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Saltstone SSRT Tank Flammability Analysis

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ABSTRACT

The Salt Solution Receipt Tanks (SSRTs) are receipt and surge tanks for the Saltstone Facility of the Savannah River Site (SRS). The waste stream to be fed into the SSRTs is a low level waste salt solution from the SRS tank farms which includes the stream from the Modular Caustic Side Solvent Extraction Unit (MCU) and in the future the Salt Waste Processing Facility (SWPF). Besides the continuous generation of hydrogen and dimethyl mercury, the MCU Stream is also known for the presence of ammonia and a number of organics. A flammability model has been developed to evaluate the concentrations of all species of flammable gases and the time to Composite Lower Flammability Limit (CLFL) for different liquid levels and temperatures. Results of the calculation indicated that the minimum ventilation flow to keep the flammable gases below 25% CLFL is 3.3 scfm. In the case of a loss of purge and the absence of atmospheric breathing, the minimum time to CLFL is 263 days. If the atmospheric breathing is available, the minimum time to CLFL increases to 762 days.

INTRODUCTION

Two 60,000 gallon (working capacity) Salt Solution Receipt Tanks (SSRTs) are installed at the Saltstone Processing Facility (SPF) to serve as receipt and surge tanks for the low level waste salt solutions from the SRS Tank Farms. The addition of these tanks at SPF will add inline surge capacity for low level waste transfers, and allows Tank 50 to be returned to a blend and feed service to support operation of the new Salt Waste Processing Facility (SWPF) being built in J-Area (Ref. 1). It is also planned that SSRT will be receiving waste from the Modular Caustic Side Solvent Extraction Unit (MCU), which is known to contain ammonia and many species of Volatile Organic Compounds (VOCs). Besides the VOCs, hydrogen and dimethyl mercury are generated continuously in time. Measures must be taken to prevent the overall flammable gas concentration from reaching the flammability limit.

The purpose of this paper is to present the methodology used to evaluate the concentrations of all the flammable gases in the vapor space of the SSRT and to determine the time to reach the Composite Lower Flammability Limit (CLFL) for different SSRT tank levels and temperatures. This paper also presents the methodology used to calculate the minimum ventilation flow required to keep the hydrogen/ammonia/VOCs gas mixture concentration below 25% or 60% CLFL during steady state operation.

MATHEMATICAL MODEL

Since SSRT 1 and SSRT2 are of similar design, only SSRT1 is used for this analysis. The SSRT has an outside diameter of 26 ft and a height of 19.5 ft. The overflow volume of SSRT is 65,500 gal, but its minimum and maximum operating volumes are 8,235 gal and 60,000 gal, respectively. There are a variety of flammable chemicals in the waste liquid and their concentrations are given in Table 1. One exception is hydrogen, which is being generated continuously by radiolysis. Another exception is dimethyl mercury, which is a product of the chemical reaction of mercury in the liquid waste. Since mercury reaction is controlled by the rate constant, the dimethyl mercury concentration in the vapor space is also a function of time. All inputs used in this analysis are documented in Reference 1.

Table 1 Flammable Gas Concentrations in the MCU Waste Solution

Flammable Gas	Value
Ammonia	200 mg/L
Butanol	1.03 mg/L
Isopar L	87.5 / 11 ppm*
Isopropanol	0.25 mg/L
Methanol	0.25 mg/L
Norpar 13	0.75 mg/L
Hydrogen generation rate @95°C	1.41×10^{-8} ft^3/hr/gal
Mercury concentration (initial)	358 mg/L
Dimethyl Mercury initial concentration	1.1 mg/L

* With a salt solution density of 1,300 g/L [Ref. 1], 87.5 ppm is equivalent to 114 mg/L

Calculation of CLFL in SSRT

For a multi-flammable gas mixture, the CLFL concentration can be calculated from the Le Chatelier's Law [Ref. 2]:

$$\mathrm{CLFL} = \left[\sum_{i=1}^{\mathrm{all}} \frac{f_i}{\mathrm{LFL}_i} \right]^{-1} \tag{1}$$

where

f_i = mole fraction of flammable gas species i in the flammable gas mixture
LFL_i = Lower Flammability Limit (LFL) of flammable gas species i

Since the equilibrium vapor pressures of ammonia and the VOCs are controlled by the temperature or their solubility, these gases are conservatively assumed to be released instantaneously from the salt solution for a loss of ventilation event. Therefore, hydrogen and dimethyl mercury are the two flammable gases with their concentrations changing with time. Under these conditions, it can be shown that the "target" fraction of CLFL of the mixture of these flammable gases is given by [Ref. 3]:

$$\Gamma_{\text{Target}} = \sum_{j}^{All} \frac{C_j}{LFL_j} = F + \sum_{i} \frac{C_i}{LFL_i} \qquad \text{; i = 1, 2,.. for } NH_3 \text{ and all VOCs} \tag{2}$$

where C_i and LFL_i are respectively the concentration of the i-th flammable gas in the vapor space and its Lower Flammability Limit (LFL). In addition, *F* is the sum of fractions of LFLs of hydrogen and dimethyl mercury; i.e.,

$$F = \frac{C_H}{LFL_H} + \frac{C_{DM}}{LFL_{DM}} \tag{3}$$

where C_H and C_{DM} are the concentrations of hydrogen and dimethyl mercury in the vapor space, which are given by the following relationships [Ref. 1]:

$$C_H(t) = C_H^o e^{-Bt} + \frac{\dot{G}}{B}(1 - e^{-Bt}) \tag{4}$$

$$C_{DM}(t) = \Psi \left[\frac{K}{B_0 - K} C_{Hg}^0 \left(e^{-Kt} - e^{-B_0 t} \right) + C_{DM_liq}^0 \, e^{-B_0 t} \right] \tag{5}$$

where C_H^0 = initial hydrogen concentration, in fraction

$\dot{G}$ = hydrogen generation rate, in 1/s

B = dimensionless breathing rate, in fraction/s

K = formation constant of dimethyl mercury, in 1/s

C_{Hg}^0 = initial mercury concentration in liquid, in g/L

$C_{DM_liq}^0$ = initial dimethyl mercury concentration in liquid, in g/L

$$\Psi = \text{constant} = \frac{H_{DM} V_{liq} A_1}{\left(V_{liq} + H_{DM} V_{vap}\right)}, \text{ in L/g} \tag{6}$$

$$B_0 = \text{modified breathing rate} = \frac{H_{DM} V_{vap}}{V_{liq} + H_{DM} V_{vap}} B, \text{ in 1/s} \tag{7}$$

H_{DM} = Henry's Constant of dimethyl mercury, unitless

$$A_1 = \text{Conversion factor} = \frac{22.4\, L/mol}{230.7\, g/mol} \left(\frac{273.15 + T}{273.15} \right), \text{ in L/g} \tag{8}$$

In this analysis, the initial hydrogen concentration is deemed to be negligible. Also, it has to be noted that the formation constant of dimethyl mercury is a function of temperature, which is given by the following correlation [1]:

$$K = 1.5911 \times 10^{-12}\, T^2 + 1.0816 \times 10^{-10}\, T + 2.2315 \times 10^{-9} \tag{9}$$

<u>Calculation of Vapor Pressures</u>

The concentrations of ammonia and the VOCs are governed by their vapor pressures. For the ammonia and those VOCs that are miscible in the waste solution such as ammonia, butanol, isopropanol, and methanol, they are not controlled by the pure substance vapor pressures but by their Henry's Law constants.

The ammonia concentration in the vapor space is determined from the Henry's Law:

$$C_{va} = H_a * C_{la} \tag{10}$$

where H_a = Henry's Law constant for ammonia, dimensionless
C_{la} = concentration of ammonia in liquid, g/L

Swingle [Ref. 4] gives the Henry's Law constant as a function of temperature (K) for temperatures up to 90°C for a 12.6 M Na^+, 2.3 M OH^- salt solution:

$$ln\,[K_H] = -7.577 + 2571.3/T + 0.003076T \tag{11}$$

The dimensionless form of the Henry's Law constant H_a can be obtained from [Ref. 4]:

$$H_a = \frac{1}{K_H RT} \tag{12}$$

where R is the Universal gas constant, which is equal to 0.08205 L-atm/(mole-K). To be consistent with the units, the density of water (1 kg/L) is used to be multiplied to K_H. To convert the ammonia concentration to vol %, the following equation is used:

$$C_a = \frac{C_{va}}{MW_a} V_m \times 100\% \tag{13}$$

where MW_a *is the m*olecular weight of ammonia (17.03 g/mol) and V_m is the molar volume of gas at the tank operating temperature.

The vapor pressures of butanol, isopropanol, and methanol are also determined by their Henry's Law constants in a similar fashion. The formulae for the Henry's Law constants of these alcohols are given in Table 2. On the other hand, Isopar L® and Norpar 13 are not miscible in the waste solution and their concentrations are controlled by their pure substance vapor pressures. The formulae for calculating their vapor pressures are also listed in Table 2.

Table 2 Vapor Pressures and Henry's Law Constants [Ref. 1]

Flammable	Formula for Calculating Henry Vapor Pressure
Butanol	$H_a = 2.38 \times 10^{-5} T^2 - 0.0009T + 0.0111$, T in °C up to 50°C
Isopar® L	Log(P_v, mm Hg) = A – B/(T + C), where A = 7.482, B = 1867, C = 219.3, and T is in °C
Isopropanol	H_a = 0.002, up to 50°C
Methanol	H_a = 0.0203, up to 50°C
Dimethyl-mercury	H_a = 0.31, at 25°C, corrected for temp using vapor pressure ratio, Log(Pv, mm Hg) = A – B/(T + C), where A = 6.914, B = 1293, C = 227.67, and T is in °C
Norpar 13	P_v (mm Hg) = $0.0016 T^2 - 0.1067 T + 2.1107$, T in °C up to ~68°C

Calculation of LFLs

The LFLs of all flammable gases used in this analysis are given in the following table.

Table 3 LFL Formulae for all Flammable Gases [Ref. 1]

Flammable	LFL Formula	LFL at 25°C
Hydrogen	$LFL_H = LFL_{H@25C}[1 - 0.0011(T - 25)]$, T in °C	4%
Ammonia	$LFL_a = -1.14186E-06\,T^3 + 1.45363E-04\,T^2 - 1.23602E-02\,T + 1.62376E+01$, T in °C	NA
Butanol	$LFL_{but} = 7.2E-06\,T^2 - 5.06E-03\,T + 1.994$, T in °C	NA
Isopar® L	$LFL_{iso} = LFL_{iso@25C}\left(\frac{T + 273.15}{298.15}\right)^{-0.51536}$, T in °C	0.656%
Isopropanol	$LFL_{ipp} = LFL_{ipp@25C} - \frac{0.75}{H_c}(T - 25)$, T in °C, and H_c = 448 kcal/mol	2.2%
Methanol	$LFL_{meth} = LFL_{meth@25C} - \frac{0.75}{H_c}(T - 25)$, T in °C, and H_c = 159 kcal/mol	6.7%
Norpal 13	$LFL_{nor} = LFL_{nor@25C} - \frac{0.75}{H_c}(T - 25)$, T in °C, and H_c = 2,183.39 kcal/mol	0.6%
Dimethyl Mercury	$LFL_{DM} = LFL_{DM@25C} - \frac{0.75}{H_c}(T - 25)$, T in °C, and H_c = 481.8 kcal/mol	2.98%

Calculation of Time to CLFL

With the concentrations of all flammable determined, the time to CLFL for SSRT can be calculated by solving Equation 2 simultaneously with Equations 3, 4, and 5. Because of the transcendental natures of the equations, the present analysis uses EXCEL GOSEEK to iterate on time until the target CLFL fraction reaches the desired value.

Calculation of Ventilation Flow

Per NFPA 69 fire protection requirement [Ref. 6], the initial hydrogen concentration should be kept below 25% CLFL. For a steady-state ventilation flow, the equilibrium hydrogen concentration is the ratio of the hydrogen generation rate and the total gas flow; i.e.

$$Target\ \%*CLFL = \frac{Q_f}{Q_v + Q_f} \tag{14}$$

where

Target% = "target" fraction of CLFL
Q_f = flow rate of the flammables, cfm (at tank temperature)
Q_v = ventilation flow rate, cfm.

Solving Equation (14) for Q_v leads to:

$$Q_v = Q_f \frac{1 - \text{Target\%} * CLFL}{\text{Target\%} * CLFL} \tag{15}$$

The flammables include hydrogen, ammonia, and all the VOCs. Therefore, the volumetric flow rates of each flammable must be determined. In the present analysis, only the volumetric generation rate of hydrogen is known and specified. During a steady state operation, the ventilation prevents ammonia and the VOCs from reaching their equilibrium vapor pressures and therefore an alternative method has to be used to determine their evolution rates and the overall CLFL concentration.

The release rates for all flammables emerging from the liquid are based on the Stefan's Law for mass diffusion by postulating all flammable gases (except hydrogen) are at their vapor pressures at the liquid surface. As a result, the mass diffusion flow rate of the i-th flammable evolving from the liquid surface (in kg/s) is [Ref. 7]:

$$\dot{m}_i = \frac{D_i P\ MW_i A}{R_o T(x_2 - x_1)} \ln \frac{P - P_2}{P - P_{1,i}}, \tag{16}$$

where D_i = diffusion coefficient of i-th flammable in air, m^2/s
P = atmospheric pressure, 101,325 Pa
MW_i = molecular weight of the i-th flammable, kg/mol
R_0 = Universal gas constant = 8.314 J/mol-K
T = tank temperature, K
x_2 = distance from tank bottom to tank top, m
x_1 = distance from tank bottom to liquid surface, m
P_2 = partial pressure of the flammable at tank top ≈ 0 N/m^2
$P_{1,i}$ = vapor pressure of the i-th flammable at liquid surface, N/m^2
A = liquid surface area, m^2.

Diffusion coefficients listed in the handbooks generally have different reference temperatures. According to Reference 7, diffusion coefficients have a 3/2 power dependence on the temperature, which is used in this analysis to correct them to the operating temperature. For conservatism, all the mass diffusion rates are evaluated at the overflow level such that it has the shortest diffusion length. With all diffusion rates determined, the total molar diffusion rate, excluding hydrogen, is:

$$\dot{n}_{total} = \sum_i \frac{\dot{m}_i}{MW_i}\left(1000\frac{g}{kg}\right), \qquad \text{in mol/s} \qquad (17)$$

and subsequently the total flammable gas volumetric flow is the sum of the generation rates of hydrogen and the VOCs; i.e.,

$$Q_f = Q_{h_\max} + \dot{n}_{total} V_m \left(60\frac{s}{\min}\right)\left(0.0353\frac{ft^3}{L}\right), \qquad \text{in cfm} \qquad (18)$$

The determination of all gas evolution/diffusion rates also enables the calculation of the CLFL concentration during steady state operation. This is accomplished by using Eq. (1) with the mole fraction Y_i inferred from the ratio of the individual gas diffusion rate to the total flammable gas flow rate.

Substituting Q_f and the CLFL into Eq. (15), the required ventilation flow Q_v can be determined. For consistency, this ventilation flow is further corrected to 25°C and becomes Q_{vs} expressed in scfm.

RESULTS OF ANALYSIS

Table 4 summarizes the ventilation flow requirements to maintain 25% and 60% CLFL for the SSRT at operating temperatures of 40 and 50°C. The maximum temperature of 50°C is chosen as the upper bound due to limitations in the Henry's Law coefficients for isopropanol and methanol that could potentially invalidate this analysis at temperatures greater than 50°C.

Table 4 Ventilation Flow Requirement to Maintain 25% and 60% CLFL in SSRT

Temperature (°C)	Liquid volume, (gal)	25% CLFL (scfm)	60% CLFL (scfm)*
40	65,500	1.76	0.73
50	65,500	3.25	1.34
50	8,235	0.48	0.20

* scfm is based on the temperature of 25°C

From Table 4, it can be seen that the ventilation flow needed to keep the flammable gas concentration below 25% CLFL is only 3.25 scfm, which occurs at the overflow level with the temperature of 50°C.

The results of the time-to-CLFL calculations are shown in Tables 5a and 5b. From these tables, it can be seen that the minimum time-to-CLFL is 263 days, which occurs at the overflow level with an operating temperature of 50°C. If atmospheric breathing is available, the minimum time to CLFL increases to 762 days.

Table 5a Minimum Times to Reach 100% CLFL Following Loss of Purge (87.5 ppm Isopar L)

Temperature (°C)	MCU Liquid Volume (gallons)	Time to CLFL No Breathing (days)	Time to CLFL with Breathing (days)
40	65,500	1,290	infinite
48	65,500	476	infinite
50	65,500	263	762
50	8,235	66,740	infinite

Table 5b Minimum Times to Reach 100% CLFL Following Loss of Purge (11 ppm Isopar L)

Temperature (°C)	MCU Liquid Volume (gallons)	Time to CLFL No Breathing (days)	Time to CLFL With Breathing (days)
40	65,500	1,290	infinite
48	65,500	476	infinite
50	65,500	263	762
50	8,235	111,539	infinite

Temperature Sensitivity Analysis

A temperature sensitivity study was performed for the SSRT. The goal seek function in Excel was used to calculate the maximum operating temperature to maintain < 60% CLFL for a target period of time (25 and 100 days) at the overflow volume following a loss of purge with and without breathing. The results of the calculations are shown in Table 6. It can be seen that the results are not sensitive to breathing. With 25 days to 60% CLFL, the maximum permissible temperature is 42.63°C. If the time to 60% CLFL is increased to 100 days, the maximum permissible operating temperature decreases to 41.81°C. This means that the result is very sensitive to the operating temperature.

Table 6 Maximum Operating Temperature for Target Time to 60% CLFL at Overflow (87.5 ppm/11 ppm Isopar L)

Time to 60% CLFL (days)	Max T to stay < 60% CLFL (^oC)	
	No Breathing	With Breathing
25	42.63	42.64
100	41.81	42.03

Time to Reach LFL for Hydrogen Only

The time to the LFL of hydrogen alone based on the salt solution stream hydrogen generation rate is calculated to evaluate the impact of hydrogen generation versus the volatiles concentration on time to CLFL. The results are shown in Table 7 for the time to LFL of hydrogen only at overflow level for the salt solution stream over a range of operating temperatures.

Table 7 Times to Reach 100% Hydrogen LFL Following a Loss of Purge

Temperature (^oC)	Liquid Volume (gallons)	Time to LFL No Breathing (days)	Time to LFL With Breathing (days)
40	65,500	2,788	infinite
50	65,500	2,671	infinite
60	65,500	2,562	infinite

These results clearly show that the volatile organics at elevated temperatures are driving the time to CLFL for the salt solution stream in the SSRT. The times to LFL based on radiolytic hydrogen generation alone are greater than seven years and relatively insensitive to temperature.

CONCLUSION

Results of calculation indicated that a minimum ventilation flow to keep the It has found that the minimum ventilation flow to keep the flammable gases below 25% CLFL is 3.3 scfm. In the case of a loss of purge and the absence of atmospheric breathing, the minimum time to CLFL is 263 days. If the atmospheric breathing is present, the minimum time to CLFL increases to 762 days.

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