phosphoric acid is a weak acid and does not dissociate completely, there exist a low pH limit. Assuming a maximum concentration of 85.5% H_3PO_4 in water with a solution density of 1.70 g/ml (Lange's), the molar concentration of H_3PO_4 would be:

$$\frac{1.70\text{ g}}{\text{ml}} \times \frac{1000\text{ ml}}{\text{L}} \times \frac{0.855\text{ g } H_3PO_4}{\text{g solution}} \times \frac{\text{mole } H_3PO_4}{98\text{ g}} = \frac{14.8\text{ mol}}{\text{L}}$$

Using this concentration, equation A10, and $pH = -\log [H^+]$, and similar calculations as was done for hydrofluoric acid, the lower limit pH is calculated as 0.48, with $[H^+] = 0.33$ mol/L.

3. Neutralization Treatment Efficiencies for Acid Solutions

For neutralization of acid solutions, the treatment efficiencies can be expressed as the mass percentage of the listed acid that has been neutralized. The calculation follows Equation A11.

Equation A11: $$\text{Treatment Efficiency} = \frac{(I-E)}{I} \times 100$$

where I = acid concentration before treatment
E = acid concentration after treatment

For strong mineral acids such as sulfuric, nitric and hydrochloric acid, the acid concentration is directly proportional to the $[H^+]$ concentration which is directly related to pH. This can be illustrated by using the $[H^+]$ values directly from Table A1 for the pre- and post-treatment pH values.

Example A3: A sulfuric acid wastestream of pH 2 is treated with a mild base to raise the effluent to pH 3. Therefore, the $pH_{before} = 2$, and the $pH_{after} = 3$. Using Table 1, the following $[H^+]$ values are obtained:

$$[H^+]_{before} = 0.01 \frac{mol}{L}$$

$$[H^+]_{after} = 0.001 \frac{mol}{L}$$

Substituting these values into Equation A11, the treatment efficiency is given by:

$$\text{Treatment Efficiency} = \frac{0.01 - 0.001}{0.01} \times 100$$

$$= 90.0 \text{ percent}$$

Example A4: An HCl acid waste stream of pH 2 is neutralized to pH 4. Therefore, the $pH_{before} = 2$, and the $pH_{after} = 4$. Using Table 1, the following $[H^+]$ values are obtained:

$$[H^+]_{before} = 0.01 \frac{mol}{L}$$

$$[H^+]_{after} = 0.0001 \frac{mol}{L}$$

Substituting these values into Equation A11, the treatment efficiency is given by:

$$\text{Treatment Efficiency} = \frac{0.01 - 0.0001}{0.01} \times 100$$

$$= 99.0 \text{ percent}$$

As illustrated in the above examples, a small change in the pH of a solution results in a large treatment efficiency due to the logarithmic nature of the pH scale. Specifically, a pH change of one unit results in a treatment efficiency of 90 percent, whether the pH change is from pH 1 to pH 2 or from pH 4 to pH 5. Table 2 in the previous document was developed by calculating various treatment efficiencies for different pH changes using $[H^+]$ values from Table A1. Table 2 was developed for strong mineral acids.

For weak mineral acids such as phosphoric acid and hydrofluoric acid, the efficiency values in Table 2 are closely approximate, but not exact, since the acid concentration is not linearly proportional to $[H^+]$ or pH. For example, in Example 3 in the previous document, a phosphoric acid stream whose pH changed from 2.4 to 4.6 had a treatment efficiency of 99.85%. If Table 2 is used (for a <u>pH change</u> of 2.2), the treatment efficiency is estimated at 99.4%.

Summary of Equations Used to Develop Table 1

Note: $10^{-pH} = [H^+]$

Sulfuric Acid H_2SO_4

$$\frac{lbs}{gal} = \frac{10^{-pH} \times 98.08 \times 3.78}{454}$$

or

$$\frac{lbs}{gal} = \frac{[H^+] \times 98.08 \times 3.78}{454}$$

Nitric Acid HNO_3

$$\frac{lbs}{gal} = \frac{10^{-pH} \times 63.01 \times 3.78}{454}$$

or

$$\frac{lbs}{gal} = \frac{[H^+] \times 63.01 \times 3.78}{454}$$

Hydrochloric Acid HCl

$$\frac{lbs}{gal} = \frac{10^{-pH} \times 36.46 \times 3.78}{454}$$

or

$$\frac{lbs}{gal} = \frac{[H^+] \times 36.46 \times 3.78}{454}$$

Phosphoric Acid H_3PO_4

$$\frac{lbs}{gal} = \left\{ \frac{(10^{-pH})^2}{0.0075} + 10^{-pH} \right\} \times \frac{98.0 \times 3.78}{454}$$

or

$$\frac{lbs}{gal} = \left\{ \frac{[H^+]^2}{0.0075} + [H^+] \right\} \times \frac{98.0 \times 3.78}{454}$$

Hydrofluoric Acid HF

$$\frac{\text{lbs}}{\text{gal}} = \left\{ \frac{(10^{-pH})^2}{0.00035} + 10^{-pH} \right\} \times \frac{20.01 \times 3.78}{454}$$

or

$$\frac{\text{lbs}}{\text{gal}} = \left\{ \frac{[H^+]^2}{0.00035} + [H^+] \right\} \times \frac{20.01 \times 3.78}{454}$$

REFERENCES:

CRC Handbook of Chemistry and Physics. 1988-89. 69th edition. CRC Press, Inc. Boca Raton, FL. Pgs. B-94, B-113, D-163.

Kirk-Othmer Encyclopedia of Chemical Technology. Third Edition. Volume 10. Fluorine Compounds, Inorganic. 1980. John Wiley & Sons, New York, NY. Pg. 734.

Lange's Handbook of Chemistry. Thirteenth Edition. 1985. McGraw-Hill Book Co., New York, NY. Pg. 11-27