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Rev. 1

ISOPAR® L RELEASE RATES FROM SALTSTONE USING SIMULATED SALT SOLUTIONS

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J.R. Zamecnik, M.G. Bronikowski, A.D. Cozzi, R.E. Eibling, C.A. Nash.

July 2008

Revision 0:

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February 2006

Environmental & Chemical Process Technology
Savannah River National Laboratory
Aiken, SC 29808

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1.0 EXECUTIVE SUMMARY

The Modular Caustic-Side Solvent Extraction (CSSX) Unit (MCU) and the Salt Waste Processing Facility (SWPF) will produce a Decontaminated Salt Solution (DSS) that will go to the Saltstone Production Facility (SPF). Recent information indicates that solvent entrainment in the DSS is larger than expected. The main concern is with Isopar® L, the diluent in the solvent mixture, and its flammability in the saltstone vault. If it is assumed that all the Isopar® L is released instantaneously into the vault from the curing grout before each subsequent pour, the Isopar® L in the vault headspace is well mixed, and each pour displaces an equivalent volume of headspace, the maximum concentration of Isopar® L in the DSS to assure 25% of the lower flammable limit is not exceeded has been determined to be about 4 ppm. The amount allowed would be higher if the release from grout were significantly less.

The Savannah River National Laboratory was tasked with determining the release of Isopar® L from saltstone prepared with a simulated DSS with Isopar® L concentrations ranging from 50 to 200 mg/L in the salt fraction and with test temperatures ranging from ambient to 95 °C. The results from the curing of the saltstone showed that the amount of Isopar® L released versus time can be treated as a percentage of initial amount present; there was no statistically significant dependence of the release rate on the initial concentration. The majority of the Isopar® L that was released over the test duration was released in the first few days. The release of Isopar® L begins immediately and the rate of release decreases over time. At higher temperatures the immediate release rate is larger than at lower temperatures. Initial curing temperature was found to be very important as slight variations during the first few hours or days had a significant effect on the amount of Isopar® L released. Short scoping tests at 95 °C with solvent containing all components (Isopar® L, suppressor trioctylamine (TOA), and modifier Cs-7SB) except the BOBCalixC6 extractant released less Isopar® L than the tests run with Isopar® L/TOA. Based on these scoping tests, the Isopar® L releases reported herein are conservative.

Isopar® L release was studied for a two-month period and average cumulative release rates were determined from three sets of tests each at 95 and 75 °C and at ambient conditions. The overall average releases at were estimated for each temperature. For the 95 and 75 °C data, at a 5% significance level, the hypothesis that the three test sets at each temperature had the same average percent release can be rejected, suggesting that there was a statistically significant difference among the three averages seen in the three experimental tests conducted.

An upper confidence limit on the mean percent release required incorporation of variation from two sources: test-to-test variation as well as the variation within a test. An analysis of variance that relies on a random effects model was used to estimate the two variance components. The test-to-test variance and the within test (or residual) variance were both calculated. There is no indication of a statistically significant linear correlation between the percent Isopar® L release and the Isopar® L initial concentration. From the analysis of variance, upper confidence limits at confidences of 80-95% were calculated for the data at 95 and 75 °C. The mean Isopar® L percent releases were 67.33% and 13.17% at 95 and 75 °C, respectively. The upper confidence limits found are:

	95 °C	**75 °C**
Mean	67.33	13.17
% Confidence	**% Release Upper Confidence Limit**	
95	91.88	21.43
94	89.36	20.58
93	87.37	19.91
92	85.74	19.36
91	84.37	18.90
90	83.19	18.50
89	82.15	18.15
88	81.24	17.85
87	80.41	17.57
86	79.67	17.32
85	78.99	17.09
84	78.36	16.88
83	77.78	16.68
82	77.24	16.50
81	76.73	16.33
80	76.25	16.17

The ambient conditions tests did not show any difference between data sets; the mean release was 4.81% and the 95% upper confidence limit was 6.01%.

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LIST OF ACRONYMS

BOBCalixC6	calix[4]arene-bis(tert-octylbenzo-crown-6)
CSSX	Caustic-Side Solvent Extraction
Cs-7SB modifier	1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol
DSS	Decontaminated Salt Solution
DWPF	Defense Waste Processing Facility
GC-MS	gas chromatography - mass spectrometry
IR	infrared (IR) spectroscopy
LFL	lower flammability limit
MCU	Modular CSSX Unit
ng/μL	nanograms per microliter (equivalent to mg/L)
PMP	polymethylpentene
ppm	parts per million, herein defined as mg/kg (mass basis)
s_d	sample standard deviation
SPF	Salt Production Facility
SRNL	Savannah River National Laboratory
SWPF	Salt Waste Processing Facility
TOA	trioctylamine
VOA	volatile organic compound
WSE	Waste Solidification Engineering

2.0 INTRODUCTION

Revision 1 of this report was written primarily to clarify the data, interpretation, and conclusions drawn. This revision was requested by the DOE as part of Waste Solidification Engineering's request to restart the Saltstone Processing Facility with limited amounts of Isopar® L present in the feed from Tank 50. No new data has been added to the report, except to reference similar work at 55 °C that was subsequently performed. Somewhat different interpretations have been made for some of the data including a more rigorous statistical treatment of the data. The Isopar® L release at 95 °C reported herein is the release after 40 days versus the release at 13 days reported in Revision 0. The new values are higher and account for Isopar® L that was released between 30 to 40 days that was probably actually released during the first three days.

The salt in the waste tanks at the Savannah River Site (SRS) will be stabilized by making it into saltstone, which will be poured into vaults and buried. The radioactive components of the salt, mainly ^{137}Cs, will be removed and encapsulated in glass prior to making saltstone. Stabilizing the residual ^{137}Cs activity in saltstone has been studied and found feasible at low curie levels.[1] However, the solvent extraction process for removing ^{137}Cs does entrain organic solvent in the decontaminated salt to be treated.[2,3]

In general, the idea of stabilizing organic compounds in grouts and cements is thought to be a simple solution to waste disposal. The idea, however, is much more complicated and expensive than simply adding organics to cement and mixing.[4] Organic compounds act as plasticizers that can inhibit curing, which can allow more of the compounds to escape. Semi-volatile organic compounds can be stabilized to some extent by the addition of clays and various adsorbents to solidification mixtures; however, this adds bulk and cost to the final waste disposal. Volatile organic compounds (VOCs) are usually not stabilized in this manner because of loss upon initial mixing prior to curing.[5] One case does exist in which it may be useful to treat VOCs via solidification, and that is the case where the VOC is at a very low concentration in the waste being stabilized.

The Saltstone Production Facility (SPF) will receive the Decontaminated Salt Solution (DSS) stream from the Modular CSSX Unit (MCU) and the Salt Waste Processing Facility (SWPF). These streams are expected to contain low concentrations of entrained solvent. Recent information on the solvent droplet size in the DSS stream indicates that the drops will be smaller than assumed in the MCU decanter design basis. A smaller droplet size stays entrained longer so, the amount of expected carryover has increased. The higher solvent concentration in the MCU exit stream may cause flammability concerns in the SPF. The release rates of the volatile solvent component, Isopar® L, are needed in order to assess possible flammability issues in the saltstone vault.

NFPA 69 requires the flammable material concentration to be below 25% of the lower flammability limit (LFL) in the vapor space of the vault if no safety interlocks are installed. If all of the Isopar® L is released instantaneously into the vault vapor space when pouring saltstone slurry, the allowable Isopar® L concentration in the DSS is 4 ppm.[6] If the release is not instantaneous, but slower due to a finite diffusion rate of Isopar® L through saltstone slurry, the presence of other organic components in the solvent such as Cs-7SB modifier and trioctylamine (TOA), or grout interactions with these components, the acceptable limit of entrained solvent could be significantly higher than 4 ppm. As the maximum expected Isopar® L concentration in the DSS sent to SPF under normal process conditions was determined through small scale testing at the Savannah River National Laboratory (SRNL) to be 88 ppm,[7] determining the Isopar® L release rate from saltstone is imperative.

SRNL was tasked with determining the Isopar® L release rates from curing grout at various temperatures expected in the saltstone vault.[8] The release rates were to be determined from saltstone prepared with a simulated DSS solution containing Isopar® L concentrations ranging from 50 ppm to 200 ppm and the expected ratio of TOA to Isopar® L to be used in the CSSX process. The rates were to be determined at three temperatures ambient (~25 °C), 75 °C, and 95 °C. These temperatures cover the full range expected in the saltstone vaults from initial mixing to the increase in temperature while curing due to hydration reactions.

3.0 EXPERIMENTAL

The experiment to determine the release of Isopar® L is very simple conceptually. First, mix the expected premix with a simulated DSS containing the requisite amount of entrained solvent. Then, pour the wet saltstone mixture into an airtight vessel, raise the saltstone to temperature, and use a method to collect and measure the Isopar® L given off over time.

The experimental method developed for studying the benzene evolved from tetraphenylborate decomposition during saltstone curing was used.[9] The benzene method[10] captures the offgas from a saltstone sample using a charcoal tube (SKC Anasorb® CSC Catalog# 226-01) while the sample cures. The charcoal tube with the captured offgas is then stripped of the Isopar® L with carbon disulfide (CS_2) and analyzed by gas chromatography – mass spectrometry (GC-MS). Minor changes in the experimental setup and method were made to adapt this method for Isopar® L and TOA. Because of experimental method changes such as having to inject a volatile organic into the saltstone mixture, using Teflon™ ferrules rather than o-rings on the vessels, and using an autosampler for the GC-MS, the tests on the initial set of samples (replicate 'a') were somewhat scoping in nature. Applying the lessons learned from these first tests, two sets of replicate samples ('b' and 'c') were run together starting a month later.

In addition to the three sets of tests described above, two scoping experiments were performed with essentially the same experimental setup. The first scoping experiment tested the use of infrared (IR)-spectroscopy as an instantaneous in-line method to measure Isopar® L. The second consisted of a set of scoping experiments with DSS simulant after it had been run through a set of centrifugal contactors. The DSS simulant contained all the components of the full solvent {the Isopar® L diluent, the TOA suppressor, the 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol (Cs-7SB) modifier}, except the calix[4]arene-bis(tert-octylbenzo-crown-6) extractant (BOBCalixC6).

3.1 Experimental Setup

The vessel used to contain the saltstone mixture is shown in Figure 3-1 along with the trap used to hold the carbon tubes. The vessel was made of thick-walled glass with a 65-mm outside diameter (o.d.) and 58-mm inside diameter (i.d.). The straight wall height was 76 mm high, and the total height not including the length of the ports was approximately 90 mm. The vessel was designed so that the saltstone would fill approximately two thirds of the volume of the vessel. Both the vessel and trap were plastic coated for safety.

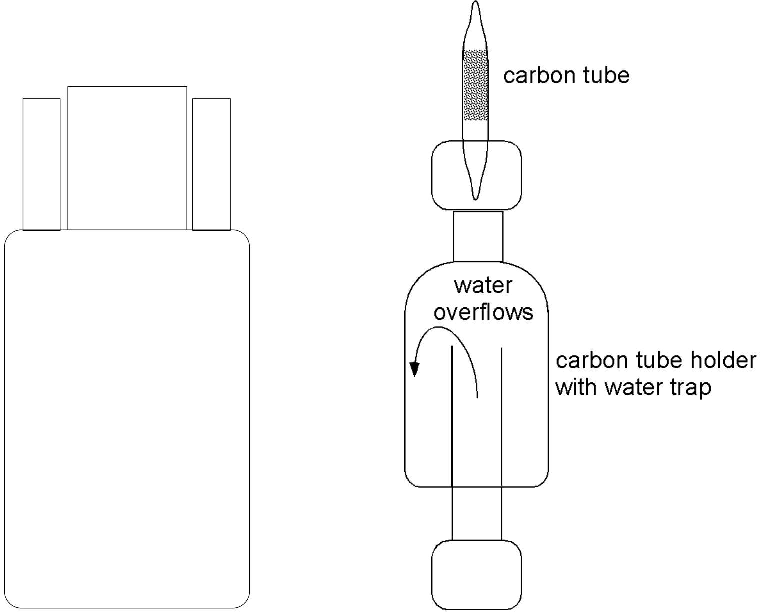
The vessel has three ports: a large 1-in. diameter port for the initial addition of saltstone and two smaller ports. The 1-in. diameter port is closed throughout the experiment with a #25 Teflon™

plug, which was recess ground on the bottom to 1/8-in. depth for sealing without an o-ring. Two smaller ports were made to hold a #7 screw plug for input and output ports.

The inlet and outlet ports were connected via a #7 Teflon™ plug with a ¼-in. i.d. and Teflon™ ferrule to Teflon™ tubing. The tubing was connected to a female quick connect for the inlet port and to the water trap on the outlet port. The quick connect was outside of the oven and the vessel was inside the oven when running the experiment.

The water trap in Figure 3-1 is used to trap water that may condense in the line. It is 7 cm long with the inner ¼-in. i.d. tube being 3.5 cm long. The trap is connected to both the vessel and the carbon tube with a #7 Teflon™ plug with a ¼-in. i.d. and Teflon™ ferrule. The carbon tube is held in place by the ferrule when the plug is tightened. The carbon tube is open to the atmosphere, thus gases added to the system or released from the saltstone are allowed to effuse out of the system. The Isopar® L released from the saltstone is captured by the carbon tube.

Two other vessel types were made for the tests. Both had the same volume but had different port configurations. The first, a 'spike' vessel, had an extra inlet port which was used to spike the vessel with a known quantity of solvent. A #7 Teflon™ plug was used with an inlet port valve screwed into it. The other vessel type was used for the full solvent tests. It was basically the same as the other vessels but had ¼-in. o.d. glass inlet and outlet ports with a nub on each of them rather than a Teflon™ fitting. They were connected to the Teflon™ tubing via ~2-in. long Teflon™-coated Tygon™ or Viton™ tubing.



(not to scale)

Figure 3-1 Geometry of Test Vessels

Figure 3-2 shows the experimental setup for the first set of samples ('a') prior to the addition of replicate samples 'b' and 'c'. Here the 75 °C oven is open and the 95 °C oven is to the right. In the oven, four filled sample vessels and an empty spiking vessel are seen. Outside the oven, the female quick connects on the inlet ports are on the right and the traps which hold the carbon collection tubes are on the left. The Teflon™ tubes which connect the vessel and the traps go through the hole in the oven. For the ambient experiment the outlet tube length was ~6 inches and no tubing was used on the inlet. The inlet of the ambient tests had the female quick connect screwed into a #7 Teflon™ plug. The temperature logger for both ovens can be seen on the top of the oven on the left.

3.2 Saltstone Mixing

Saltstone was made by mixing the simulated DSS solution with the premix and a spike of solvent solution. Typically, 117 g of DSS were weighed into a 250-mL, straight sided polymethylpentene (PMP) wide-mouth jar. The PMP was not expected to absorb Isopar® L to a large extent during the short mixing time. Next, 138 g of premix were added to the jar, and the contents were mixed by vigorously shaking by hand. At this point, the Isopar® L, as a mixture of Isopar® L and TOA, was quickly added using a microliter syringe. The jar was closed and shaken again by hand. The resultant saltstone slurry was added to a weighed vessel through the 1-in. port with input and output ports plugged. The 1-in. port was tightly closed, and the vessel was weighed to determine the amount of saltstone added. The vessel was then put into the oven and attached to inlet and outlet ports. The replicate ‘a’ samples were placed into ovens at room temperature and then the heat was turn on; the replicate ‘b’ and ‘c’ samples were placed into the ovens that were already at temperature.

Figure 3-2 Filled Vessels Installed in Oven

3.2.1 Simulated DSS

Simulated DSS was prepared as an “average salt solution” as described in WSRC-RP-2000-00361, Rev. 0, with minimal component omission. CsCl was not added to the DSS as per the customer request.[11] Five liters of this salt solution were made for use in the tests. The salt solution make up is given in Table 3-1.

The initial concentrations of Isopar® L to be tested were nominally 50 ppm, 100 ppm, and 200 ppm. Here, the 100-ppm concentration corresponds approximately to the maximum expected amount in the DSS from MCU.[7] Including the other organic components would theoretically decrease the vapor pressure of the Isopar® L by simple dilution:

$$P_i^{vap} = x_i P_i^{sat} \tag{1}$$

where P_i^{vap} = vapor pressure of Isopar® L

x_i = mol fraction Isopar® L in organic phase

P_i^{sat} = saturation vapor pressure of Isopar® L

Therefore, leaving out these organics should lead to a more conservative estimate of Isopar® L release from saltstone. However, these other organic components may help with the mixing of Isopar® L with the simulated DSS and saltstone.

The suppressor TOA was added to the Isopar® L at the level (0.003 M) expected to be in the CSSX baseline solvent.[12] The added TOA is not expected to change the vapor pressure of Isopar® L significantly because of its low concentration in the Isopar® L solvent. The amount of Cs-7SB modifier in the CSSX solvent, 0.75 M, would decrease the vapor pressure, and hence the release of Isopar® L and so was not included. The expense and low likeliness of effects of BOBCalixC6 precluded its use. The Isopar® L/TOA solution makeup is given in Table 3-2. This solution was used as a spike in all the experiments except the scoping work that used full component solvent (minus the BOBCalixC6) from the 2 cm contactor testing. To make the DSS approximately 200 ppm, 100 ppm, or 50 ppm in Isopar® L concentration, 31 µL, 15.5 µL, or 7.5 µL, respectively, of the Isopar® L/TOA solution were added to the samples; the actual target concentrations resulting from these additions were 204, 102, and 49.4 ppm, respectively.

Table 3-1 Composition of DSS Simulant

Compound	Mass (g)	Component	Target Concentration (M)
DI H_2O	3542		
$Al(NO_3)_3 \cdot 9H_2O$	525	AlO_2^-	0.28
NaOH (50 wt%)	1275	OH^-	2.06
$NaNO_3$	499	NO_3^-	2.03
$NaNO_2$	173	NO_2^-	0.5
KNO_3	7.60	K^+	0.015
$Na_2CO_3 \cdot H_2O$	93.00	CO_3^{2-}	0.15
Na_2SO_4	99.00	SO_4^{2-}	0.14
NaCl	7.00	Cl^-	0.024
NaF	5.90	F^-	0.028
$Na_2HPO_4 \cdot 7H_2O$	9.40	PO_4^{3-}	0.007
$Na_2C_2O_4$	13.40	$C_2O_4^{2-}$	0.02
$Na_2SiO_3 \cdot 9H_2O$	42.60	SiO_3^{2-}	0.03
$Na_2MoO_4 \cdot 2H_2O$	0.086	MoO_4^{2-}	0.00007
NH_4NO_3	0.401	NH_3	0.001
$CuSO_4 \cdot 5H_2O$	0.027	Cu	2.2E-5
Na_2CrO_4	1.170	Cr	1.4E-3
$Zn(NO_3)_2 \cdot 6H_2O$	0.184	Zn	1.2E-4
$Pb(NO_3)_2$	0.015	Pb	1.1E-5
$Fe(NO_3)_3 \cdot 9H_2O$	0.051	Fe	2.6E-5
$SnCl_2 \cdot 2H_2O$	0.031	Sn	2.0E-5
$Hg(NO_3)_2 \cdot H_2O$	0.0006	Hg	2.5E-7

Table 3-2 Composition of Isopar® L/TOA Solution

Compound	g	M
Isopar® L	2.3052	---
TOA	0.0028	0.003

3.2.2 Premix

The premix composition and water-to-premix ratio used were based on recommendations made in previous testing and are listed in Table 3-3.[13] The water-to-premix ratio is defined as the ratio of the mass of evaporable water from the waste (at ~110 °C) to the combined mass of cement, slag, and fly ash. The premix materials were obtained from the SPF.

Table 3-3 Premix Formulations for Processing

Premix	Water/Premix
45 wt % Class F Fly Ash (FA) 45 wt % GGBFS[a] (Slag) 10 wt % Cement	0.60

[a] Ground granulated blast furnace slag

3.2.3 Samples

The initial samples in set ‘a’ were made for each of the Isopar® L concentrations and temperatures listed in Table 3-4. One replicate was cured at each of the temperatures to determine the effect of curing temperature on the Isopar® L release rate. The two replicate sets ‘b’ and ‘c’ at each temperature were added about a month after the initial sample set had begun. The delay between the ‘a’ set and the ‘b’ and ‘c’ sets gave time to better understand the experimental system and the measurement method. A blank (simulant saltstone which contained no Isopar® L) was also made and run at each temperature.

As noted earlier, a spike vessel was run at each temperature. These vessels were routinely spiked with a known amount of the Isopar® L/TOA mixture and were used as a relative recovery standard. Initially, 10 µL of the solution were spiked with a standard Hamilton™ syringe, but in later spikes 5 µL were used to better match the lower Isopar® L release amounts.

Table 3-4 Matrix of Blend Concentrations and Test Temperatures

	Isopar® L Concentrations Tested (ppm)	Curing Temperatures Tested (°C)
Salt Solution	50	Ambient
	100	75
	200	95

3.3 Isopar® L Sampling and Measurement

3.3.1 Sampling

The Isopar® L collection method was based on a National Institute for Occupational Safety and Health (NIOSH) method for benzene sampling.[10] The curing saltstone samples were vented through a carbon tube located at the end of the vessel outlet tube immediately after a water trap. The carbon tube is a glass tube having two activated carbon beds separated by an inert filter. The first bed is intended to capture all of the Isopar® L and the second bed is intended to confirm no breakthrough from the first bed occurred. Venting through the carbon tube is intended to ensure that any Isopar® L released prior to sampling will pass through the carbon bed and that the sample vessel does not pressurize.

Sampling was done as follows. A vessel was selected for sampling. A male quick connect on a nitrogen line was inserted into the female connector on the input port. Pure nitrogen gas (99.99%) at ~90 mL/min was then used to then purge the headspace prior to removing the carbon tube for Isopar® L analysis. This flow rate is within the range of 10 < flow rate < 200 mL/min recommended in Reference 10. The nitrogen was purged through the vessel for 5 minutes. This volume represents a minimum of five volume changes in the vessel headspace for filled vessels and two volume changes for empty vessels. After the purge was complete, the carbon tube was replaced with a new one. After removal, the carbon tubes were labeled by the vessel number followed by the number of the samples taken from that vessel, and the time the sample was taken was recorded.

Vessels put in the oven at the same time were purged in sequence, including blanks and the spike vessel which was spiked with the Isopar® L/TOA solution. For example, the five vessels put in for the initial 95 °C test were purged sequentially. These five vessels would have nominal Isopar® L concentrations (in the DSS fraction of saltstone) of 200 ppm, 100 ppm, 50 ppm, and 0 ppm (the blank), and 5 or 10 μL of Isopar® L/TOA solution (the recovery spike standard), respectively. After sampling a sequence, the standard vessel would be re-spiked with 5 or 10 μL of the initial Isopar® L/TOA solution. At subsequent times, the vessels were sampled in the same sequence.

Sampling was done with decreasing frequency as samples aged since the amount of Isopar® L released was expected to decrease with time. For the ‘a’ set, the samples were taken on days 1, 3, and 6 and then weekly. Final samples were taken after two months time. For the ‘b’ and ‘c’ replicates, especially in the 95 °C case, samples were initially taken more frequently to better quantify the amount of Isopar® L released during the first few days of the experiment. The ‘b’ and ‘c’ replicates were sampled for a month after initial sampling was complete.

3.3.2 Isopar® L Measurement

The method for recovery of the Isopar® L from the carbon beds also parallels the method described in Reference 10. The collected sample tubes were opened and the two carbon beds were separated into individual vials. The front bed was labeled sample #-FR and the back labeled sample #-BK. One milliliter of CS_2 was added to each vial to desorb the Isopar® L. The vial was capped, mildly shaken, and allowed to sit for at least 30 minutes before analysis. Samples that were required to sit for more than two hours prior to being run were refrigerated.

Desorbed samples that were known to contain a large amount of Isopar® L were diluted in methanol to bring the concentration into the calibration range of the analytical instrument. Generally, only the spike vessel tubes and tubes collected within the first week of sampling were diluted. Dilution was done by taking 2 μL of the CS_2 desorbed sample and adding it to 1 mL of methanol.

Five μL of Isopar® L were also injected onto new carbon tubes to determine the desorption efficiency of CS_2 and several other solvents. The carbon beds were desorbed with 1 mL of CS_2, hexane, or methanol, and the vials were processed as samples. These tests demonstrated that efficient desorption of the activated carbon required the use of CS_2 (as specified in the NIOSH methods). The alternative desorption solvents were considered for waste minimization and safety due to the toxicity, high flammability and low autoignition temperature of CS_2. Hexane was less effective and methanol was poor at desorbing Isopar® L from activated carbon, as expected, due to the highly polarity of methanol and the very nonpolar nature of both Isopar® L and activated carbon. Methanol was mainly used to dilute the higher concentration samples and for the solvent with some standards.

Initial Isopar® L standards for analysis were made in CS_2, but the CS_2 was found to evaporate during use, resulting in inaccuracies. Later standards were made in methanol and were more stable as they did not evaporate as quickly like the CS_2 standards. Methanol was also used for dilution of samples desorbed by CS_2 that were at concentrations higher than the calibration range of the GC-MS.

3.3.3 Sample Analysis

Isopar® L was determined by analysis with a gas chromatograph coupled to a mass spectrometer (GC-MS). The Isopar® L was measured by setting the MS to mass 57, the most prominent mass fragment for the Isopar® L organic compounds, and measured the mass 57 signal over the time interval that Isopar® L elutes from the GC. Compounds with longer retention times, such as TOA, or shorter retention times, like CS_2 or methanol, are not counted. At least three concentrations of Isopar® L were used to develop a linear calibration of the instrument.

Three different GC-MS instruments were used during this work because of instrument failures. These different GC-MS instruments were of the same type and made by the same manufacturer (quadrupole mass spectrometers made by Agilent). The instrument failures were in the vacuum system in the first instrument and an electronics failure in the second instrument. Each GC-MS was functionally verified by examining the mass spectrum of a standard compound (perfluorotributylamine) for the proper fragmentation and isotopics and then mass calibrated prior to use. The data review for the standards and the samples also considered whether unusual changes in instrumental response had occurred. At the time samples were analyzed, all of the instruments were functioning properly.

Samples were run on the GC-MS equipped with an auto sampler to provide faster sample turnaround. Using the auto sampler, a whole sequence of samples including the Isopar® L/TOA spike sample were run together. The analysis sequence generally followed the order: four Isopar® L concentration standards, a sequence of samples, another Isopar® L concentration standard, another sequence of samples, etc., followed by two more Isopar® L concentration standards.

Four standard concentrations were used to calibrate the GC-MS: 1.08 ng/µl, 10.8 ng/µl, 108 ng/µl and 542.5 ng/µl. These standards were used to make a linear calibration curve for determining the Isopar® L concentration in the desorbed sample (ng/µl) of each sample as a function of the chromatogram peak area.

The concentration of Isopar® L determined for the sample desorbed from the carbon tube is subject to a collection efficiency; i.e., only some fraction of the Isopar® L present on the carbon tube is actually recovered. Therefore, the actual amount of Isopar® L on a carbon tube is calculated by adjusting for this efficiency ε_d:

$$M = \frac{V_d}{\varepsilon_d} f\,A \tag{2}$$

where M = mass of Isopar® L on carbon tube (ng)

V_d = volume of desorbed sample (1000µL)

ε_d = desorption efficiency (0-1)

f = calibration factor $\left(\frac{\text{ng}}{\mu\text{L}\bullet\text{peak area}}\right)$

A = peak area (arbitrary units)

The recovery of the spike vessel (recovery standard) was used to adjust the recoveries determined from the sample analyses, as shown below. Note that the concentration in ng/µL can be used because the sample volume for both the sample and the spike are 1000 µL. The calibration is assumed to be linear with an intercept of zero.

$$\mu\text{L Isopar}^{®}\text{ L released} = \frac{\dfrac{\text{ng}}{\mu\text{L CS}_2}\ \begin{matrix}\text{Isopar}^{®}\text{ L measured}\\ \text{in desorbed sample}\end{matrix}}{\dfrac{\text{ng}}{\mu\text{L CS}_2}\ \begin{matrix}\text{Isopar}^{®}\text{ L measured}\\ \text{in spike vessel}\end{matrix}} \times \mu\text{L Isopar}^{®}\text{ L added to spike vessel}$$

This calculation can also be written in terms of the chromatogram peak areas because the Isopar® L concentration in each sample is proportional to the peak area.

$$\mu\text{L Isopar}^{®}\text{ L released} = \frac{\begin{matrix}\text{Peak Area for Isopar}^{®}\text{ L}\\ \text{measured in desorbed sample}\end{matrix}}{\begin{matrix}\text{Peak Area for Isopar}^{®}\text{ L}\\ \text{measured in spike vessel}\end{matrix}} \times \mu\text{L Isopar}^{®}\text{ L added to spike vessel}$$

For this calculation, desorption efficiency is assumed to be the same for both the sample and the spike; with this calculation method, desorption efficiency does not need to be determined.

The Isopar® L released in percent is then calculated from the amount released and the amount initially added to the saltstone sample:

$$\%\ \text{Isopar}^{®}\text{ L released} = 100 \times \frac{\mu\text{L Isopar L}^{®}\text{ released}}{\mu\text{L Isopar L}^{®}\text{ initially in saltstone}}$$

3.4 Scoping Tests

3.4.1 IR Measurement Method

A scoping test of the use of IR-spectroscopy as an instantaneous in-line method to measure Isopar® L was done. Initial testing showed that water, Isopar® L, and TOA had distinct spectra. A saltstone sample was spiked with 100 ppm of the Isopar® L/TOA solution and attached to a 20-cm long path cell in an IR-spectroscopy instrument (Nicolet, Nexus 670 FT-IR). A 20-mL/min nitrogen purge was run, and spectra were taken every half hour for three days at ambient temperature.

3.4.2 Full Solvent with Contactor

Four short term scoping tests with full CSSX solvent (except BOBCalixC6) were run at 95 °C. The scoping tests were used to determine if the full component solvent released a similar amount of Isopar® L from saltstone as the Isopar® L/TOA tests and if the Isopar® L was well mixed when made into saltstone. In these scoping tests, the solvent was dyed to determine if the Isopar® L was well mixed in the saltstone. Each set of tests were run in triplicate; a total of 12 saltstone samples were made. The simulated DSS had been cycled through a bank of 2-cm contactors to produce the aqueous phase samples for saltstone testing. The equipment and general operation were similar to those of the previous work with these contactors.[6] Specifics for these runs included the following:

Condition	First Run, 9/21/2005	Second Run, 9/27/2005
DSS flowrate	22.9 mL/min	22.8 mL/min
Solvent flowrate	7.8 mL/min	7.6 mL/min
DSS Simulant pre-filtration	No	Yes
Average Temperature	23.7 ^{o}C	25.0 ^{o}C
Approximate product size delivered for testing	350 mL	650 mL*
*Half run and delivered for grout immediately, half run and aged for 1 hour before grouting		

The solution from each contactor run was split into three parts and put into glass separatory funnels so that samples could be drawn while excluding any top organic layer that might form. Separatory funnels were gently swirled before sample removal so that sample liquids were homogeneous.

Contactor Mixing versus Shaking Test
The difference between the amount of Isopar® L given off when the full solvent is added with shaking and when it is run through a contactor was determined in this test. Three samples containing 10 µL of full solvent added to the saltstone and mixed by shaking as done in previous tests were prepared. In a second set of three samples, the simulant salt solution and full solvent were run through 2-cm centrifugal contactors for mixing to simulate the expected DSS product. Contactor-mixed and shaken saltstone samples were made alternately to reduce any bias due to any setting of the saltstone during the time from sample preparation until all samples were placed in the oven and the oven was turned on. That is, first a 10-µL spike sample was made as in previous Isopar® L/TOA saltstone preparations. Then, a contactor DSS sample was weighed out, premix was added, and the sample was shaken. The remaining four samples were then made, and the oven was turned on.

Contactor Mixing – Immediate Mixing with Premix versus Mixing After One Hour
The difference between the amount of Isopar® L given off when the contactor product with full solvent is immediately mixed with the premix and when it is allowed to sit for an hour prior to mixing was looked at in the next test.

In this test, three saltstone samples were prepared from a solution mixed in the contactors that was put into separatory funnels and then immediately sampled from the bottom. This method of contactor solution introduction would mimic somewhat the removal of the DSS from the decanter tank in MCU where the DSS is removed from beneath the surface where the Isopar® L concentration should be lower. Three additional saltstone samples were prepared from a solution mixed in the contactors that was allowed to separate for an hour before removing the solution from the bottom of the separatory funnel. After all six samples were made, the oven was turned on.

4.0 RESULTS & DISCUSSION

The release of Isopar® L from saltstone was measured as a function of time at several temperatures and initial concentrations. Experiments were run at three temperatures: 95 °C, 75 °C, and ambient (~25 °C). Each Isopar® L concentration was tested at each temperature in triplicate, an initial sample 'a' and replicates 'b' and 'c'. The Isopar® L release is presented as a percentage of the total added. Cumulative release curves for all temperatures are calculated and discussed.

4.1 Isopar® L Measurement Standards and Analysis

Figure 4-1 shows a typical calibration curve of peak area versus Isopar® L concentration for the GC-MS. Figure 4-2 shows a typical plot of the calibration slope versus time for a set of analyses. The concentration of Isopar® L in each unknown sample was then calculated from the prior calibration curve slope.

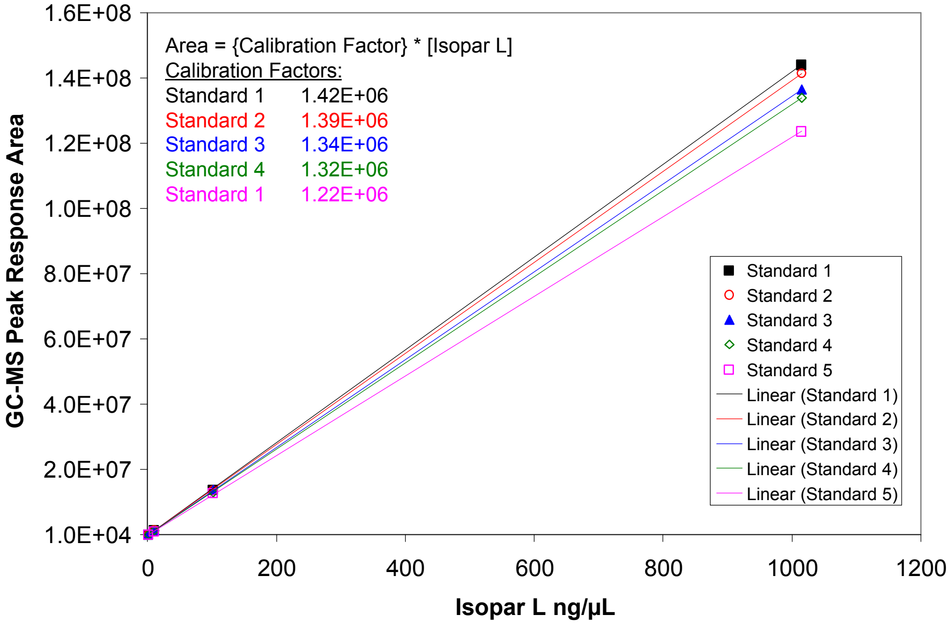


Figure 4-1 Typical GC-MS Calibration Curves

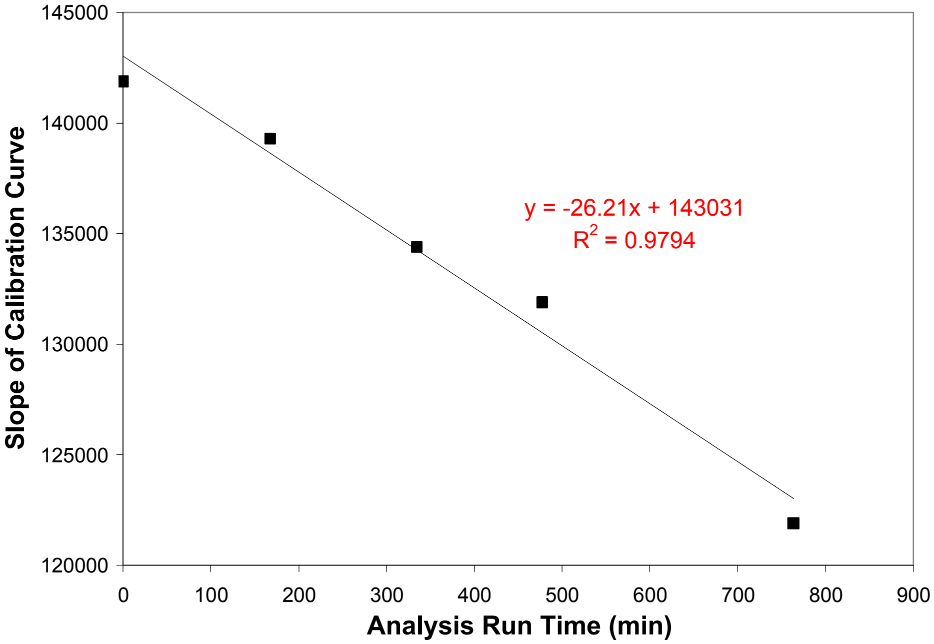


Figure 4-2 Typical Slope of GC-MS Calibration Curve Versus Time

Desorption efficiencies (ε_d) for the recovery of Isopar® L from the carbon sampling tubes was also measured. Desorption efficiencies of 89.6 % and 83.3% were measured for an average of 86.5±8.9% (2σ). In subsequent work on Isopar® L release at 55 °C,[15] the desorption efficiency was determined to be 92.4±8.7% ($2s_d$). As described previously, the desorption efficiency is not required for the calculations of the Isopar® L amounts on the carbon tubes.

4.1.1 Recovery and Analysis

Sampling frequencies for each vessel were adjusted so that measurable quantities of Isopar® L would be collected on the carbon sampling tubes. In some cases, the amounts collected were much greater than anticipated, but not greater than the capacity of the sampling tube. However, some samples, notably the initial 95 °C samples and 10-µL spikes, were outside the GC-MS calibration range. For these initial results, the ratio of the integrated area of the sample to the integrated area of the spike was used to determine Isopar® L amount; use of this ratio precludes the need for the GC-MS calibration because the area of the spike sample serves as the calibration factor. For the replicate 'b' and 'c' samples, the sample tubes which were expected to be outside of the calibration range were diluted in methanol prior to running on the GC-MS. Both the original sample and sample dilution were then run in sequence on the GC-MS. For these samples, the ratio of the measured Isopar® L amount to the measured spike amount was used to determine the Isopar® L amount as previously described in Section 3.3.3.

For a vessel spiked with 10 µL of Isopar® L/TOA solution, the concentration of Isopar® L in the CS_2 solution following desorption of the carbon bed is calculated to be 7700 ng/µL, assuming a 0.77 g/mL Isopar® L density and 100% collection efficiency. Taking into account the tube desorption efficiency of approximately 86%, the GC-MS response should be in the 6000–7000 ng/µL range and half that for the 5 µL spike. The spike results, with the GC-MS calibrated with the Isopar® L in methanol calibration standards, were generally in this range.

The difference in the results from using only the peak areas of the undiluted samples and the calculated concentrations from the diluted samples was examined using the spike results. For the first instrument used, the recoveries of the five 95 °C spike results were 97.8±23.0% ($2s_d$) for the undiluted samples and 91.7±31.4% for the diluted samples. For the other instrument, the recoveries of the fourteen 95 °C spike results were 87.6±48.2% and 81.6±43.4%, respectively, for the undiluted and diluted samples. This large variability in the spike recoveries led to using the ratio of the sample measurement to the spike measurement for each set of samples. Recall that the recovery percentage cancels out when the sample results are scaled to the spike results (Section 3.3.3).

Carbon tubes for blanks analyzed were found to contain no Isopar® L. The carbon tube backs that were analyzed for samples also had no or negligible Isopar® L and consequently a large number were not analyzed; if the amount of Isopar® L on the front half carbon was close to the capacity of the carbon, then the back half was analyzed. For the tube that had been put in the collection port backwards (back half towards the vessel), both the front and the back results of this tube were added to determine the Isopar® L released.

4.2 Isopar® L Release Initial Results

4.2.1 General Observations of Saltstone Curing

Saltstone made with the recipe used (Table 3-3) was very fluid and hardened leaving no surface water after three days at ambient temperature. Immediately after mixing, the saltstone poured easily. Less than 1% of the saltstone did not pour into the vessels when the samples were being made. Thus each sample vessel contained about 255 g of uniform dark gray material.

The saltstone samples at ambient temperature separated with time. After a few hours one could see ~1-2 mm of bleed water on top of each sample and the dark gray color (of Figure 3-2) was replaced by a dark gray black on the bottom of each sample. After three days the samples were a light tan gray on the top ~2 mm, darker gray throughout with various heights of gray black on the bottom. The gray black portion ended up being from 1 to 15 mm in height.

The saltstone samples run at 75 °C and 95 °C reacted differently than the ambient case. The heated samples did not lose the surface bleed water in three days and did not have a gray black layer on the bottom. The samples stayed a uniform gray throughout the experiment. Upon initial mixing the samples were a dark gray. After two hours in the oven, the liquid remaining on top and on the bottom of the samples was brown, as shown in Figure 4-3. The brown color of the bleed water disappeared within 24 hours. Typical heated saltstone samples after the brown color disappeared are shown in Figure 4-4. The bleed water remained on the top of the 95 °C and 75 °C samples for ~20 and 27 days, respectively.

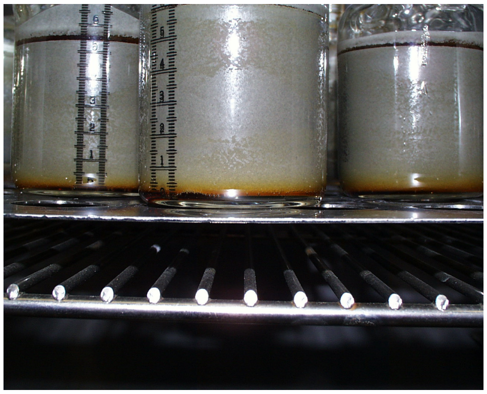


Figure 4-3 Saltstone After a Few Hours at 75 °C and 95 °C

The heated samples were found to rise in the vessels due to a ‘piston effect’. The 95 °C samples began rising after one day and the 75 °C samples started by day three. A possible explanation can be offered for this behavior. Vapor escaping from the saltstone appears to have been released from both ends of the saltstone monolith, resulting in the monolith rising inside the vessel since the top surface was open to the atmosphere. The bleed water from the curing saltstone could have acted as a lubricant for the monolith to slide upward much like a piston.

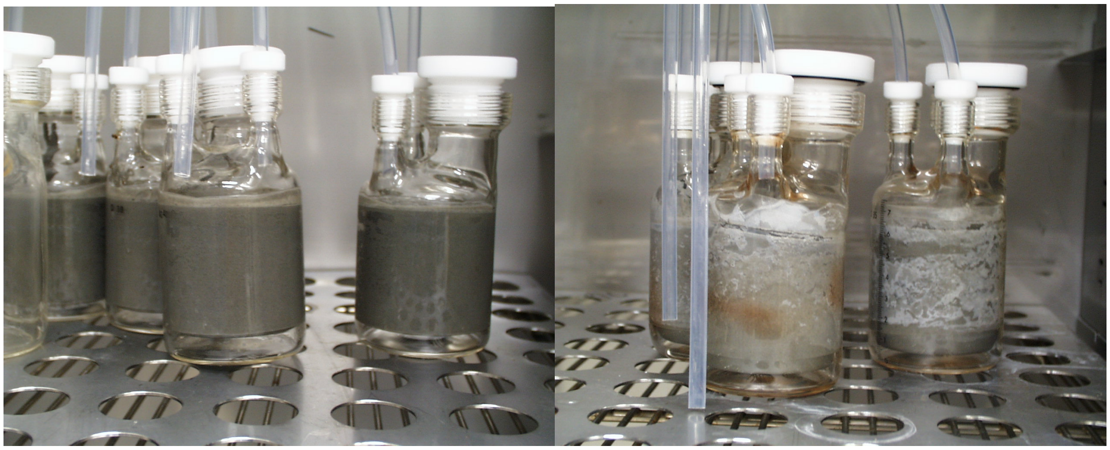


Figure 4-4 Saltstone After 1 Week at 75 °C (left) and at 95 °C (right)

Figure 4-4 shows what the samples looked like both immediately after raising on the left side and after drying of bleed water took place. On the left, a uniform layer of bleed water covers the sides of the vessel. The samples rose anywhere from 0.5 to 1.5 cm during the experiment. As the bleed water is removed by incorporation into the saltstone matrix or by evaporation, light gray dry saltstone is seen on the top and side of the vessel. The depth of the dry saltstone slowly grows as seen on the right of the figure. At some point after 30 days, it may have been that the bleed water on the side of the vessel could not hold the gas in the lower void and the samples fell. At this time, a sudden increase in the Isopar® L release was seen for these samples. A few samples did not fall, perhaps because they were held up by the dried saltstone on the side of the vessels.

4.2.2 Initial Releases

The results from the first set 'a' experiments are shown in Figure 4-5 and Figure 4-6. Each point represents the amount of Isopar® L collected on a carbon tube due to the release from the sample during the time interval the tube was sampling. For example, the first point for 200 ppm at 95 °C of 64% is the amount of Isopar® L released from the sample in one day. The second point of 11% for this 200-ppm sample is the amount of Isopar® L released from the sample from day 1 to day 4. The most important aspect shown by the initial data in Figure 4-5 and Figure 4-6 is that most of the Isopar® L is released within the first few days of making the saltstone. In all cases, the amount of Isopar® L released decreases with time after the first few days. In the heated samples, the decrease is substantial. The magnitude of the Isopar® L released was found to increase with increasing temperature.

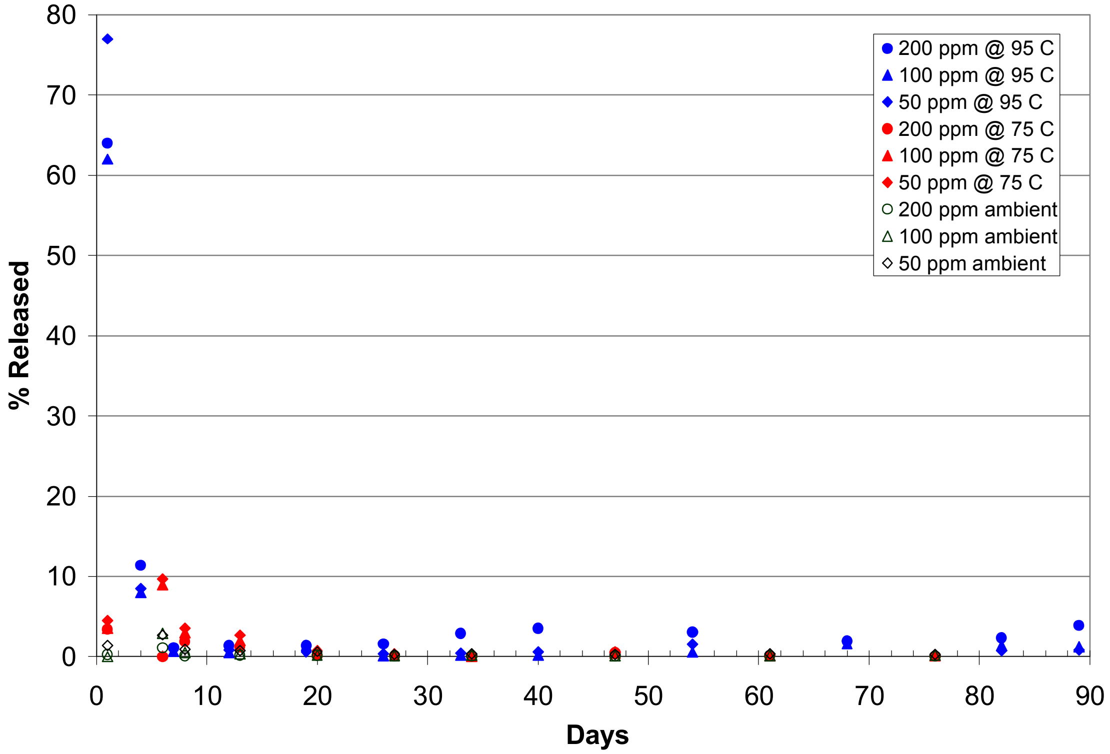


Figure 4-5 Set 'a' Isopar® L % Released from Saltstone

Figure 4-6 presents the same data plotted as %Released per Day on an expanded y-scale. The release rates for all of the data are shown to decrease quickly from the start of the test until about 20-30 days. At 20 to 30 days, the 95 °C rates start to increase; the 200-ppm data in this region are especially variable. These data are shown with a y-axis magnified even more in Figure 4-7. The increased release of Isopar® L for the 95 °C samples occurs at the same time these samples were observed to drop in the vessels. Thus, the increases seen in the heated sample rates may be due to Isopar® L that was actually released earlier in the tests when the samples rose in the vessels. Had the samples not risen, one would have expected the Isopar® L release to only decrease in time.

The release of Isopar® L from the bottom of the vessels suggests that voids or cracks produced during large-scale saltstone production, such as in the vaults, could be expected to retain the Isopar® L that could be released suddenly when an open path for release occurs.

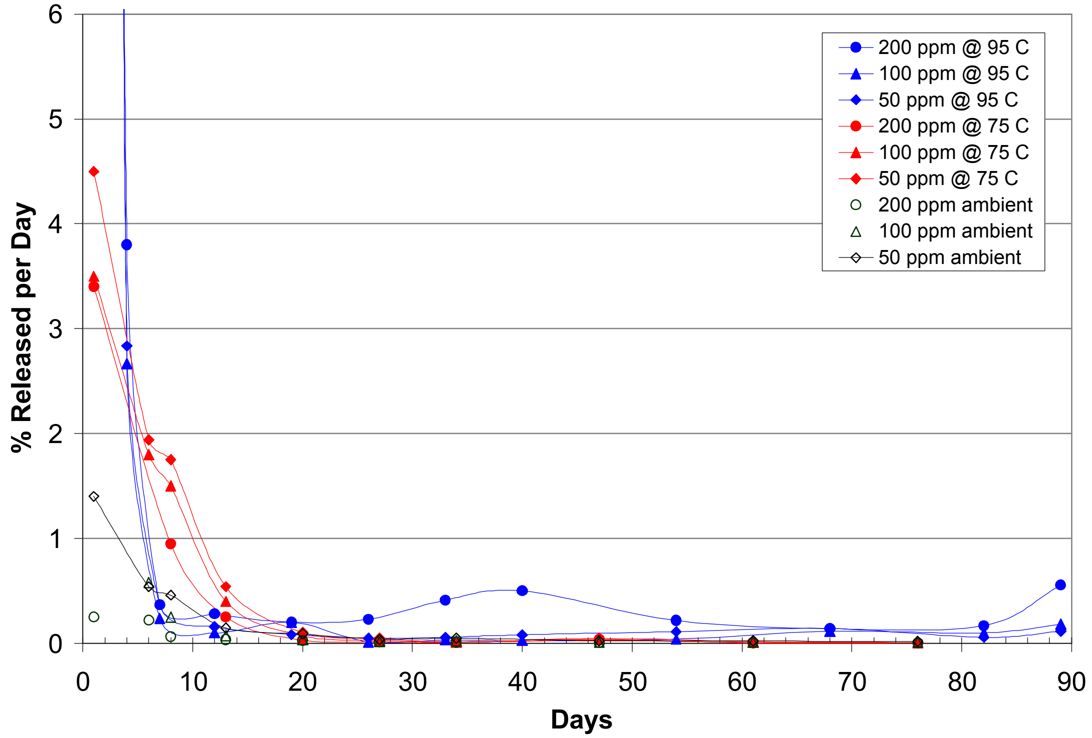


Figure 4-6 Set 'a' Isopar® L Percent Released per Day from Saltstone – Expanded Y-Axis

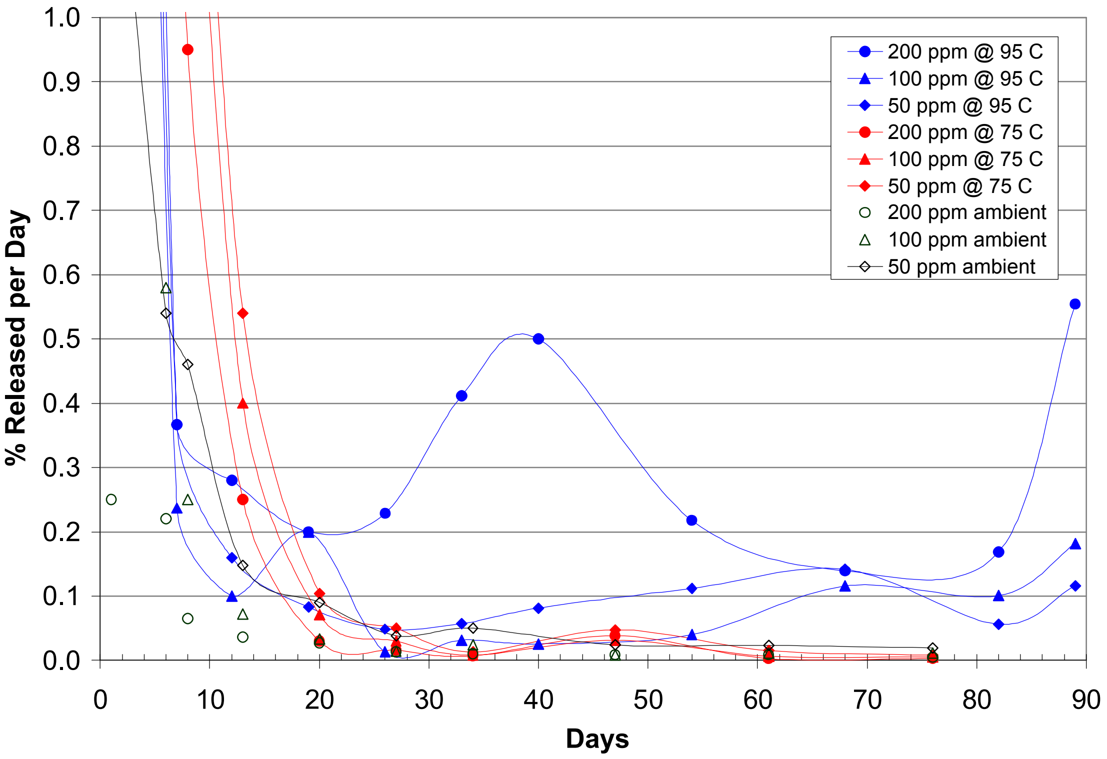


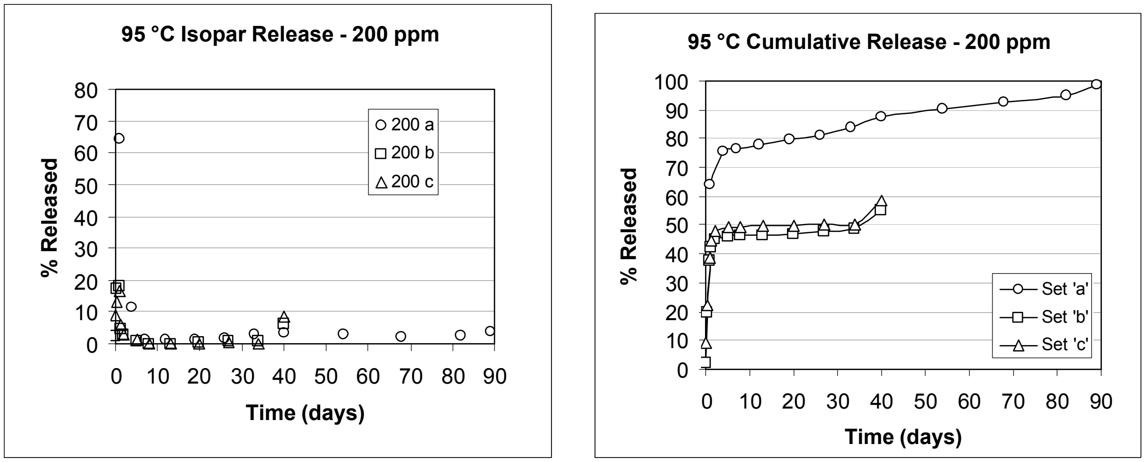
Figure 4-7 Set 'a' Isopar® L Percent Released per Day from Saltstone – Expanded Y-Axis

4.3 Isopar® L Release – All Data Sets

Replicate sample sets ‘b’ and ‘c’ were made in the same manner and with the same material as the initial set ‘a’ samples. The duration of these replicate tests was 40 days. The sampling frequency used for the replicates was the same as used previously except at 95 °C. In the 95 °C case, more frequent samples were taken in the first few days due to the increased amount of Isopar® L expected to be given off during that time.

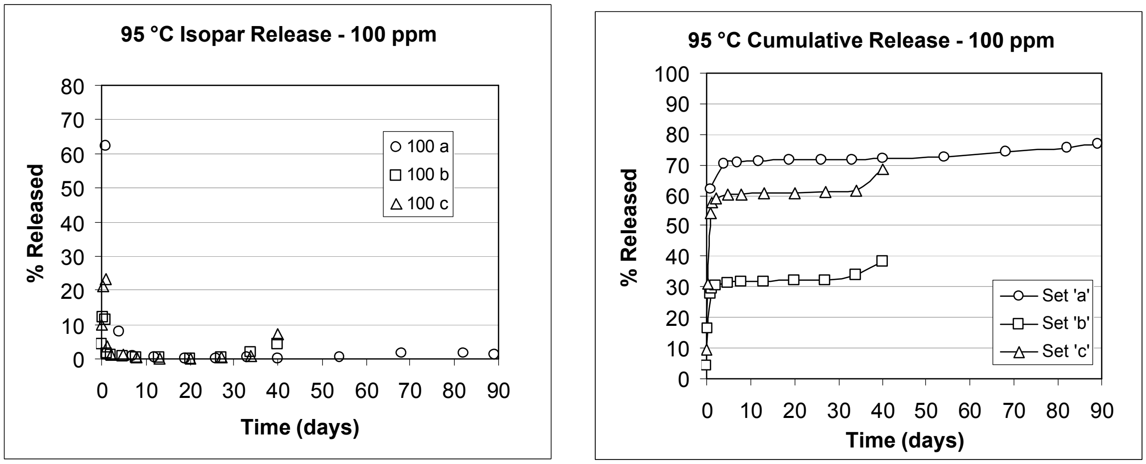
The Isopar® L release is plotted in Figure 4-8 through Figure 4-10 as a function of time for all the samples. Releases are presented as both carbon tube sample analyses and cumulative releases as a percentage of the initial amount of Isopar® L added that was released. The Isopar® L release for sets ‘a’, ‘b’, and ‘c’ are given on the same graph for each temperature and Isopar® L concentration for comparison.

Although the releases are expected to be the same for sets ‘a’ and for sets ‘b’ and ‘c’, differences were observed. The general release trends are the same. The greatest amount of Isopar® L is released within the first few days for all samples. The amount of Isopar® L released decreases with time. Considerably more Isopar® L is released at the higher temperatures. Differences in the release data are noticeable in the spread of the cumulative release plots. The resulting differences will be discussed for each temperature.



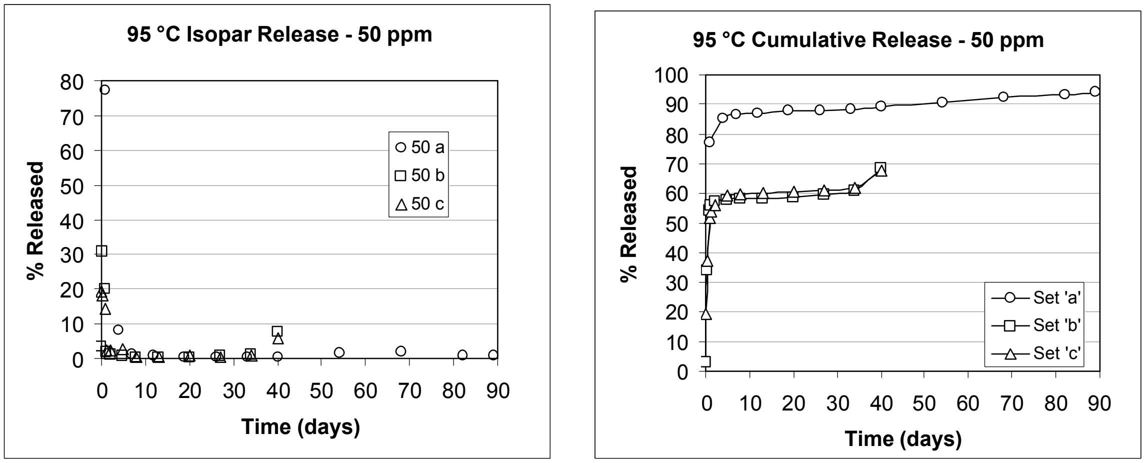
a) 95 °C 200 ppm Isopar® L release

d) 95 °C 200 ppm cumulative release



b) 95 °C 100 ppm Isopar® L release

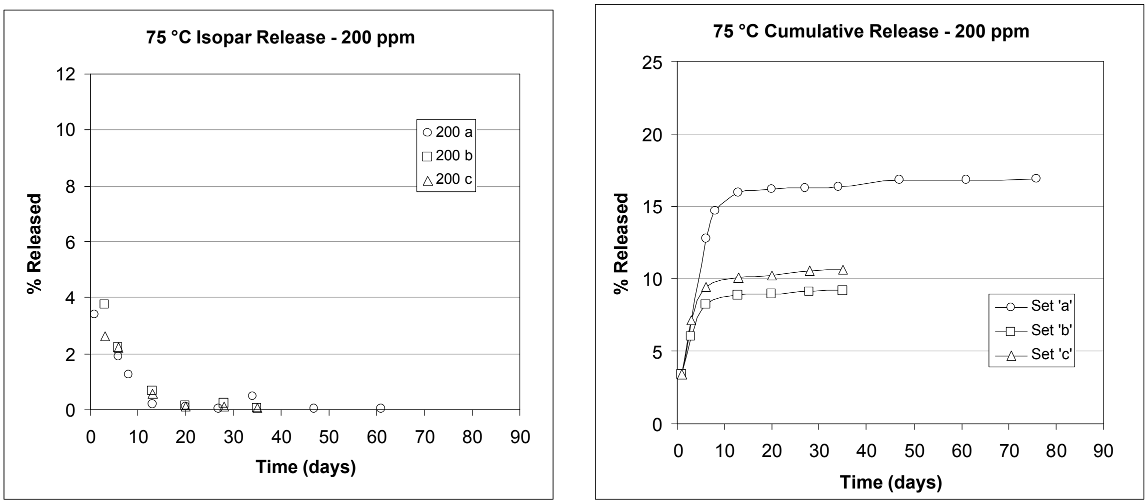
e) 95 °C 100 ppm cumulative release



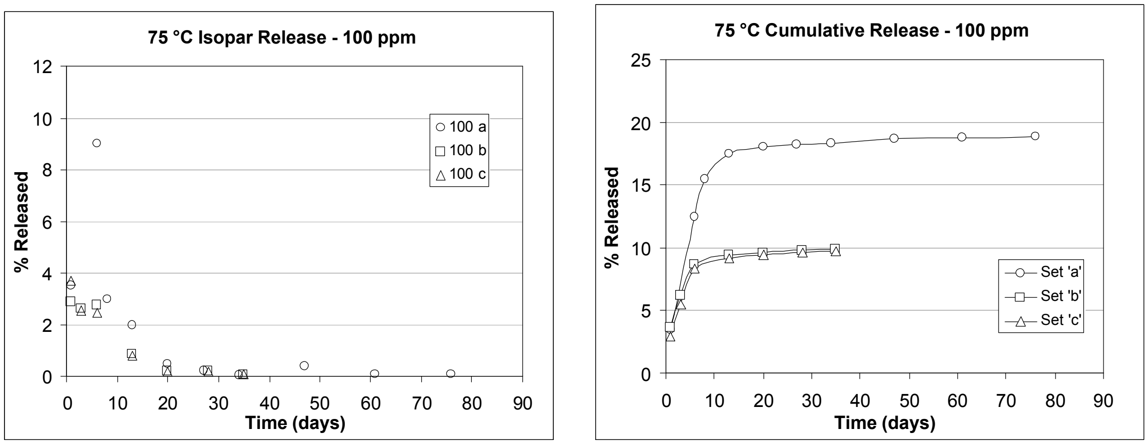
c) 95 °C 50 ppm Isopar® L release

f) 95 °C 50 ppm cumulative release

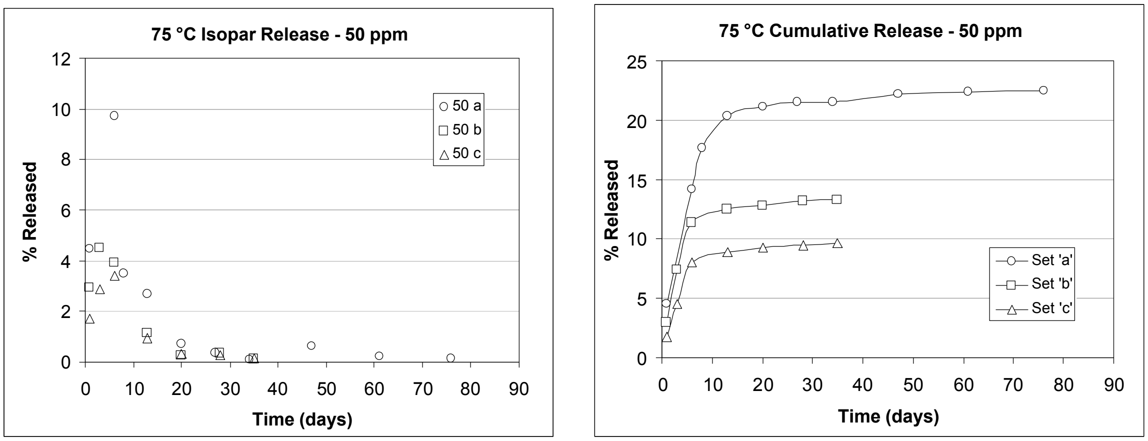
Figure 4-8 Isopar® L Release (a-c) and Cumulative Relief (d-f) for 50 ppm, 100 ppm and 200 ppm Isopar® L at 95 °C



a) 75 °C 200 ppm Isopar® L release d) 75 °C 200 ppm cumulative release

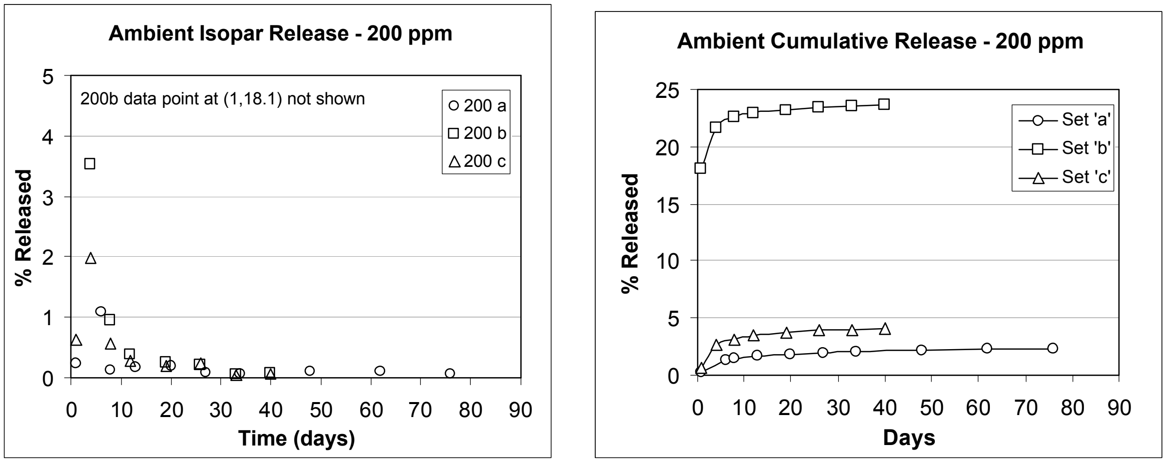


b) 75 °C 100 ppm Isopar® L release e) 75 °C 100 ppm cumulative release



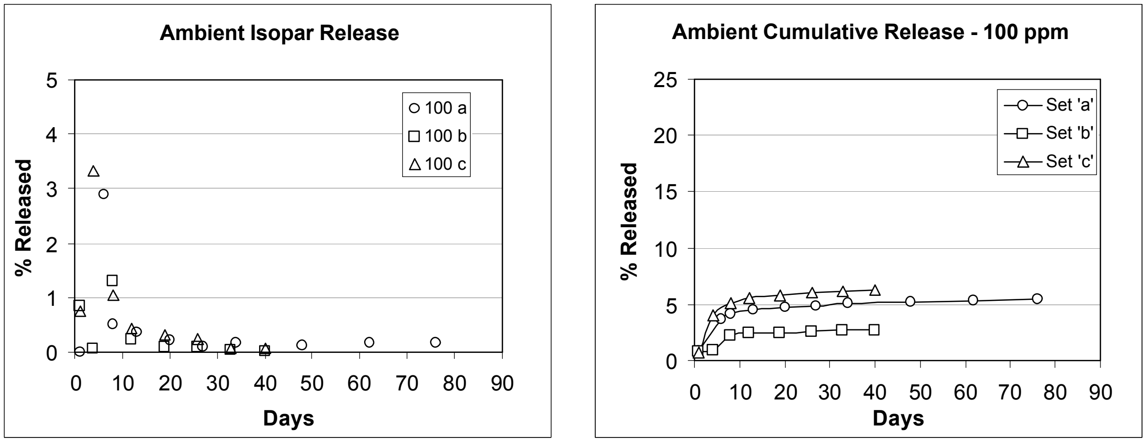
c) 75 °C 50 ppm Isopar® L release f) 75 °C 50 ppm cumulative release

Figure 4-9 Isopar® L Release (a-c) and Cumulative Relief (d-f) for 50 ppm, 100 ppm and 200 ppm Isopar® L at 75 °C



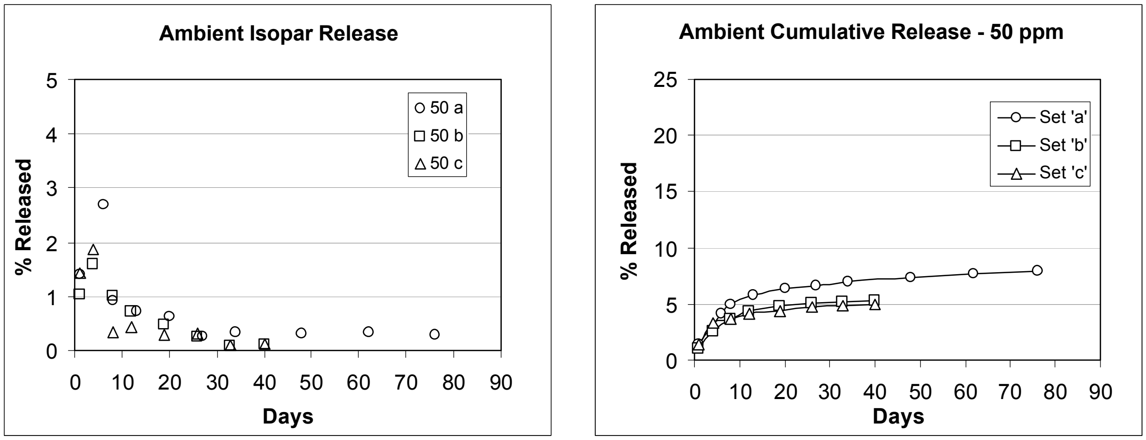
a) ambient 200 ppm Isopar® L release

d) ambient 200 ppm cumulative release



b) ambient 100 ppm Isopar® L release

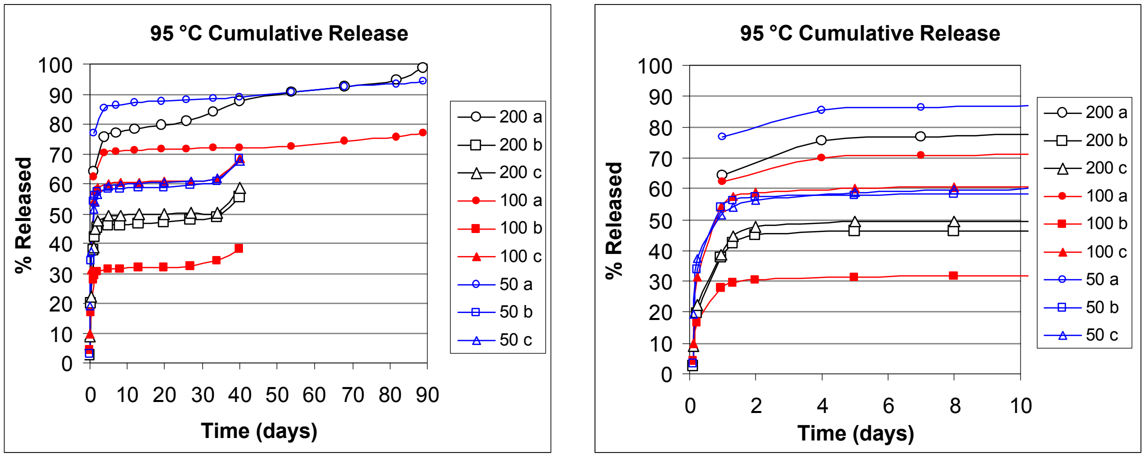
e) ambient 100 ppm cumulative release



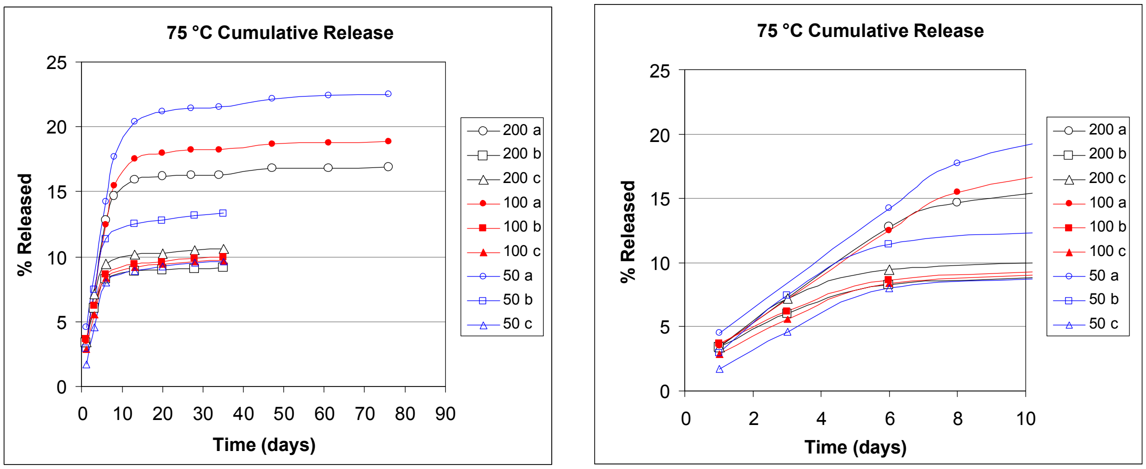
c) ambient 50 ppm Isopar® L release

f) ambient 50 ppm cumulative release

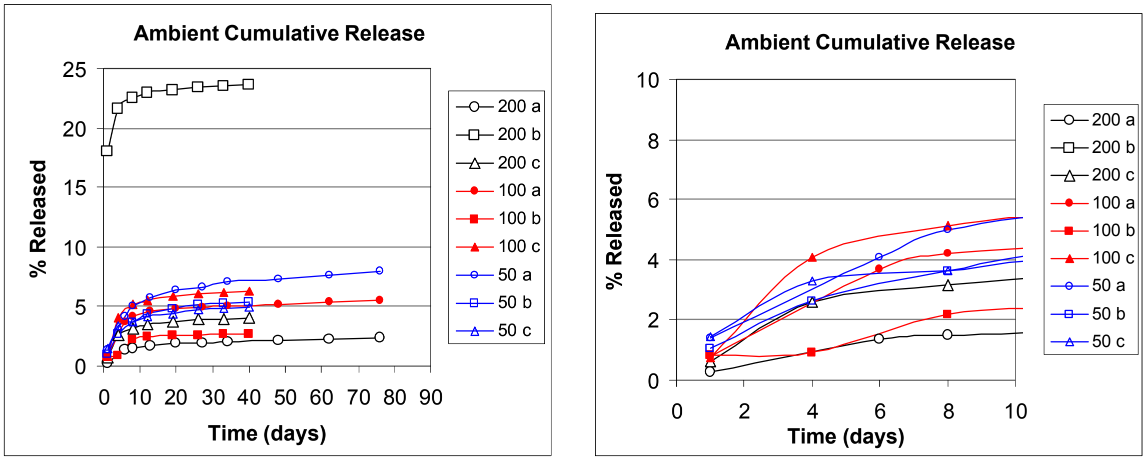
Figure 4-10 Isopar® L Release (a-c) and Cumulative Relief (d-f) for 50 ppm, 100 ppm and 200 ppm Isopar® L at Ambient Temperature



a) Isopar® L release at 95 °C



b) Isopar® L release at 75 °C



c) Isopar® L release at ambient temperature

Figure 4-11 Cumulative Releases of Isopar® L for All Concentrations of Isopar® L at Each Temperature – Full and Expanded Scales

Figure 4-8 shows the results of the 95 °C samples. Two differences in the 95 °C results can be seen. The first difference is that unlike the data for the 75 °C and ambient replicates, an upturn in the percent Isopar® L between 30–40 days is seen. The increases in sets 'b' and 'c' are greater than the small increase in set 'a'. These increases correspond to when the saltstone mass dropped to the bottom of the vessel after having risen during the first several days.

The second difference is that all of the set 'a' tests have a greater total release. The sets 'b' and 'c' were spiked with the same amount of the Isopar® L/ TOA solution as the 'a' tests so the releases would be expected to be the same. One possible error could have been that some of the amount released initially from sets 'b' an 'c' was not captured. However, the ports were found to be tightly sealed, so it is unlikely that a large amount of Isopar® L released initially was not captured.

The set 'a' spike vessels were loaded prior to oven heat-up. A possible explanation for the high set 'a' results is that due to this being the first test run, more time was taken in spiking the empty vessel with the Isopar® L/TOA standard, so the door remained open longer with the heater operating than in subsequent spike additions. Because the door was open, the heater would have increased its output significantly to try to maintain the setpoint temperature. When the door was shut, the heater may have overshot the 95 °C setpoint, which could have caused greater Isopar® L release than would have occurred at 95 °C. The spiking of the spike recovery vessel was performed much more quickly during subsequent samplings for set 'a' and for all of sets 'b' and 'c'. The thermal mass of the larger number of saltstone samples after all three sets were in the oven would also minimize any overshoot. Unfortunately, during the first week of the 95 °C set 'a' tests, the temperature logger data was lost during transfer of this data to a computer, so any increase in temperature cannot be quantified.

Figure 4-9 shows the results of the 75 °C samples. The main difference in the 75 °C results is that the set 'b' and 'c' releases are again lower than the set 'a' sample results. The greater release from set 'a' can be explained, as in the 95 °C case, by an increase in temperature during the initial setting of the saltstone. In set 'a', the oven was mistakenly set to 95 °C instead of 75 °C. Although the oven was above 75 °C for less than 15 minutes, the temperature of the oven momentarily reached 91 °C.

For the 75 °C data, three data points at the start of the tests are missing due to evaporation of the desorbed samples in the vials to be analyzed by the GC-MS. To estimate the cumulative releases at 75 °C, the three data points that were missing were replaced with the average of the other experiments. The six day set 'a' 200-ppm result was lost and was replaced by the average (9.4%) of the set 'a' 100-ppm and 50-ppm results. Results from the first sampling of the 200-ppm sets 'a' and 'b' samples are also missing and both have been replaced by the set 'a' sample result of 3.4%; this value is probably high because all of the set 'a' values are higher.

Figure 4-10 shows the results of the ambient samples. Differences between the set 'a' and the sets 'b' and 'c' data are small; only the set 'b' 200-ppm data are significantly different from the comparative data sets. The first data point for the set 'a' 200-ppm sample indicates an 18% release of Isopar® L. This 18% release cannot be explained, but two possibilities exist. The first is that the saltstone may not have been mixed thoroughly when made, so that a significant portion of the Isopar® L remained closer to the surface of the saltstone where it would evaporate more easily. The second, and more likely explanation, is that the desorbed sample partially evaporated (CS_2 would preferentially evaporate) prior to or while being analyzed, so the solution would be artificially concentrated in Isopar® L. All of the saltstone samples were mixed by the same person in the same way, so the second explanation is more plausible. Therefore, the 18% release data point in set ‘b’ will not be used to determine the average cumulative releases. The set ‘a’ release at 200 ppm is approximately half of the set ‘c’ value. When the set ‘a’ sample was made up, the first carbon tube slipped through the sample port into the vessel and remained there with the open end just above the saltstone surface. The carbon probably adsorbed a portion of the Isopar® L released, thereby lowering the amount that was adsorbed on the carbon tube attached to the sample port.

Figure 4-11 shows the cumulative release data for all concentrations as a function of temperature for comparison. The results for the set ‘a’ samples at 95 °C and 75 °C are definitely higher than the sets ‘b’ and ‘c’ results. The slope of the cumulative release distributions level out after a few days and remain relatively flat until day 30 when the saltstone samples drop in the vessels. A Fick’s diffusion coefficient could possibly be obtained with this data for Isopar® L diffusing through solid saltstone.

The most important aspect of the cumulative releases from the shorter term data is that the release at a temperature begins immediately. At higher temperatures the release rate is substantially larger. The time it takes for the Isopar® L rate to plateau is also temperature dependent. The ambient samples take more than ten days to plateau while those at 95 °C take only a day. From the plateau, minor differences in initial temperature for the 75 °C and 95 °C results were seen, as were the time of setting before the oven was turned on. This suggests that the initial temperature for the first few days after pouring saltstone determines how much Isopar® L is given off.

When looking at all the results, the data do not show statistically that the percent release of Isopar® L is a function of initial concentration; however, it appears that additional data sets that would decrease the uncertainty in the data might show that statistical differences do exist.

The slope of the cumulative release curves level out after a few days and remain relatively flat. A Fick’s Law diffusion coefficient could possibly be obtained with this data for Isopar® L diffusing through solid saltstone. Although useful for longer term release, it would not be useful for the short term release. The most important aspect of the Isopar® L release is that it begins immediately. Higher temperatures give initial release rates that are substantially larger. The time for the Isopar® L rate to plateau is also temperature dependent. The ambient samples take more than ten days to plateau while those at 95 °C take only about one day.

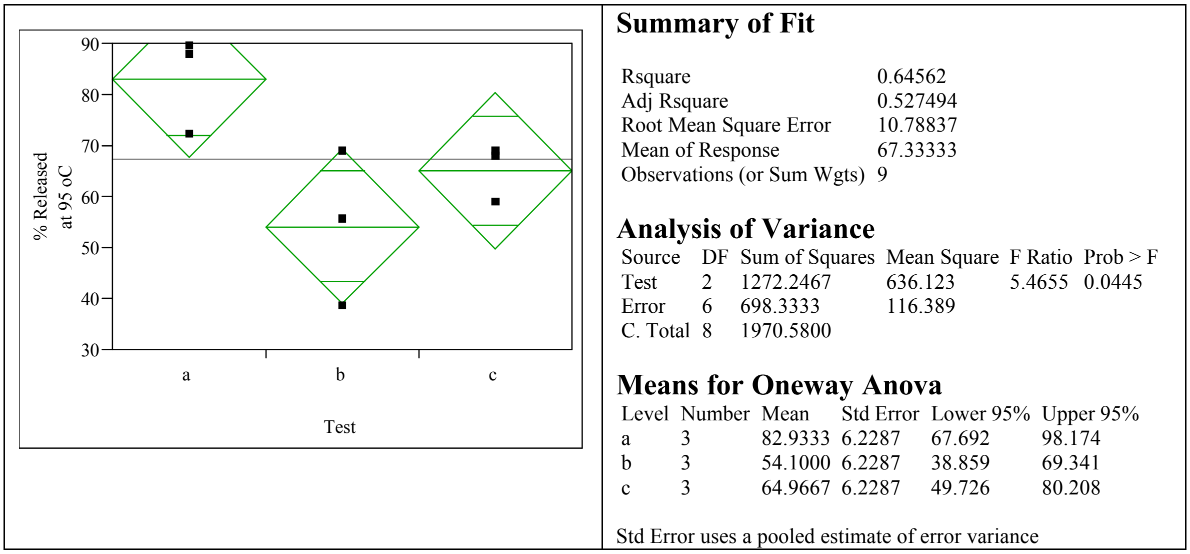
Finding out whether the higher diffusion rate at the higher temperatures or a change in the saltstone properties determines the magnitude of the Isopar® L released would take more experimentation. But one can speculate that the saltstone pore size becomes set very early on in the curing process. Small changes in temperature during the initial curing can then change the final release dramatically. Higher temperatures would create larger pores that would be more interconnected than at lower temperatures. Thus with drying more Isopar® L would be released at the higher temperature. The setting difference is large enough so that in the long term almost 100% of the Isopar® L was released from the 200-ppm, 95 °C initial sample in three months.

4.3.1 Statistical Analysis of Isopar® L Release Data

The goal of this section is to develop an upper confidence limit on the mean percent Isopar® L release at each temperature. Only the upper confidence limit is important to safe operation of Saltstone; lower confidence limits are not needed because lower than average release poses no safety hazard. JMP Version 6.0.3[15] from SAS Institute, Inc. was used to conduct this analysis. How should the available test results be used to support this effort?

4.3.1.1 Statistical Analysis of 95 °C Data

An initial statistical investigation of the experimental data is provided in Figure 4-12. In this exhibit, an analysis of variance is used to test for a difference in the mean percent Isopar® L releases over the three tests (Note: for the statistical analyses, the term ‘test’ is synonymous with ‘set’ used elsewhere in this report. The ‘tests’ are ‘a’, ‘b’, and ‘c’). From this Figure, the overall average release was estimated as 67.3%, and at a 5% significance level, the hypothesis that the three tests had the same average percent release can be rejected. Thus, these data suggest that there was a statistically significant difference among the three averages seen in the three experimental tests conducted.



Summary of Fit

Rsquare	0.64562
Adj Rsquare	0.527494
Root Mean Square Error	10.78837
Mean of Response	67.33333
Observations (or Sum Wgts)	9

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Test	2	1272.2467	636.123	5.4655	0.0445
Error	6	698.3333	116.389		
C. Total	8	1970.5800			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
a	3	82.9333	6.2287	67.692	98.174
b	3	54.1000	6.2287	38.859	69.341
c	3	64.9667	6.2287	49.726	80.208

Std Error uses a pooled estimate of error variance

Figure 4-12 Isopar® L Release at 95 °C – Oneway Analysis of % Release By Test

Figure 4-12 indicates that as the upper confidence limit on the mean percent release at 95 °C is determined it must incorporate variation from two sources: test-to-test variation as well as the variation within a test. For the variation within a test, consider Figure 4-13, which provides a plot of the data showing the initial Isopar® L concentration of the feed for each of the three tests. There is no indication of a statistically significant linear correlation between the percent Isopar® L release and the Isopar® L concentration of the feed. Thus, the percent Isopar® L release for a given run within a test does not appear to depend on the Isopar® L concentration of the feed, when that concentration falls within the interval of these tests (i.e., from 50 to 200 ppm).

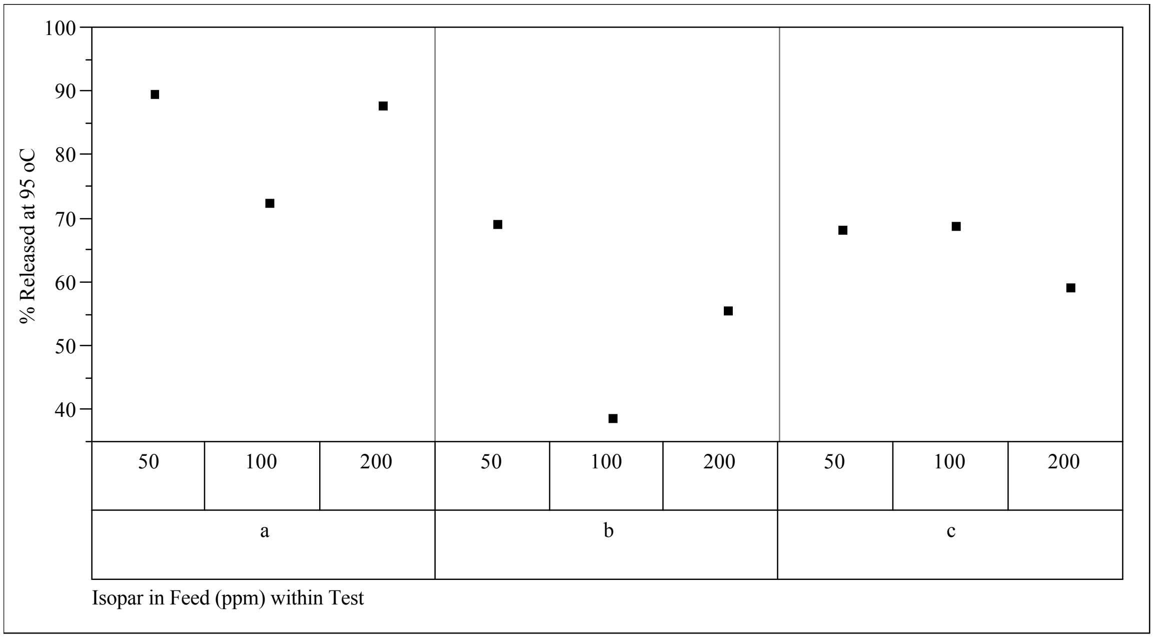
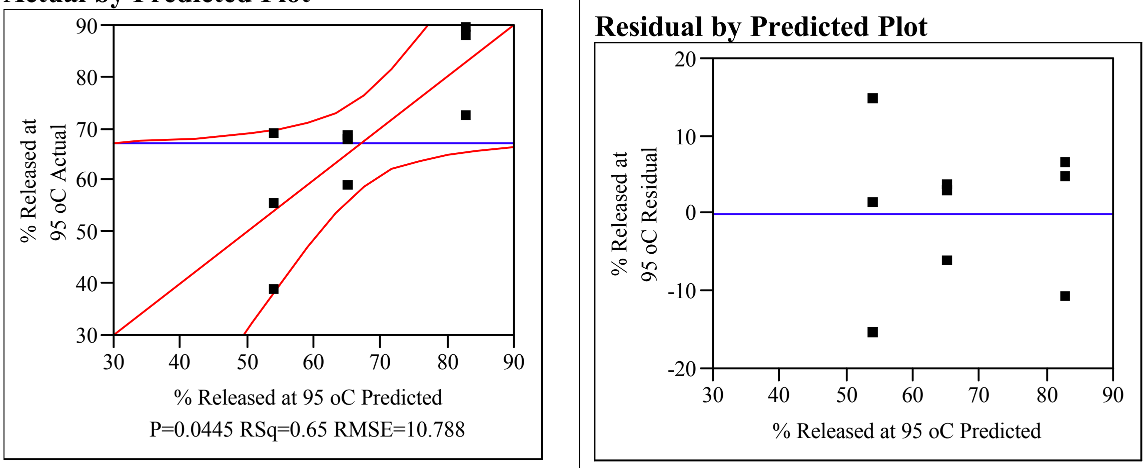


Figure 4-13 Isopar® L Percent Release at 95 °C by Isopar® L Feed Concentration within Test

Figure 4-14 provides the basis for estimating the components of variation of interest at 95 °C. These components are the test-to-test variance and the within test variance. Figure 4-14 is an analysis of variance that relies on a random effects model (discussed below) to estimate the two variance components. The test-to-test variance is estimated to be 173.24 (or a standard deviation of 13.16 % Release). The within test (or residual) variance component is estimated to be 116.39 (or a standard deviation of 10.79 % Release). There are only 2 degrees of freedom associated with the estimate of the test-to-test variance, while there are 6 degrees of freedom associated with the within test variance due to the “pooling” of the data across the three tests to estimate the within test variance.

Response Result (%)
Whole Model



Summary of Fit

RSquare	0.64562
RSquare Adj	0.527494
Root Mean Square Error	10.78837
Mean of Response	67.33333
Observations (or Sum Wgts)	9

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	1272.2467	636.123	5.4655
Error	6	698.3333	116.389	Prob > F
C. Total	8	1970.5800		0.0445

Expected Mean Squares

The Mean Square per row by the Variance Component per column

EMS	Intercept	Test&Random
Intercept	0	0
Test&Random	0	3

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Test&Random	173.2448	59.815
Residual	116.3889	40.185
Total	289.6337	100.000

These estimates based on equating Mean Squares to Expected Value.

Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Test&Random	116.389	6	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Test&Random	1272.25	636.123	2	5.4655	0.0445

Figure 4-14 Isopar® L Release at 95 °C – Analysis of Variance of a Random Effects Model

Information from Figure 4-14 also provides the basis for determining confidence intervals for the mean Isopar® L release. The underlying statistical model for an Isopar® L percent release measurement is given by:

$$y_{ij} = \mu + a_i + \varepsilon_{ij} \tag{3}$$

for i=1, …, n tests and j = 1, …, r; runs per test where y_{ij} represents the percent Isopar® L measurement for the jth run of the ith test, μ is the true (unknown) mean percent Isopar® L release, a_i is the random effect from testing for the ith test, and ε_{ij} is the random effect from the jth run within the ith test. Also, the a_i's are independent, random variables and are assumed to follow a normal distribution with mean zero and (unknown) variance σ_a^2. The ε_{ij}'s are independent, random variables and are assumed to follow a normal distribution with mean 0 and (unknown) variance σ_ε^2. And, finally, the a_i's and ε_{ij}'s are assumed to be independent. In this situation, where there are n = 3 random tests and r = 3 runs per test (i.e., n × r = 9 total measurements), an upper 100(1-α)% confidence interval for the mean percent Isopar® L release is given by:

$$\bar{y} + t(\alpha, n-1) \times \sqrt{\frac{\sigma_a^2}{n} + \frac{\sigma_\varepsilon^2}{n \times r}} \qquad (4)$$

where t(α,n-1) is the upper α-tail of the Student's t distribution with n-1 degrees of freedom. The MS Num term in Figure 4-14 is an estimate of

$$\sqrt{r\sigma_a^2 + \sigma_\varepsilon^2}$$

The average release, $\bar{y}$, from the nine tests was 67.33 ppm as shown in Figure 4-14. Thus, the upper 100(1-α)% confidence interval for the mean percent Isopar® L release may be re-written as

$$67.33 + t(\alpha, 2) \times \sqrt{\frac{636.123}{9}} \qquad (5)$$

or

$$67.33 + t(\alpha, 2) \times 8.407 \qquad (6)$$

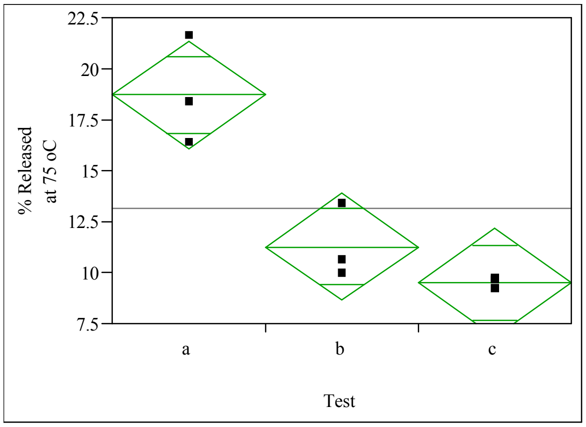
From Equation (6), the standard error (or standard deviation) of $\bar{y}$ is given by 8.407 % Release. Table 4-1 provides values for the upper confidence limit on the mean percent Isopar® L release at 95 °C for various confidence levels.

Table 4-1 Determination of Values for Upper Confidence Limits on the Mean for 95 °C Data

% Confidence	% Release Upper Confidence Limit	% Confidence	% Release Upper Confidence Limit
95	91.88	87	80.41
94	89.36	86	79.67
93	87.37	85	78.99
92	85.74	84	78.36
91	84.37	83	77.78
90	83.19	82	77.24
89	82.15	81	76.73
88	81.24	80	76.25

4.3.1.2 Statistical Analysis of 75 °C Data

Figure 4-15 begins the analysis of the experimental data from the 75 °C testing in the same manner as was used for the 95 °C data. The results from this analysis of variance yield an estimate of the overall average release at 75 °C of 13.17%, and at a 5% significance level, the hypothesis that the three tests had the same average percent release at this temperature can be rejected. Thus, these data suggest that there was a statistically significant difference among the three averages seen in the three experimental tests conducted at this temperature.



```
Oneway Anova
Summary of Fit

Rsquare                      0.873283
Adj Rsquare                  0.831044
Root Mean Square Error       1.866964
Mean of Response             13.16667
Observations (or Sum Wgts)          9

Analysis of Variance
Source   DF      Sum of       Mean  F Ratio   Prob >
                Squares     Square                 F
Test      2   144.12667    72.0633  20.6748   0.0020
Error     6    20.91333     3.4856
C.        8   165.04000
Total

Means for Oneway Anova
Level  Number     Mean  Std Error  Lower 95%  Upper 95%
a           3  18.7333     1.0779     16.096     21.371
b           3  11.2667     1.0779      8.629     13.904
c           3   9.5000     1.0779      6.862     12.138

Std Error uses a pooled estimate of error variance
```

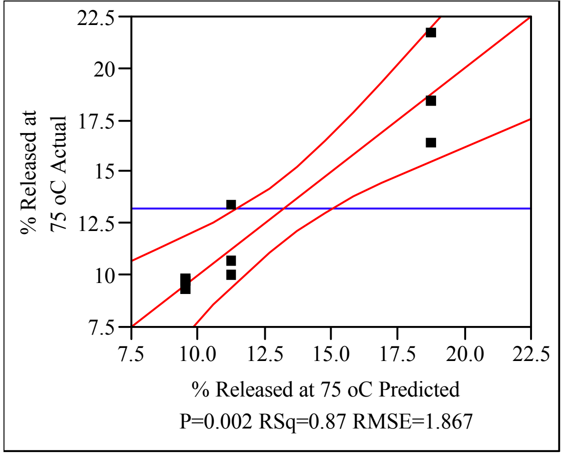
Figure 4-15 Oneway Analysis of % Released at 75 °C By Test

Thus, Figure 4-15 indicates that the development of an upper confidence limit on the mean percent release at 75°C should follow the same approach as used for the 95 °C testing. Figure 4-16 provides the results of the analysis of variance of the random effects model that was utilized above when applied to the data from the 75 °C testing. Using the information from this exhibit in the same manner as was done for the 95 °C testing yields an average percent release of 13.17% with a standard deviation for the sample mean of 2.83%.

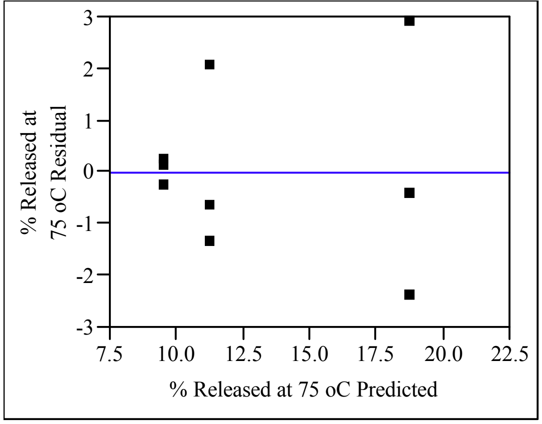
Response % Released at 75 °C

Whole Model

Actual by Predicted Plot



Residual by Predicted Plot



Summary of Fit

RSquare	0.873283
RSquare Adj	0.831044
Root Mean Square Error	1.866964
Mean of Response	13.16667
Observations (or Sum Wgts)	9

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	144.12667	72.0633	20.6748
Error	6	20.91333	3.4856	Prob > F
C. Total	8	165.04000		0.0020

Expected Mean Squares

The Mean Square per row by the Variance Component per column

EMS	Intercept	Test&Random
Intercept	0	0
Test&Random	0	3

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Test&Random	22.85926	86.769
Residual	3.485556	13.231
Total	26.34481	100.000

These estimates based on equating Mean Squares to Expected Value.

Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Test&Random	3.48556	6	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Test&Random	144.127	72.0633	2	20.6748	0.0020

Figure 4-16 Analysis of Variance of a Random Effects Model for the 75 °C Data

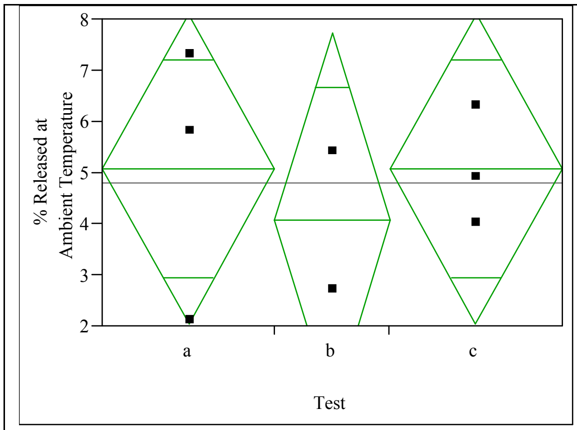
Table 4-2 was prepared to provide the values for the upper confidence limit on the mean percent Isopar® L released at 75 °C for various confidence levels.

Table 4-2 Determination of Values for Upper Confidence Limits on the Mean at 75 °C

% Confidence	% Release Upper Confidence Limit	% Confidence	% Release Upper Confidence Limit
95	21.43	87	17.57
94	20.58	86	17.32
93	19.91	85	17.09
92	19.36	84	16.88
91	18.90	83	16.68
90	18.50	82	16.50
89	18.15	81	16.33
88	17.85	80	16.17

4.3.1.3 Statistical Analysis of Ambient Temperature Data

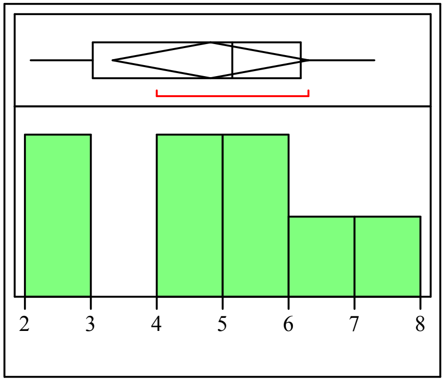
Figure 4-17 starts the analysis of the experimental data from the ambient temperature testing in the same manner as was used for the data from the tests at the other two temperatures. The results from this analysis of variance, however, cannot reject, at a 5% significance level, the hypothesis that the three tests had the same average percent release. Thus, these data suggest that there was no indication of a statistically significant difference among the three averages seen in the three experimental tests conducted at this temperature. As a result, each of the values from each of these tests will be considered as a random draw from the population of possible Isopar® L release percentages, and it is the mean of this population that it is interest.



```
Oneway Anova
Summary of Fit

Rsquare                          0.069811
Adj Rsquare                      -0.30226
Root Mean Square Error            2.03265
Mean of Response                   4.8125
Observations (or Sum Wgts)              8

Analysis of Variance
Source     DF  Sum of Squares  Mean Square  F Ratio  Prob > F
Test        2        1.550417      0.77521   0.1876    0.8345
Error       5       20.658333      4.13167
C. Total    7       22.208750

Means for Oneway Anova
Level  Number     Mean  Std Error  Lower 95%  Upper 95%
a           3  5.06667     1.1736     2.0500     8.0834
b           2  4.05000     1.4373     0.3553     7.7447
c           3  5.06667     1.1736     2.0500     8.0834

Std Error uses a pooled estimate of error variance
```

Figure 4-17 Oneway Analysis of % Released at Ambient Conditions By Test

Specifically, an upper 100(1-α)% confidence limit for the mean percent Isopar® L release at ambient conditions is of interest. Figure 4-18 provides estimates of the population of possible Isopar® L percent releases using all of the ambient data and these results will aid in the estimation of the confidence limit. From this exhibit, the sample estimate of the mean is 4.813% and the standard deviation (or standard error) of this sample mean is 0.630%.



Quantiles

100.0%	maximum	7.300
99.5%		7.300
97.5%		7.300
90.0%		7.300
75.0%	quartile	6.175
50.0%	median	5.150
25.0%	quartile	3.025
10.0%		2.100
2.5%		2.100
0.5%		2.100
0.0%	minimum	2.100

Moments

Mean	4.813
Std Dev	1.781
Std Err Mean	0.630
upper 95% Mean	6.301
lower 95% Mean	3.323
N	8

Figure 4-18 Descriptive Statistics for the % Released at Ambient Conditions Using All of the Data

Table 4-3 was prepared to provide the values for the upper confidence limit on the mean percent Isopar® L release at ambient conditions for various confidence levels

Table 4-3 Determination of Values for Upper Confidence Limits on the Mean at Ambient Conditions

% Confidence	% Release Upper Confidence Limit	% Confidence	% Release Upper Confidence Limit
95	6.01	87	5.58
94	5.93	86	5.55
93	5.86	85	5.52
92	5.80	84	5.49
91	5.75	83	5.46
90	5.70	82	5.43
89	5.66	81	5.40
88	5.62	80	5.38

4.3.1.4 Summary of Statistical Analyses

The overall average releases at each temperature were estimated. For the 95 and 75 °C data, at a 5% significance level, the hypothesis that the three tests at each temperature had the same average percent release can be rejected, suggesting that there was a statistically significant difference among the three averages seen in the three experimental tests conducted. The ambient conditions tests showed no such difference. The mean Isopar® L percent releases are summarized in Table 4-4 along with upper confidence limits at confidences from 80–95%. The mean release values versus time at the temperatures tested are summarized in Figure 4-19.

Table 4-4 Means and Upper Confidence Limits on the Means for All Data

	95 °C	75 °C	Ambient
Mean	67.33	13.17	4.81
% Confidence	**% Release Upper Confidence Limit**		
95	91.88	21.43	6.01
94	89.36	20.58	6.46
93	87.37	19.91	6.31
92	85.74	19.36	6.19
91	84.37	18.90	6.09
90	83.19	18.50	6.00
89	82.15	18.15	5.92
88	81.24	17.85	5.85
87	80.41	17.57	5.79
86	79.67	17.32	5.74
85	78.99	17.09	5.69
84	78.36	16.88	5.64
83	77.78	16.68	5.59
82	77.24	16.50	5.55
81	76.73	16.33	5.52
80	76.25	16.17	5.48

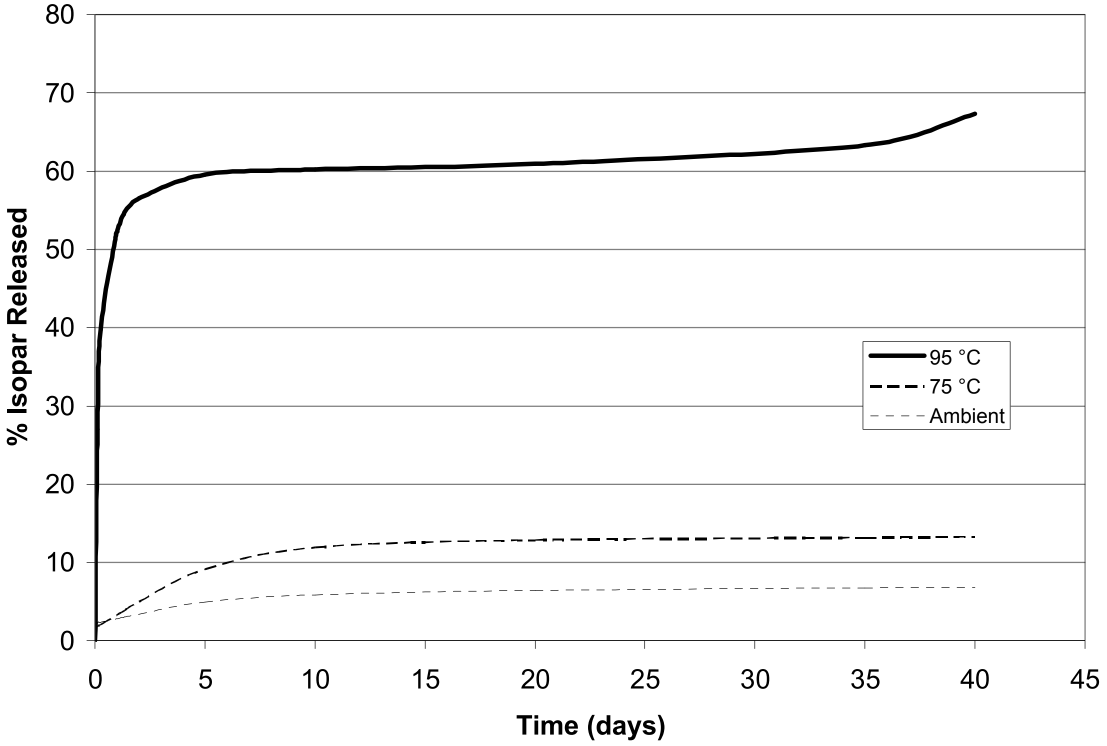


Figure 4-19 Average Cumulative Releases

4.4 Scoping Test Results

4.4.1 IR Spectroscopy Method

IR spectroscopy was found to be a non-useful method for measuring Isopar® L release at ambient temperature and the concentrations used in this study. While the IR peaks associated with water from 4000–3500 cm^{-1} and 200–1300 cm^{-1} do not interfere with the Isopar® L peaks around 2900 cm^{-1}, the water peaks are considerably more intense. The saltstone sample had an absorbance of 0.24 for the strongest water peak. Because of the high water absorbance, the 0.0008 absorbance of the largest Isopar® L peak at 2930 cm^{-1} could be considered noise. For this method to work for measuring Isopar® L from saltstone, higher Isopar® L concentrations or release rates would be needed as well as a water trap before the IR detector.

4.4.2 Full Solvent Contactor Results

The saltstone produced with full solvent by two different mixing methods was visually the same. The initial step in the two mixing methods is shown in Figure 4-20. The first method mixed the premix and salt solution by shaking. The solvent was then immediately added to the top of the saltstone mixture and shaken. The dyed solvent can be seen to fluoresce blue on top of the saltstone in Figure 4-20. After shaking, no blue fluorescence is seen when the UV lamp (380 nm) was shone on the mixed sample as shown in Figure 4-21, only the gray color of the saltstone and the reflection of the UV light on the sides of the PMP jar. In the second mixing method the full solvent and the salt solution were mixed via a contactor. The resulting simulant DSS solution was put into a separatory funnel. The solvent disengages to some extent as shown by the blue fluorescence at the top and sides of the funnel in Figure 4-20. The blue color becomes less intense closer to the bottom of the funnel indicating that the solvent is less concentrated at the bottom. The simulant DSS solution was removed from the bottom of the funnel, premix was added, and the saltstone was mixed by shaking. Like the first method no fluorescence was seen after making the saltstone samples. The concentration of the dye was diluted too much after mixing so that only the gray saltstone color could be seen.

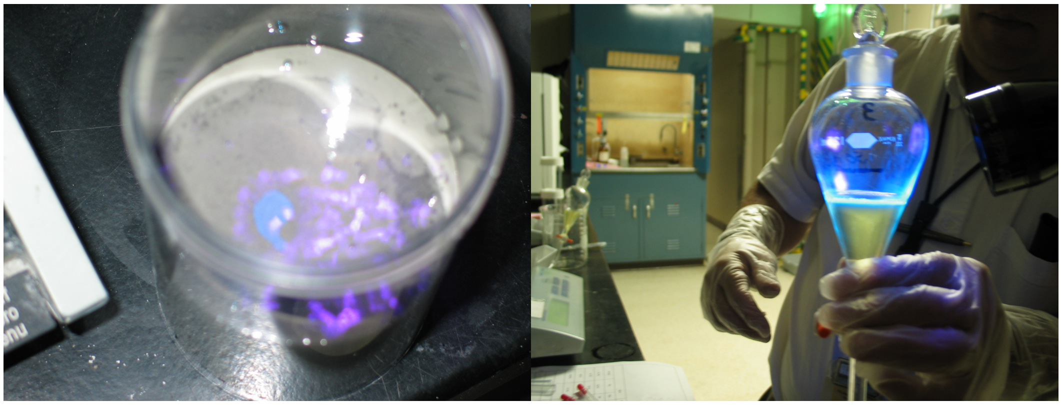


Figure 4-20 Dyed Solvent on Top of Premix and Salt Solution, and Dyed Solvent after Being Mixed with Salt Solution with a Contactor

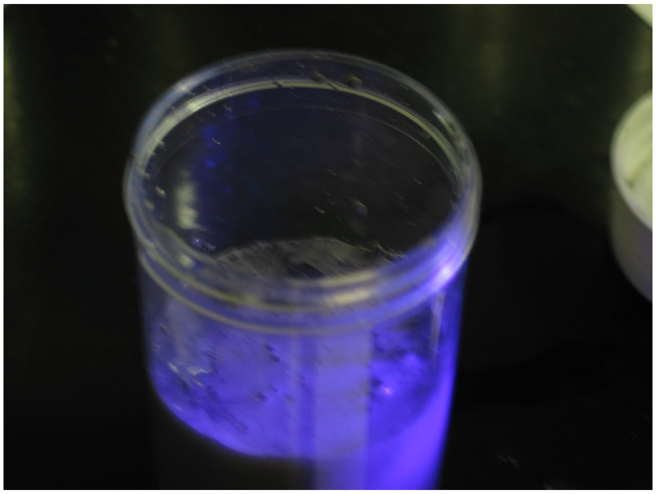


Figure 4-21 Dyed Saltstone After Mixing - No Fluorescence

No major difference was seen in the Isopar® L release at 95 °C due to the mixing method used with the full solvent. The amount of Isopar® L in each sample for the two mixing methods is shown in Figure 4-22 along with the average ng/µL Isopar® L released of the replicates. Note that the % Release cannot be plotted because the initial concentrations of Isopar® L in the contactor DSS simulant samples were not known. The straight lines that connect the averages are shown to guide the eye. Although it appears that the average Isopar® L release from the shaken samples is higher than those made with the contactor DSS simulant, the spread of the data is too large to state this as fact.

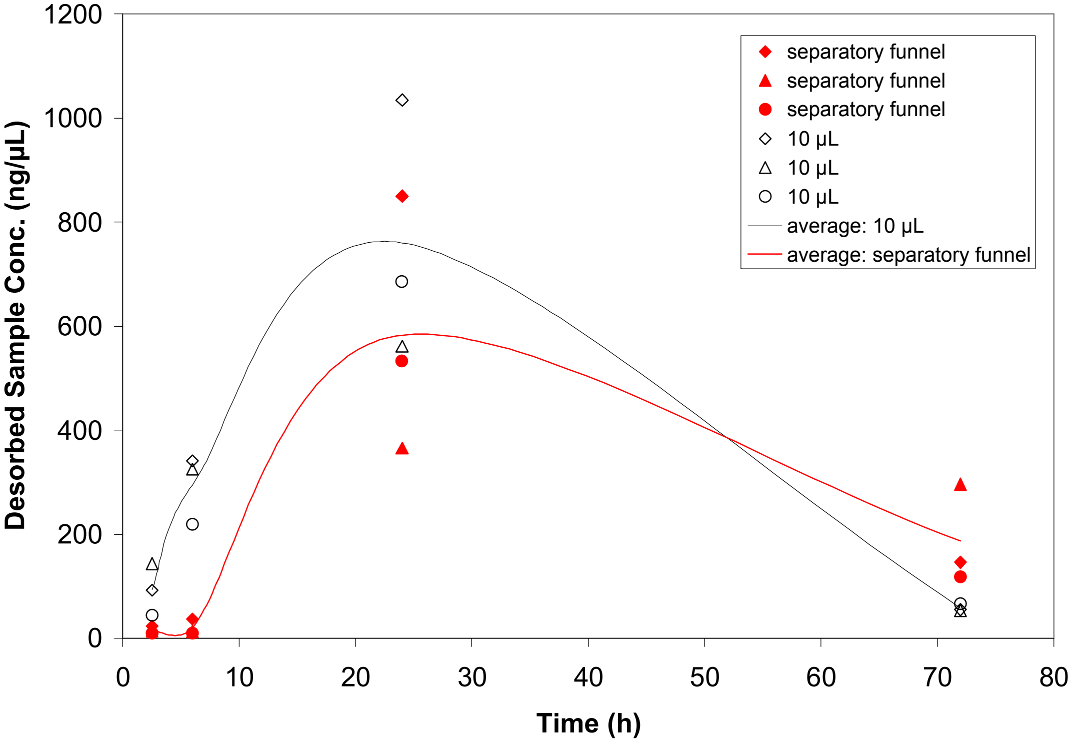


Figure 4-22 Isopar® L Release at 95 °C from Saltstone Made with Full Solvent Mixed by Two Methods

The 2.5 hour results from the contactor are slightly lower than those of the mixed sample. This induction period is not due to allowing one set of samples to remain at ambient temperature longer before the oven was turned on. As noted earlier the mixed and contactor samples were made in pairs, one contactor sample and one mixed sample at the same time, so this difference in ambient setting time affect would not be appreciable.

The induction period can be explained simply by the fact that the full solvent is more homogeneously mixed in the DSS solution by the contactor. After mixing the DSS solution with the premix to make a sample, the Isopar® L would be in smaller droplets and more thoroughly mixed throughout a sample. The Isopar® L would then need more time to diffuse through the sample or coalesce to larger droplets to initially push its way out of the setting saltstone. This induction period is not very important with respect to saltstone production as the data all fit on the same curve if the contactor sample data is shifted 2.5 hours. With production pour times in days, a 2.5 hour shift will not affect the cumulative amount of Isopar® L released.

The 10 μL full solvent addition in the scoping test was made to be comparable to the 50 ppm results of the Isopar® L /TOA tests. A direct comparison cannot easily be made due to different sampling frequencies. However, the amounts of Isopar® L released after three days in the full solvent tests were 27%, 20%, and 19% for a cumulative average of 22% ± 5% ($1s_d$). The amounts released from the contactor sample were similar in magnitude. The estimated (by linear interpolation) amounts of Isopar® L released from sets ‘b’ and ‘c’ at the third day at 50-ppm initial Isopar® L and 95 °C were 57.5% and 57.2%, respectively.

The mol fraction of Isopar® L in the full solvent is about 0.83, so if the release rate is proportional to the vapor pressure, then by Raoult's Law, the release rate should be about 17% lower than for pure Isopar® L:

$$P_{vap} = x\ P_{sat}$$

$$\text{where } P_{sat} = \text{saturation vapor pressure}$$

$$x = \text{mol fraction in liquid}$$

$$P_{vap} = \text{vapor pressure}$$

However, the release of Isopar® L from the full solvent is only about ~22/57 or 39% of the pure solvent release, so the Cs-7SB modifier appears to suppress the vapor pressure of Isopar® L more than can be accounted for by dilution. Previous work has reported similar behavior;[14] the apparent vapor pressure of Isopar® L was reported to be 41-62% of the expected values from 25-45 °C.

The second set of contactor tests took into consideration the possibility that the DSS solution would have time to separate prior to being made into saltstone. Even though there were two hours of saltstone setting time difference between the samples made with DSS solution immediately out of the contactor and those that aged for an hour, the Isopar® L released is virtually identical. Figure 4-23 shows the Isopar® L release for both the immediate and one hour curing saltstone samples along with the average ng/µl Isopar® L released of the three replicate samples. The straight lines are to guide the eye. The small increase in Isopar® L release expected for the samples that did not set two hours prior to heating is almost non-existent. Either the setting is less important for the full solvent case or it is offset by a difference in initial Isopar® L concentration.

Isopar® L concentrations for the second set of contactor tests were estimated from analysis that measured the modifier. Modifier concentrations for the immediately used contactor DSS solution were ~10% higher than after the solution was allowed to disengage for an hour. For two samples, the concentrations found were 66 and 58 mg/L for the fresh DSS solution and 49 and 46 mg/L after aging for one hour. To estimate the Isopar® L concentration, the average modifier concentration is divided by 70 wt% to get the amount of Isopar® L in the DSS solution. This number is then multiplied by the dilution factor of 45.88% used when making the saltstone. The resulting Isopar® L concentrations in the saltstone samples are then 41 ppm and 31 ppm, for the immediate and aged saltstone samples, respectively.

Finally, the average Isopar® L release for all of the scoping tests is shown in Figure 4-24. The seemingly large difference between the 10-µL mixed sample and the contactor samples release at one day can easily be explained by the initial Isopar® L concentration difference of ~20%. Coupled with the earlier variance discussion, one can state that the average Isopar® L release is the same for all the scoping experiments at 95 °C.

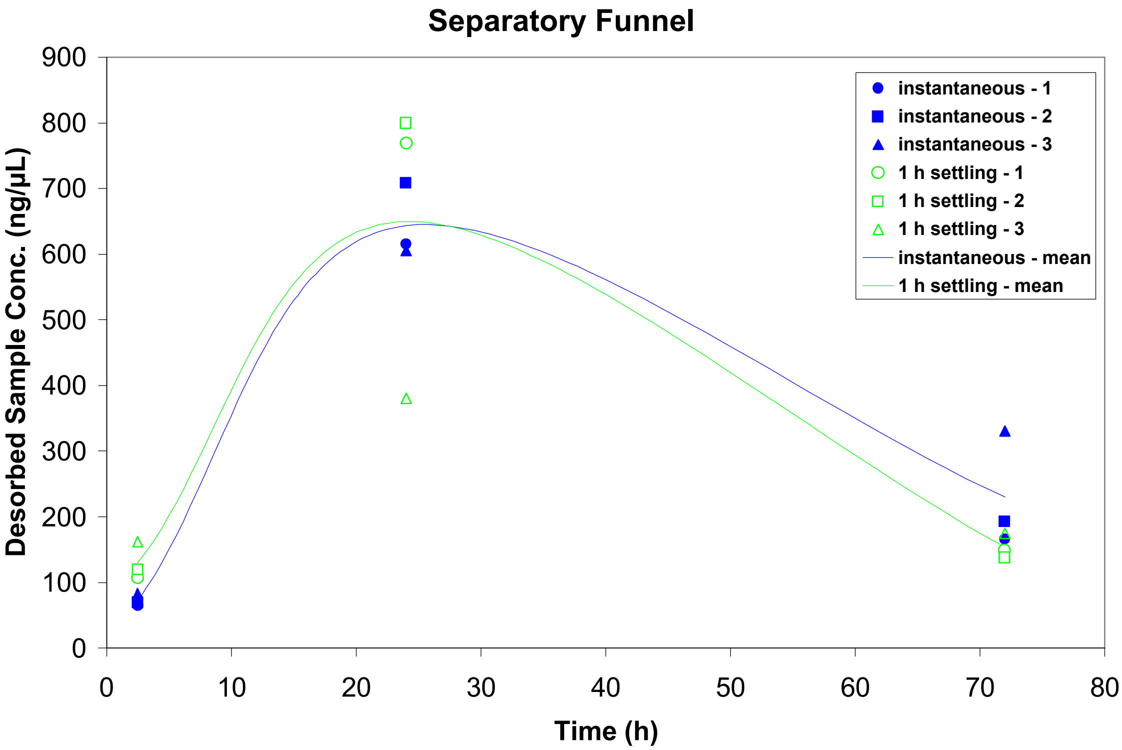


Figure 4-23 Isopar® L Release from Saltstone Made with Full Solvent Immediately and After One Hour Disengaging Time

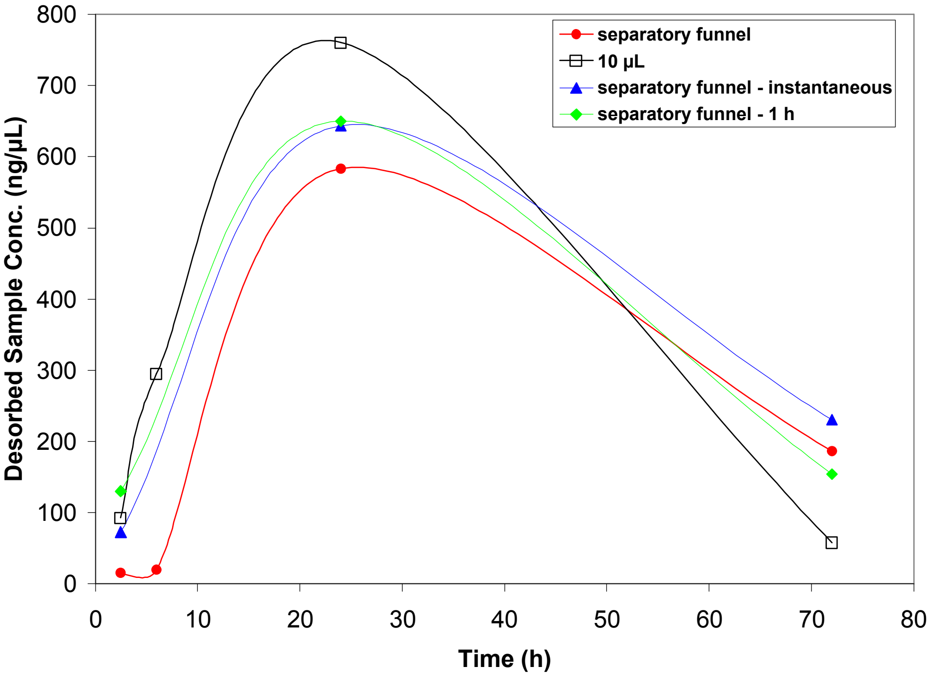


Figure 4-24 Average Isopar® L Release for All Scoping Tests

5.0 CONCLUSIONS

The release of Isopar® L has been measured from saltstone as it cured as a function of time, temperature, and Isopar® L concentration. Three Isopar® L concentrations (50 ppm, 100 ppm, and 200 ppm) were tested at ambient temperature, 75 °C, and 95 °C. The tests were run in triplicate with an initial set of samples at each temperature followed by replicate samples a month later. Isopar® L was collected on carbon tubes, desorbed with CS_2, and measured with GC-MS. The Isopar® L was not measured by FT-IR because of the large absorbance signal from water vapor.

Initial observations of the saltstone curing showed a definite difference in the ambient and higher temperature samples. At ambient temperatures the samples had no bleed water after three days. The bleed water remained on top of the 95 °C and 75 °C samples for ~20 and 27 days, respectively. Additionally, the saltstone in the higher temperature samples rose inside the vessels due to a ‘piston effect’. After about 30 days the saltstone dropped back down to the bottom of the vessel. At this time, an increase of Isopar® L release occurred due to expelling of the vapor that was below the saltstone. The Isopar® L released at that time was probably generated at the time the saltstone rose, which was about 1 to 3 days, suggesting that this increase in release should be added to the data at around 1-3 days.

The results from the curing of the saltstone showed that the Isopar® L release data can be treated as a percentage of initial concentration in the concentration range studied; the percent release was statistically not a function of the initial concentration. The Isopar® L release results show that the majority of the Isopar® L was released in the first few days. The release begins immediately and in all cases the amount of Isopar® L released decreases with time after the first few days. The magnitude of the Isopar® L released was found to increase with increasing temperature.

Cumulative release distributions showed that initial curing temperature was very important. Slight variations in temperature during the first few days appears to have affected the final Isopar® L amount released. Statistically significant differences between the set ‘a’ and sets ‘b’ and ‘c’ samples at both 95 °C and 75 °C were found and might be attributable to unplanned temperature increases during the first day of curing. Even the time a sample sat at ambient temperature before the oven was turned on was also seen to minimally affect the amount of Isopar® L released. A possible explanation of this behavior was than the saltstone pore size is set very early on in the curing process.

Short scoping tests at 95 °C with full component mixed solvent and a fluorescent dye were run. The tests showed that both the method of adding the Isopar® L as a spike into the saltstone and shaking to mix and mixing the Isopar® L with a contactor to add to premix, produced well mixed samples. The full solvent was found to release less Isopar® L than the tests run with Isopar® L/TOA only and to release less that expected due only to dilution by the Cs-7SB modifier.

Isopar® L release was studied for a two-month period and average cumulative release rates were determined from three sets of tests each at 95 and 75 °C and at ambient conditions. The overall average releases at were estimated for each temperature. For the 95 and 75 °C data, at a 5% significance level, the hypothesis that the three test sets at each temperature had the same average percent release can be rejected, suggesting that there was a statistically significant difference among the three averages seen in the three experimental tests conducted.

An upper confidence limit on the mean percent release required incorporation of variation from two sources: test-to-test variation as well as the variation within a test. An analysis of variance that relies on a random effects model was used to estimate the two variance components. The test-to-test variance and the within test (or residual) variance were both calculated. There is no indication of a statistically significant linear correlation between the percent Isopar® L release and the Isopar® L initial concentration. From the analysis of variance, upper confidence limits at confidences of 80-95% were calculated for the data at 95 and 75 °C. The mean Isopar® L percent releases were 67.33% and 13.17% at 95 and 75 °C, respectively. The upper confidence limits found are:

	95 °C	**75 °C**
Mean	67.33	13.17
% Confidence	**% Release Upper Confidence Limit**	
95	91.88	21.43
94	89.36	20.58
93	87.37	19.91
92	85.74	19.36
91	84.37	18.90
90	83.19	18.50
89	82.15	18.15
88	81.24	17.85
87	80.41	17.57
86	79.67	17.32
85	78.99	17.09
84	78.36	16.88
83	77.78	16.68
82	77.24	16.50
81	76.73	16.33
80	76.25	16.17

The ambient conditions tests did not show any difference between data sets; the mean release was 4.81% and the 95% upper confidence limit was 6.01%.

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APPENDIX

1. Example calculation of the amount of Isopar® L added to a saltstone sample.

255 g of saltstone was made up of 138 g of premix (54.12 wt%) and 117 g of simulant DSS (45.88 wt%). The addition of simulant and premix fit the constraints for the water to premix ratio of 0.60 and premix composition of 10 wt% Cement, 45 wt% Slag, and 45 wt% Fly Ash.

Thus, for 200ppm;

$$\frac{200 \text{ mg Isopar® L}}{\text{kg DSS}} \times 0.117 \text{ kg DSS} = 23.4 \text{ mg Isopar® L needed}$$

$$23.4 \text{ mg Isopar® L} \div 0.77 \text{ mg}/\mu\text{L Isopar® L} = 30.4 /\mu\text{L Isopar® L needed}$$

Since the syringe had a delivering volume of 10μL and four volumes were needed (10, 10, 10, 1), 31μL was added. Amounts added in λ (1 λ = 1 μL) were 31.0 λ, 15.5λ, and 7.5λ and give actual target concentrations of 204 ppm, 102 ppm, and 49.4 ppm in the DSS.

2. Percent Isopar® L released.

Listed below are the percentages of Isopar® L released for each sample at each temperature in tabular form. Two tables are given for each temperature. The first is for the initial samples and the second is for the replicate samples. Columns are labeled 200, 100, and 50 correspond to the samples containing DSS spiked to 200ppm, 100 ppm and 50 ppm Isopar® L. Columns labeled with 'ave' are the average percent released at that collection time (i.e. average across a row). The cum 'ave' column is the cumulative average of the average percent released listed in the 'ave' column. The column labeled 'stdev' is the standard deviation to one sigma of the percent released at a collection time (i.e. the standard deviation of the data across a row)

Utilizing this data as described in the text allows calculation of the average cumulative releases reported. The 200 ppm ambient set 'b' first data point is shown in **bold** to indicate that it was an unexpectedly high value. Average data added for missing data to make cumulative releases as described in the text is given in *italics*.

95°C 1st days	200a	100a	50a	ave	cum ave	stdev
1	64.2	62.1	77.3	67.9	67.9	8.24
4	11.4	8.00	8.27	9.22	77.1	1.89
7	1.08	0.708	1.08	0.956	78.0	0.215
12	1.43	0.480	0.803	0.904	79.0	0.483
19	1.40	0.194	0.579	0.724	79.7	0.616
26	1.60	0.090	0.341	0.677	80.4	0.809
33	2.88	0.228	0.396	1.17	81.5	1.48
40	3.50	0.178	0.573	1.42	82.9	1.81
54	3.05	0.560	1.57	1.73	84.7	1.25
68	1.95	1.62	1.98	1.85	86.5	0.200
82	2.36	1.41	0.786	1.52	88.0	0.793
89	3.88	1.27	0.814	1.99	90.0	1.65

95°C replicates days	50b	50c	100b	100c	200b	200c	ave50	ave100	ave200	ave all	replicates ave cum	stdev
0.11	3.29	19.2	4.27	9.75	2.48	9.10	11.2	7.01	5.79	8.02	8.02	6.26
0.25	30.8	18.1	12.4	21.4	17.3	13.1	24.4	16.9	15.2	18.8	26.9	6.74
0.96	20.2	14.2	11.4	23.1	18.1	16.6	17.2	17.2	17.4	17.3	44.1	4.18
1.3	1.74	2.43	1.47	3.41	4.49	6.03	2.08	2.44	5.26	3.26	47.4	1.76
2	1.28	2.31	1.08	1.20	2.80	2.92	1.80	1.14	2.86	1.93	49.3	0.844
5	0.699	2.75	0.91	1.35	1.04	1.46	1.72	1.13	1.25	1.37	50. 7	0.733
8	0.256	0.551	0.228	0.219	0.195	0.186	0.404	0.223	0.190	0.272	51.0	0.134
13	0.247	0.495	0.210	0.157	0.138	0.168	0.371	0.184	0.153	0.236	51.2	0.133
20	0.317	0.612	0.132	0.0987	0.538	0.181	0.464	0.115	0.360	0.313	51.5	0.217
27	0.948	0.254	0.324	0.280	0.756	0.274	0.601	0.302	0.515	0.473	52.0	0.301
34	1.27	0.870	1.78	0.595	1.01	0.050	1.07	1.188	0.530	0.929	52.9	0.589
40	7.55	5.92	4.21	6.98	6.50	8.66	6.74	5.60	7.58	6.64	59.6	1.51

75°C 1st days	200a	100a	50a	ave	cum ave	stdev
1	3.40	3.50	4.50	3.80	3.80	0.608
6	*9.35*	9.00	9.70	9.35	13.2	0.350
8	1.90	3.00	3.50	2.80	16.0	0.818
13	1.25	2.00	2.70	2.00	17.9	0.725
20	0.210	0.50	0.73	0.48	18.4	0.260
27	0.110	0.21	0.35	0.223	18.6	0.120
34	0.049	0.06	0.093	0.067	18.7	0.023
47	0.500	0.41	0.62	0.510	19.2	0.105
61	0.038	0.093	0.21	0.114	19.3	0.088
76	0.047	0.078	0.120	0.082	19.4	0.037

75°C replicates days	50b	50c	100b	100c	200b	200c	ave50	ave100	ave200	ave all	replicates ave cum	stdev
1	2.96	1.71	3.68	2.89	*3.4*	*3.4*	2.34	3.28	3.40	3.01	3.01	---
3	4.52	2.87	2.54	2.65	3.76	2.64	3.70	2.60	3.20	3.16	6.17	0.801
6	3.94	3.39	2.44	2.78	2.25	2.24	3.66	2.61	2.24	2.84	9.01	0.690
13	1.15	0.949	0.788	0.867	0.694	0.587	1.05	0.828	0.640	0.839	9.85	0.198
20	0.282	0.305	0.197	0.208	0.170	0.134	0.294	0.202	0.152	0.216	10.1	0.066
28	0.349	0.262	0.197	0.225	0.253	0.102	0.306	0.211	0.178	0.231	10.3	0.081
35	0.138	0.126	0.084	0.084	0.075	0.064	0.132	0.084	0.070	0.095	10.4	0.029

ambient 1st days	200a	100a	50a	ave	cum ave	sdev
1	0.25	*1.40*	1.40	1.40	1.40	---
6	1.10	2.90	2.70	2.80	4.20	0.141
8	0.13	0.50	0.92	0.71	4.91	0.297
13	0.18	0.36	0.74	0.55	5.46	0.269
20	0.19	0.23	0.63	0.43	5.89	0.283
27	0.092	0.10	0.27	0.185	6.08	0.120
34	0.073	0.17	0.35	0.26	6.34	0.127
48	0.11	0.11	0.31	0.21	6.54	0.141
62	0.12	0.16	0.33	0.245	6.79	0.120
76	0.07	0.17	0.29	0.23	7.02	0.085

ambient days replicates	50b	50c	100b	100c	200b	200c	ave50	ave100	ave200	ave all	replicates ave cum	stdev
1	1.04	1.43	0.838	0.754	**18.1**	0.628	1.24	0.796	0.783	0.938	0.938	7.00
4	1.61	1.88	0.065	3.32	3.54	1.98	1.74	1.69	2.76	2.06	3.00	1.26
8	1.01	0.349	1.30	1.04	0.959	0.560	0.680	1.17	0.760	0.870	3.87	0.349
12	0.718	0.444	0.231	0.430	0.397	0.289	0.581	0.330	0.343	0.418	4.29	0.169
19	0.483	0.297	0.090	0.306	0.270	0.207	0.390	0.198	0.238	0.275	4.57	0.129
26	0.272	0.326	0.105	0.237	0.211	0.237	0.299	0.171	0.224	0.231	4.80	0.074
33	0.101	0.101	0.049	0.082	0.074	0.041	0.101	0.065	0.0573	0.074	4.87	0.025
40	0.116	0.116	0.028	0.084	0.098	0.070	0.116	0.056	0.084	0.085	4.96	0.033