Design Considerations for Partial Neutralization Acid Injection

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ABSTRACT

It is currently estimated that, after vacuum evaporator-crystallizer of Hanford liquid wastes on the order of 10 million gallons of caustic residual liquor will remain. Partial Neutralization, the continuous addition of nitric acid to the slurry is being developed to allow additional volume reduction and reduce interim storage costs. Tests revealed that acid and liquor compositions as well as nozzle design are significant factors in the concentration of NO_x in the mild steel vessel vent system.

This report describes the available literature information relating to mixing of up to 20 gallons per minute of acid with 14,000 gallons per minute of slurry.

Very rapid and thorough mixing of the injected acid is required, since reaction of even 0.1 percent of the injected acid with sodium nitrite in the slurry would yield unacceptable levels of NO_x in the vessel vent system. The mixing time calculated by a method developed herein was used to evaluate the proposed conceptual mixing nozzle.

DESIGN CONSIDERATIONS FOR PARTIAL
NEUTRALIZATION ACID INJECTION

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DESIGN CONSIDERATIONS FOR PARTIAL NEUTRALIZATION ACID INJECTION

INTRODUCTION

Vacuum evaporator-crystallizer processing of high-level radioactive waste liquors started in November 1973 at the Atlantic Richfield Hanford Company's nuclear facility. The evaporation-crystallization process converts the liquid waste to a less mobile crystal salt cake by evaporation of water. A residual liquor about 10 percent of the feed volume is also formed. The volume of Hanford liquid waste has been reduced by about 31 million gallons as of December 31, 1976.

It is currently estimated that, after processing all available Hanford waste in the evaporator-crystallizer using current technology, on the order of 10 million gallons of residual liquor will remain. To further reduce the volume of these residual liquors, one alternative is to chemically alter the waste to allow additional evaporation-crystallization processing. Partial neutralization, the continuous addition of nitric acid to the slurry to neutralize a portion of the sodium hydroxide, converts the sodium hydroxide to sodium nitrate, which crystallizes as the slurry is concentrated. The term "partial neutralization" is used because the amount of acid must be controlled to assure the desired waste properties. Initial pilot plant tests demonstrated the potential benefits of the process using non-radioactive synthetic liquors.

In June of 1975, an initial partial neutralization test at the 242-S Evaporator-Crystallizer was shut down after 17 hours due to an unknown concentration of oxides of nitrogen (NO_x) in the mild steel vessel vent system. Further pilot plant and plant tests revealed that acid and liquor compositions as well as injector nozzle design are significant factors in the concentration of NO_x in the vessel vent system.

At this point, an engineering study was undertaken to establish a theory for the relationship of injector design and NO_x generation. This report describes the available literature information relating to mixing of the injected acid with the slurry. A conceptual design for an acid injector system is also presented and evaluated in light of the mixing theory developed.

SUMMARY

Very rapid and thorough mixing of the injected acid is required, since reaction of even 0.1 percent of the injected acid to form NO_x would yield unacceptable levels of NO_x in the vessel vent system. Based on the observed levels of NO_x in plant tests, turbulence in the slurry pipe (Reynolds Number 75,000 to 150,000) is inadequate to provide the mixing required.

Injection of a high-velocity high turbulence stream into a static fluid results in rapid entrainment and mixing of the ambient fluid. The time required for an increment of acid to be thoroughly mixed with an adequate quantity of static slurry can be calculated as a function of fluid properties, acid flow rate and nozzle size. This mixing time can be used to sample the inherent mixing capability of various nozzle sizes.

An injector nozzle design is proposed which incorporates three separate nozzles to cover the range of acid flows needed. The mixing times calculated for these nozzles are shorter than the mixing time calculated for the injector which gave satisfactory performance in the plant.

The trajectory of the centerline of the injected stream has been determined to assure that the high velocity stream does not strike the far wall of the slurry piping. Actual jet penetration ranges from about two inches for one-quarter inch diameter jets to about six inches for three-eighths inch diameter jets injected into a six foot per second cross flowing stream.

DISCUSSION

Background

The primary and desired reaction between nitric acid and the waste slurry is the neutralization of sodium hydroxide to increase the solubility of sodium aluminate. This allows additional evaporation (volume reduction) without precipitating undesirable sodium aluminate salts. Desirable sodium nitrate solids are also produced by the evaporation. Close to the acid injection point, zones of only moderate mixing between the acid and waste may be found. Where the acid-waste blend is still acidic, reactions of nitric acid and sodium nitrite are possible. This reaction can evolve oxides of nitrogen (NO_x), some of which are not soluble in a caustic media. The unabsorbed NO_x , released by the waste at the vapor-liquid interface, passes through the process condenser and enters the vessel vent system through a steam jet condenser system which maintain the vacuum within the evaporator. In the vessel vent system, NO_x has the opportunity to react with air and vapor water to form nitric acid. This acid, if formed in appreciable concentrations, can readily corrode the mild steel vent system.

The acid injectors used to date in the 242-S Evaporator-Crystallizer were designed upon the basis that the turbulence in the recirculation loop and recirculation pump would rapidly mix up to 20 gallons per minute of acid with the 14,000 gallons per minute of slurry. Very rapid and thorough mixing is required, since reaction of even 0.1 percent of the injected acid to form NO_x will lead to unacceptable concentrations of NO_x in the vessel vent system. The recirculation pump is located approximately ten feet downstream from the acid injector. With the slurry moving at a velocity of six to eight feet per second, less than two seconds elapse before the acid waste mixture reaches the pump where thorough mixing is insured. The Reynolds Number of the slurry line ranges from 75,000 to 150,000, depending upon the density and viscosity of the liquor.

The first injector tested in the 242-S Evaporator-Crystallizer was a one inch diameter pipe which extended six inches into the 28 inch diameter slurry recirculation loop. Table 1 shows the results of the tests for three and six molar acid. The test using three molar acid was successful, discharging less than 500 parts per million of NO_x to the vessel vent system. The test using six molar acid was terminated shortly after start-up due to NO_x of 50,000 parts per million or greater being discharged.

A second injector consisting of a three inch pipe extending 26 inches into the recirculation loop with thirteen 0.13 inch diameter holes was also tested. Table 1 contains the results of tests using three, six, and nine molar acid. Once again, the three molar tests were successful, but tests run with acid over three molar concentration discharged high concentrations NO_x to the vessel vent system.

These tests indicate that the turbulence within the recirculation loop is not adequate to avoid reactions evolving NO_x . While three molar acid could be used, higher concentrations of acid allow additional flexibility in the use of partial neutralization. Since the turbulence of the slurry cannot be changed, a study of the theory of mixing fluids was undertaken to determine the relationship between injector design and mixing.

MIXING THEORY

Injection of a high velocity stream into a static fluid has been studied by several investigators to determine how the static fluid is entrained (mixed) with the injected fluid. "As the direct result of turbulence generated at the borders of a submerged jet, the fluid within the jet will undergo both lateral diffusion and deceleration and at the same time fluid from the surrounding region will be brought into motion (reference 3)." By increasing the velocity and Reynolds Number of the jet, the surrounding fluid mixes with the jet at a higher rate. Increasing the rate at which the surrounding waste entrains, reduces the time required to mix the acid into the waste, thereby reducing the opportunity for NO_x evolution.

No equation or expressions were found which quantitatively defines the entrainment of a jet injected perpendicular into a cross flowing stream. The following equation, however, quantitatively describes the entrainment of a turbulent jet (Reynolds Number above 5,000) injected into a quiescent ambient fluid. (see Figure 1)(reference 5).

$$Q_x = \left(\frac{X}{4.3D} - 1 \right) Q_0 \quad (1)$$

X = distance from the nozzle (inches)

Q_x = volume of liquid entrained per unit time at distance X , cubic inches per second.

Q_0 = volume of liquid leaving the nozzle per unit time, cubic inches per second

D = inside diameter of the nozzle (inches)

This equation can be used to compare the inherent entrainment (mixing) capabilities for a variety of nozzle designs.

For each slurry and acid combination, there is a distinct amount of entrainment necessary to neutralize the acid depending upon the acid concentration and the hydroxide ion concentration of the slurry. Knowing the flow rate of the acid and molarity of the acid and slurry, the necessary rate of slurry entrained, Q_c is

$$Q_c = \frac{[H^+]}{[OH^-]} Q_o \quad (2)$$

$[H^+]$ = hydrogen ion concentration of the acid

$[OH^-]$ = hydroxide ion concentration of the slurry

Q_c = critical volume of liquid entrained to attain acid neutralization

Once Q_c is evaluated and the diameter of the nozzle is chosen, the point of penetration, X_f , where the jet is neutralized, can be calculated by rearranging Equation 1.

$$X_f = 4.30 (R + 1) \quad (3)$$

R = ratio of the hydrogen ion concentration in the acid to the hydroxide ion concentration in the slurry.

Mixing times, that is the time required for an increment of acid to move from the injection point ($x = 0$) to the point of neutralization ($x = X_f$) can be calculated by using a momentum balance. Knowing the density of the slurry and the injected acid, the velocity of the jet as a function of X from 0 to X_f can be determined by a momentum balance over a small increment of distance ΔX as follows:

$$V_x = \frac{V_o M_o}{M_x} \quad (4)$$

$$V_o = \frac{4 Q_o}{\pi D^2} \quad (5)$$

$$M_o = Q_o P_o \quad (6)$$

$$M_x = M_o + \left(\frac{X}{4.30} - 1 \right) Q_o P_s \quad (7)$$

The time required for an increment of acid to be neutralized can be determined by (see Appendix for additional information):

$$T = \int_{x=0}^{x=X_f} \frac{dx}{V_x} \quad (8)$$

$$T = \frac{4.3\pi D^3}{4 Q_0} (R + 1) \left[1 + \frac{\rho_s}{\rho_a} \left(\frac{R - 1}{2} \right) \right] \quad (9)$$

V_0 = velocity of jet at discharge, inches per second

V_x = velocity of jet at distance x , inches per second

M_0 = Mass of acid injected, pounds per second

M_x = Mass of slurry entrained at distance x , pounds per second

ρ_a = density of acid (pounds mass per cubic inch)

ρ_s = density of slurry (pounds mass per cubic inch)

T = time required for an increment of acid to be neutralized

The neutralization time determined is for injection into a static fluid. While the neutralization time would be shorter in a turbulent stream, comparison of neutralization times should allow evaluation of alternate injection designs.

TRAJECTORY

The high injection velocities required to assure rapid neutralization, create a possibility of the acid stream striking the slurry pipe wall opposite the injector. The trajectory of an injected stream into a cross flowing ambient has been studied (references 2 and 4) and the following equations developed:

[valid for $x/d < 17$]

$$\frac{y}{d} = 1.31 P^{-.74} \left(\frac{x}{d} \right)^{0.37} \quad (10)$$

$$P^2 = \frac{\rho_s v_0^2}{\rho_a V_0^2} \quad (11)$$

y = distance in cross stream direction (inches)

x = distance in down stream direction (inches)

d = nozzle diameter (inches)

ρ = density of fluids (ρ_a in jet, ρ_s in stream) (pounds per cubic inch)

v_0 = stream velocity (inches per second)

V_0 = initial jet velocity (inches per second)

The equation indicates that high exit velocities and large nozzle diameters increase cross stream penetrations; while low exit velocities and small nozzle diameters result in minor cross stream penetration. Actual jet penetration ranges from about two inches for one-quarter inch diameter jets to about six inches for three-eighths inch diameter jets injected into a cross stream flowing at six feet per second.

DESIGN

Nozzle Size

A high exit velocity favors rapid entrainment which also requires a high pressure drop through the nozzle. The nozzles described below are based upon 48 pounds per square inch available for pressure drop across the injection orifice. The maximum design basis is 4 gallons per minute of 12 molar acid diluted to 3, 6 and 9 molar, allowing for less than maximum flow rates and still assuring rapid neutralization.

The Reynolds Number for various nozzle diameters at several flow rates are shown in Figure 2. The line marked "maximum flow" denotes the maximum rate Reynolds Number attainable for each flow rate due to pressure drop. Note the nozzle sizes of 0.40, 0.325 and 0.25 inches, when used with the proper flow rate, maintain the Reynolds Number above 35,000 for flow rates from 3 to 18 gallons per minute. Note also that there is an overlapping of flow rates between nozzle sizes.

The relative neutralization times for injection of various acid molarities are presented in Table II. Note that times are all shorter than for the case of 3M acid in the 1-inch pipe nozzle. This is expected to result in acceptable levels of NO_x evolution.

For ease of installation, the three nozzles should be installed as a unit in a pipe assembly resembling that used for the single nozzle. This assembly, which can be changed with a remotely operated crane provides separate flow paths located from the acid supply, through the shielding wall into the evaporator-crystallizer slurry loop. Manual valves at the acid supply take-off select the appropriate injector nozzle. A schematic of the injector construction is shown in Figure 4.

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TABLE I242-S EVAPORATOR-CRYSTALLIZER
PROCESS TEST RESULTS

<u>Injector Used</u>	<u>Injected Nitric Acid Molarity</u>	<u>Slurry Sodium Hydroxide Molarity</u>	<u>Jet Reynolds Number</u>	<u>NO_x (Parts per Million)</u>	<u>Acid Flow (Gallons per Minute)</u>
1"*	3	2.42	29,000	350	12.0
1"	6	1.20	13,400	50,000	5.5
1"	3	1.59	29,000	230	12.0
3"***	3	1.66	11,000	1,760	7.3
3"	6	1.80	6,200	50,000	4.1
3"	9	3.60	8,200	50,000	4.13

* one hole

** thirteen 0.13 inch diameter holes

TABLE IIJET NEUTRALIZATION TIMES IN
QUIESCENT CAUSTIC

Nozzle Diameter (inches)	Injected HNO ₃ Molarity	Caustic Molarity	Acid Flow Gallons per minute	Jet Reynold's Number	Neutralization Time (Seconds)
1.049	3.0	4.0	12.0	29,000	0.123
0.4	3.0	4.0	18.0	141,000	0.00452
0.4	3.0	4.0	10.0	78,000	0.00814
0.325	3.0	4.0	12.0	116,000	0.00364
0.325	6.0	4.0	5.0	43,000	.0198
0.25	6.0	4.0	7.0	78,000	0.00643
0.25	9.0	4.0	3.0	33,000	0.0202

FIGURE 1
ENTRAINMENT OF A SUBMERGED CIRCULAR JET

FIGURE 2

Reynolds Number vs. Nozzle Diameter for
Various Flow Rates

0.4" Nozzle

0.325" Nozzle

0.25" Nozzle

FIGURE 3

JET PROFILE FOR INJECTION INTO A 6 FEET PER SECOND CROSS FLOW

FIGURE 4

THREE NOZZLE ACID INJECTOR

APPENDIX

$$T = \int_{X=0}^{X_f} \frac{dx}{V_x}$$

Using equations 4, 5, 6, 7, definition for V_x and collecting terms the integral becomes

$$T = \frac{\pi D^2}{4Q_o \rho_a} \left(\int_{X=0}^{X=X_f} \rho_a dx + \frac{\rho_s}{4.3D} \int_{X=0}^{X=X_f} X dx - \rho_s \int_{X=0}^{X=X_f} dx \right)$$

Integrating and substituting $X_f = 4.3D (R + 1)$ (Equation 3)

$$T = \frac{\pi D^2}{4Q_o \rho_a} \left(\rho_a (4.3D)(R + 1) + \rho_s \left(\frac{4.3D (R + 1)^2}{2} \right) - \rho_s 4.3D (R + 1) \right)$$

Which simplifies to

$$T = \frac{4.3 \pi D^3}{4Q_o} (R + 1) \left[1 + \frac{\rho_s}{\rho_a} \left(\frac{R - 1}{2} \right) \right]$$