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ISOPAR® L RELEASE RATES FROM SALTSTONE USING SIMULATED SALT SOLUTIONS

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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 Deactivated 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 allowable concentration of Isopar® L in the DSS sent to SPF has been calculated at approximately 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 mg/L 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 Isopar® L release data can be treated as a percentage of initial concentration in the concentration range studied. 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 is larger than at lower temperatures. In one test at 95 °C essentially all of the Isopar® L was released in three months. Initial curing temperature was found to be very important as slight variations during the first few days affected the final Isopar® L amount released. Short scoping tests at 95 °C with solvent containing all components (Isopar® L, extractant, suppressor, and modifier) released less Isopar® L than the tests run with Isopar® L. Based on the scoping tests, the Isopar® L releases reported herein are conservative.

Isopar® L release was studied for a two-month period and average cumulative yield distributions were produced. From an SPF pouring perspective where saltstone will be poured in a shorter time period of one to two weeks, prior to being capped, the release of Isopar® L occurring in two weeks is more important. The average percentages of Isopar® L released after 13 days from saltstone are, to one sigma standard deviation: 60% ± 17% at 95 °C, 13% ± 4.3% at 75 °C, and 4.6% ± 1.2% at ambient temperature.

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LIST OF ACRONYMS

BOBCalix	calix[4]arene-bis(tert-octylbenzo-crown-6)
CSSX	Caustic-Side Solvent Extraction
CS-7SB	1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol
DSS	Deactivated Salt Solution
DWPF	Defense Waste Processing Facility
GC-MS	gas chromatography coupled with mass spectrometric detection
IR	infrared (IR)-spectroscopy
LFL	lower flammability limit
MCU	Modular CSSX Unit
PMP	Poly methyl Pentene
SPF	Salt Production Facility
SRNL	Savannah River National Laboratory
SWPF	Salt Waste Processing Facility
TOA	Trioctylamine
VOA	Volatile organic compound

2.0 INTRODUCTION

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 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 absorbants 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, Ispoar® 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 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 Isobar® 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 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 coupled with mass spectrometric detection (GC-MS). Minor changes in the experimental setup and method were made to adapt and quantify this method for Isopar® L and TOA. The minor changes such as using Teflon ferrules on the vessels and an autosampler for the GC-MS made running a set of initial samples prudent in case unforeseen problems arose. Two sets of replicate samples were run together starting a month later.

In addition to the testing 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 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 (BOBCalix).

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 o.d. and 58-mm i.d. The straight wall height is 76 mm high, and the total height not including the length of the ports is approximately 90 mm. It 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.

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 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 ports than the usual vessels. The first had an extra inlet port which was used to spike the vessel with a known quantity of solvent. Again a #7 Teflon plug was used with a 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. They were connected to the Teflon tubing via ~2-in. long Teflon-coated Tygon or Viton tubing.

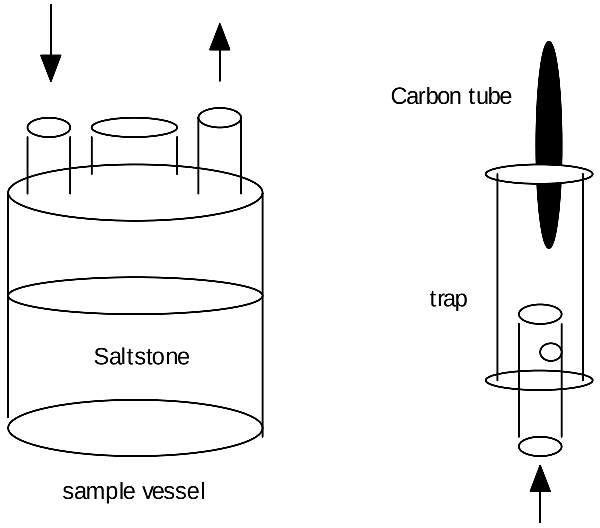


Figure 3-1. Geometry of test vessels.

Figure 3-2 shows the experimental setup for the first set of samples prior to the addition of replicate samples. 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. Basically, 117 g of DSS were weighed into a 250-mL, straight sided Poly methyl Pentene (PMP) wide-mouth jar. The PMP was not expected to absorb Isopar® L to a large extent during mixing. 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. After a set of samples was placed into the oven, the oven was turned on.

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 both initial and replicate tests. The salt solution make up is given in Table 3-1.

The initial concentrations of Isopar® L to be tested were 50 ppm, 100 ppm, and 200 ppm . Here, the 100 ppm concentration corresponds to the maximum expected amount in the DSS from MCU.[7] Excluding the other organic components will theoretically increase the vapor pressure of the Isopar® L and hence lead to a more conservative estimate of Isopar® L released from saltstone. However, the 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 expected to be in the CSSX baseline solvent.[12] The added TOA is not expected to lower the vapor pressure of Isopar® L much because of its low concentration (0.003 M) in the solvent. Rather, TOA should increase the Isopar® L release because it improves and stabilizes stripping. The large amount of modifier in the CSSX solvent would decrease the release of Isopar® L and so was not used. The expense and low concentration of BOBCalix 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 BOBCalix) from the 2 cm contactor testing. To make the DSS 200 ppm, 100 ppm, or 50 ppm in Isopar® L concentration, 31 µL, 15.5 µL, or 7.5 µL, of the Isopar® L/TOA solution were added to the samples.

Table 3-1. Composition of DSS Simulant.

Compound	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

Samples were made in triplicate for each of the Isopar® L concentrations and temperatures listed in Table 3-4. The samples were cured at each of the temperatures to determine the effect of curing temperature on the Isopar® L offgas rate. Replicates were added about a month after the initial sample set was begun. The time delay allowed an initial understanding of the system and detection method. A blank (simulant saltstone which contained no Isopar® L) was also made and run at each temperature.

As noted earlier, a standard sized vessel with four inputs was run at each temperature. These vessels were routinely spiked with a known amount of the Isopar® L/TOA solution to be used as a relative recovery standard. Initially, 10 μL of the solution were spiked with a standard Hamilton™ micropipette, 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	50 100 200	Ambient 75 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.

Vessels put in the oven at one time were purged in sequence, including blanks and the standard 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 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 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. The next time the vessels were samples they were sampled in the same sequence as previously.

Sampling was done with decreasing frequency as samples aged since the amount of Isopar® L released was expected to decrease with time. The initial samples were taken on days 1, 3, and 6 and then weekly. Final samples were taken after two months time. Replicates, especially in the 95 °C case, were taken more frequently in an attempt to better quantify the amount of Isopar® L released during the first few days of the experiment. The 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. One labeled sample #-BK and the other labeled sample #-FR. One milliliter of CS_2 was added to each vial as the eluent. The vial was capped, mildly shaken, and allowed to sit for approximately 30 minutes before analysis. If the samples were to sit for more than two hours prior to being run they were placed in the refrigerator.

Eluted 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 standard vessel tubes and tubes collected within the first week of sampling were diluted. Dilution was by taking 2 µL of the CS_2 eluted 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 various solvents. The carbon beds were desorbed with 1 mL of CS_2, hexane, or methanol, and the vials were processed as samples. Desorption efficiencies for each solvent were then calculated. The efficiencies were used to see if a less volatile solvent could be used to desorb tubes and to determine the collection efficiency of Isopar® L with CS_2 by this method.

Initial Isopar® L standards for analysis were made in CS_2 with Isopar® L by weight. Later standards were made in methanol also by weight. The methanol standards were more stable as they did not evaporate or separate, as fast as the CS_2 standards, or reflux when being run over time on an auto sampler.

3.3.3 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, a mass fragment indicative of organic compounds, and collecting the counts 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 correlation of the instrument. Three different GC-MS instruments were used during this work due to instruments breaking down.

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 spiked Isopar® L/TOA standard sample were run together. The analysis sequence generally followed the order; four Isopar® L concentration standards, a whole sequence, repeat of an Isopar® L concentration standard, a whole sequence,… two Isopar® L concentration standards. This sequencing allows both a linear correlation of the instrument with the Isopar® L concentration standards (in methanol) and a recovery standard to use as a ratio of a sample to spiked Isopar® L standard sample to remove sample variability seen in the volatile samples while waiting to be analyzed.

3.4 Scoping tests

3.4.1 IR 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 BOBCalix) 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. The tests were run in triplicate. The simulated DSS had been cycled through a bank of 2-cm contactors to produce the aqueous phase samples for grout 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 °C	25.0 °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 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.

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 looked at in the first two tests. In the first test, 10 µL of full solvent were added to the saltstone and mixed by shaking as done in previous tests. In the second, a surrogate salt solution and full solvent were run through 2-cm centrifugal contactors for mixing to model the expected DSS. Sample vessels for the first two tests were made alternately to remove any bias due to initial saltstone setting when being made prior to turning on the oven. That is, first a 10-µL spike sample was made as in previous Isopar® L/TOA saltstone preparations. Then, a contactor DSS was weighed out, premix was added, and the sample was shaken. After all six samples were made, the oven was turned on.

The difference between the amount of Isopar® L given off when the full solvent is added immediately after it has gone through a contactor and when the same solution is allowed to sit for an hour was looked at in the next tests. In the third test, a solution mixed in the contactors was put into a separatory funnel so that the solution could be removed from the bottom as would be done in the MCU with pumps. In the final test, a solution mixed in the contactors was allowed to separate for an hour before removing the solution from the bottom of the funnel to make saltstone. After all six samples were made, the oven was turned on.

4.0 RESULTS & DISCUSSION

The release of Isopar® L from saltstone has been 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 (1st) and replicates (2nd and 3rd). The Isopar® L release is presented as a percentage of the total using a relative ratio of the total added. Cumulative yield curves for all temperatures are calculated and discussed.

4.1 Isopar® L Measurement standards and analysis

Two different Isopar® L standards were used to quantify the Isopar® L release. The first were Isopar® L standards made up by weight in CS_2 or methanol. The CS_2 standards were used initially, but due to evaporation, condensing, and separation problems, all later standards were made up in methanol. Four standard concentrations were used: 1.08 ppm, 10.8 ppm, 108 ppm and 542.5 ppm. These standards were used to make a linear calibration curve for determining the Isopar® L concentration in ng/µl of each sample.

The second standard was a recovery standard consisting of a spike of a known volume of the original Isopar® L/TOA solution into an empty vessel at each temperature. The Isopar® L release of this recovery standard was collected on a carbon tube in the same manor as for the sample vessels. The spiking frequency used was the same as the sample collection frequency so a known amount of standard would go through the same environmental changes as that for the Isopar® L released from a sample. Carbon tubes from the standard spiked vessels were desorbed and analyzed on the GC-MS at the same time as the samples that they were initially collected with. Taking a ratio of the result of the Isopar® L that was released from a saltstone sample and collected on the carbon tube to that of its Isopar® L standard spike result removes the effects of the separation problems from CS_2 while the samples were being counted. The ratio also allows for an easier analysis of the data when using more than one GC-MS as instrument detection efficiencies for Isopar® L in CS_2 cancel out and do not need to be taken into account. This approach to data treatment is based on the assumption that the percentage of Isopar® L recovered and detected was the same for each sample and recovery standard in a given sample set.

Desorption efficiency or the recovery of Isopar® L from the carbon sampling tubes was also tested. Desorption efficiencies of 89.6 % and 83.3% were measured for an average of 86% ± 8% (2σ).

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 higher than anticipated, but not higher than the capacity of the sampling tube. However, some samples, notably the initial 95 °C samples and spiked standards, were outside the GC-MS calibration range. For these initial results, the ratio of the integrated area of the GC-MS for that sample to the integrated area of the GC-MS for the requisite standard spike was used to determine

Isopar® L amount. For later replicate samples, the sample tubes which were expected to be outside of the calibration were diluted in methanol prior to running on the GC-MS. Both the sample and sample dilution were then run in sequence on the GC-MS.

For a standard vessel spiked with 10 µL of Isopar® L/TOA solution, the concentration of Isopar® L in the CS_2 eluent solution following desorption of the carbon bed is calculated to be 7700 ng/µL when assuming a 0.77 g/mL Isopar® L density and 100% collection efficiency. Taking into account the tube desorption efficiency of 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, which are based on the Isopar® L in methanol calibration standards, were generally in this range. In order to better quantify the last statement the average recovery for the 95 °C spikes was calculated for two GC-MS instruments assuming 100% collection efficiency (i.e. 10 µL = 7700 ng/µL) For the one instrument, the relative recovery of the five 95 °C spike results are 98% ± 11% and 92% ± 16% respectively for the undiluted and diluted results. For the other instrument, the relative recovery of the fourteen 95 °C spike results are 87% ± 29% and 82% ± 22% respectively for the undiluted and diluted results.

Carbon tubes for the blanks were found to contain no Isopar® L in them. The carbon tube backs that were analyzed also had negligible Isopar® L and consequently a large number were not analyzed. One minor exception was for a tube which had been put in the collection port backwards. Both the front and the back results of this tube were added to determine the Isopar® L released.

Results are reported in percent of Isopar® L released from the original amount added to the 255 g saltstone sample. The results are calculated by dividing the ng/µL released by the sample by the ng/µL released by the spiked vessel, multiplying it by the amount of the standard 10 (or 5) µL per spike to get the relative amount of Isopar® L given off by the saltstone sample. This number is then divided by the amount of Isopar® L added to the vessel (31µL, 15.5µL, or 7.5 µL) to get the percent of 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 temperatures. Immediately after mixing, the saltstone had the consistency of a partially melted slushie and 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 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.

Figure 4-1. Saltstone after a few hours at 75 °C and 95 °C

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 4-1. The brown color of the bleed water disappeared within 24 hours. Typical heated saltstone samples after the brown color disappeared are shown in Figure 4-2. The bleed water remained on the top of the 95 °C and 75 °C samples for ~20 and 27 days, respectively.

One additional aspect of the heated samples is that they rose in the vessels due to a piston effect. The 95 °C samples began rising after a day and the 75 °C samples started by day three. Basically, as the bleed water percolated out of the saltstone in all directions it pushed uniformly on all sides of the vessel. Since the top of the vessel was open to the atmosphere the force on the bottom of the vessel could raise the sample. The force on the side of the vessel would be uniform with the bleed water acting as a lubricant to allow the sample to slide much like a piston.

Figure 4-2. Saltstone after 1 week at 75 °C on the left and at 95 °C on the right.

Figure 4-2 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 or 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, the bleed water on the side of the vessel cannot hold the gas in the lower void and the samples fall. A few are held up because of the dried saltstone on the side of the vessels, but the bleed water no longer separates the bottom gases from the vessel headspace thereby preventing the bottom gases from leaving the vessel.

4.2.2 Initial yields

The results from the initial experiments are shown in Figures 4-3 and 4-4. 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 Figures 4-3 and 4-4 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.

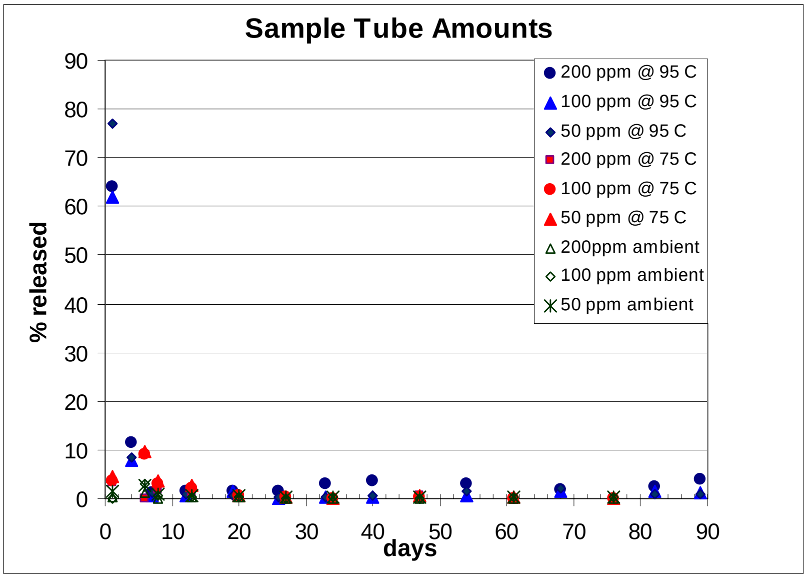


Figure 4-3. Isopar® L yield shown as % released from Saltstone.

Figure 4-4 gives a closer look at the data which shows a few other aspects of Isopar® L release in the experiment. The first is that the amount released initially increases from day one and decreases after the third day. The initial increase suggests that the Isopar® L is mixed and needs some time to disengage or diffuse through the saltstone to be released even before it sets. After the saltstone sets, the amount of Isopar® L released is much less until about 30 days after the experiment was started. At this time, the results from the ambient and heated samples diverge. The ambient results still decrease while the heated samples increase. The increased release of Isopar® L for the heated samples occurs at the same time the samples were observed to drop in the vessels. Thus, the increase seen in the heated samples is an artifact of the experiment and not an increase in Isopar® L release from the saltstone. One would expect the Isopar® L release to continue its decrease if the saltstone samples were uniform and the Isopar® L could only leave the saltstone from the top surface.

Although an artifact of the experiment, the release of Isopar® L from the bottom of the vessels is important to large scale saltstone production. Voids or cracks produced when making saltstone can be expected to retain the Isopar® L for some time. As in the experiment, the Isopar® L will be released when a path for it to percolate occurs.

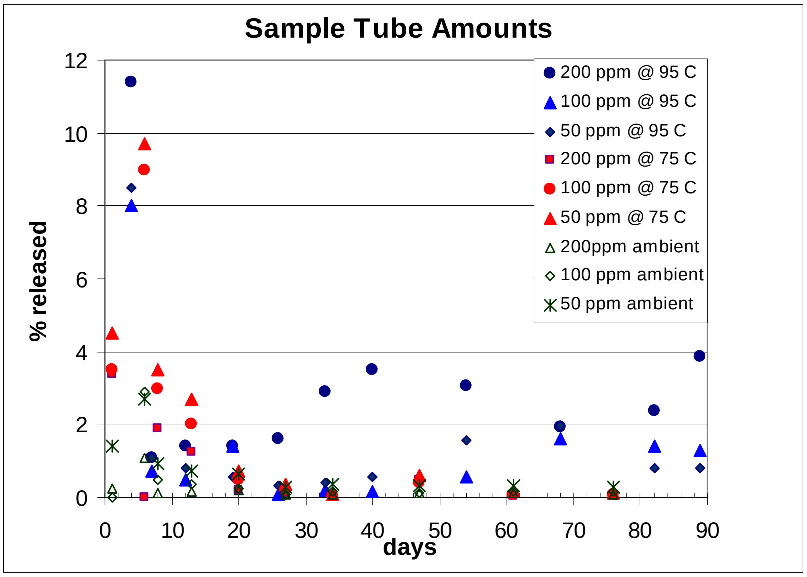


Figure 4-4. Isopar® L yield shown as % released from Saltstone expanded y axis.

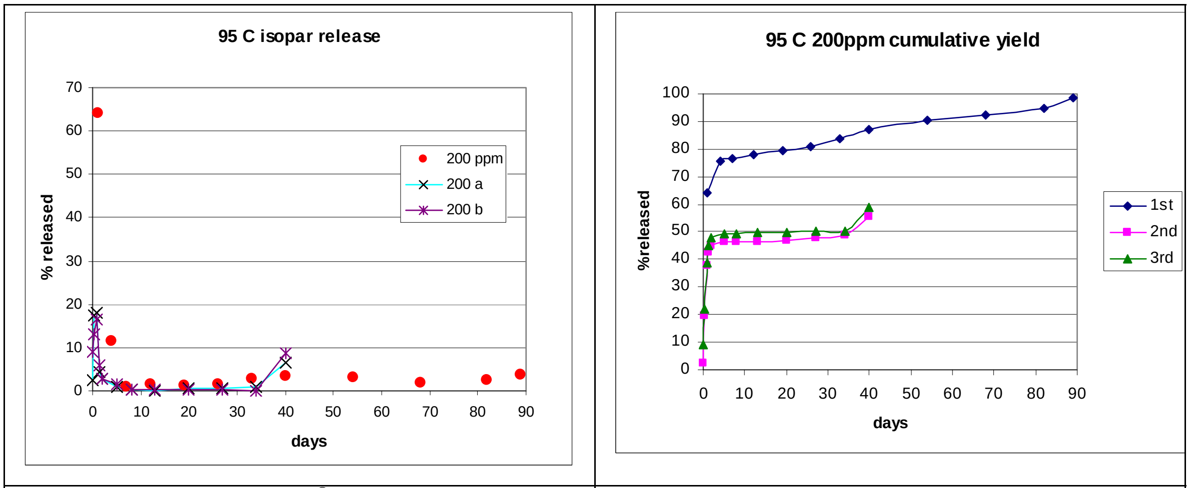
4.3 Isopar® L release replicate results

4.3.1 Isopar® L individual sample yields and cumulative yields

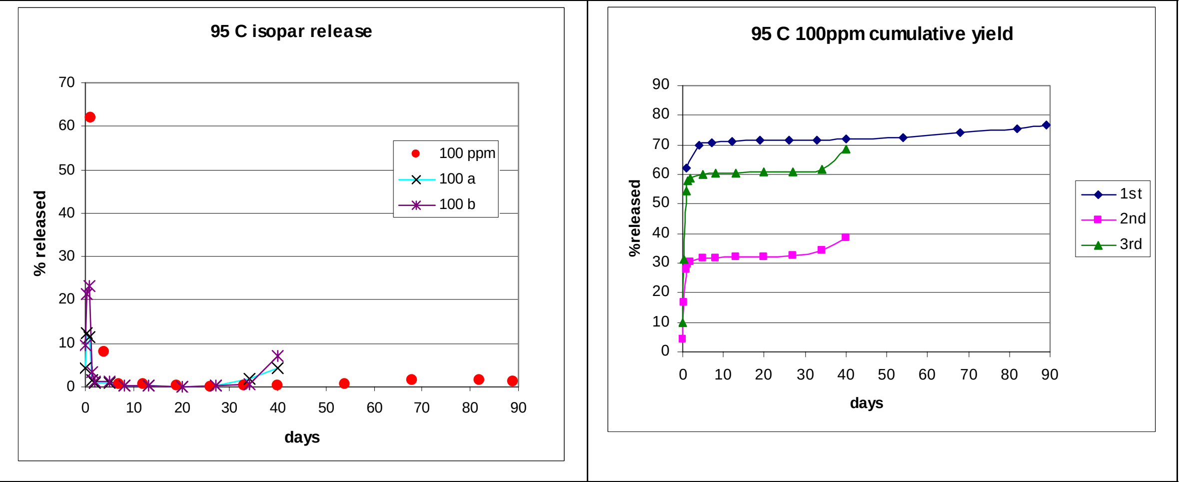
Replicate samples were made in the same manner and with the same material as the initial samples. The duration of the replicate tests was 40 days. The sampling frequency used for the replicates was the same as used previously except at 95 °C. In the 95 °C case, more frequent samples were taken in the 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 Figures 4-5 through 4-7 as a function of time for all the samples. Yields are presented as both carbon tube sample yields and cumulative yields as a percent of the initial amount of Isopar® L added that was released. The Isopar® L release for both replicate and initial samples are given on the same graph for each temperature and Isopar® L concentration for comparison. Curves for replicate samples are shown for illustrative purposes.

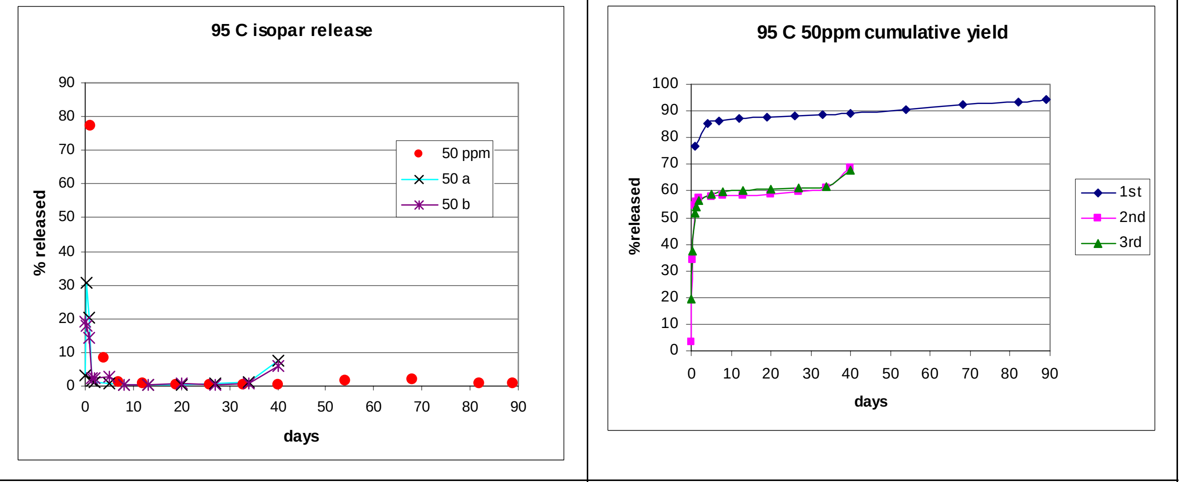
Although the yields are expected to be the same for the initial and replicate samples, there are some differences. The general release trends are the same. The greatest amount of Isopar® L is released within the first few days for all samples. The amount of Isopar® L decreases as time goes on. Considerably more Isopar® L is released at the higher temperatures. Differences in the release data are noticeable in the spread of the cumulative yield plots. The resulting differences will be discussed for each temperature.



a) 95 °C 200 ppm Isopar® L release | d) 95 °C 200 ppm cumulative yield

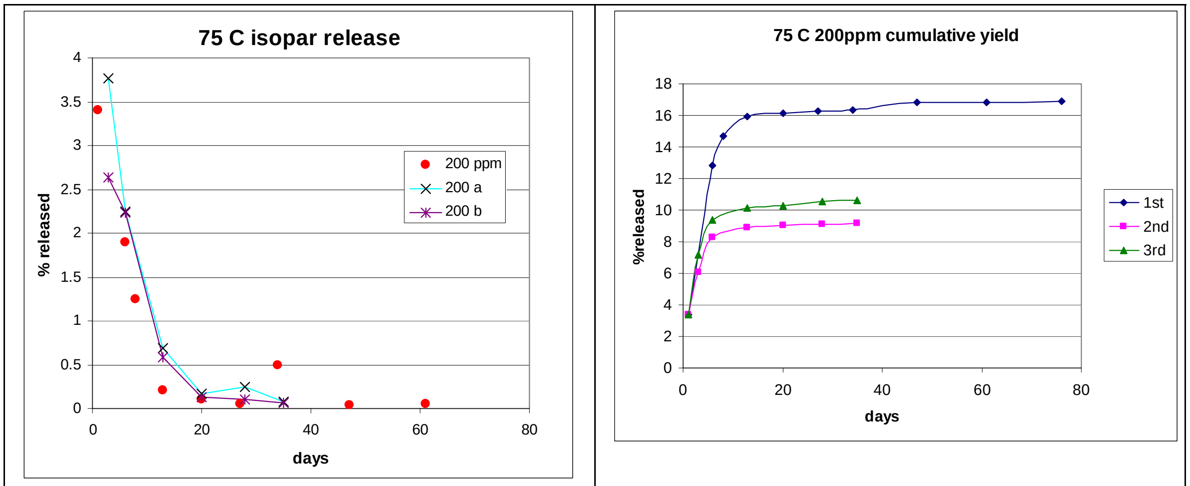


b) 95 °C 100 ppm Isopar® L release | e) 95 °C 100 ppm cumulative yield

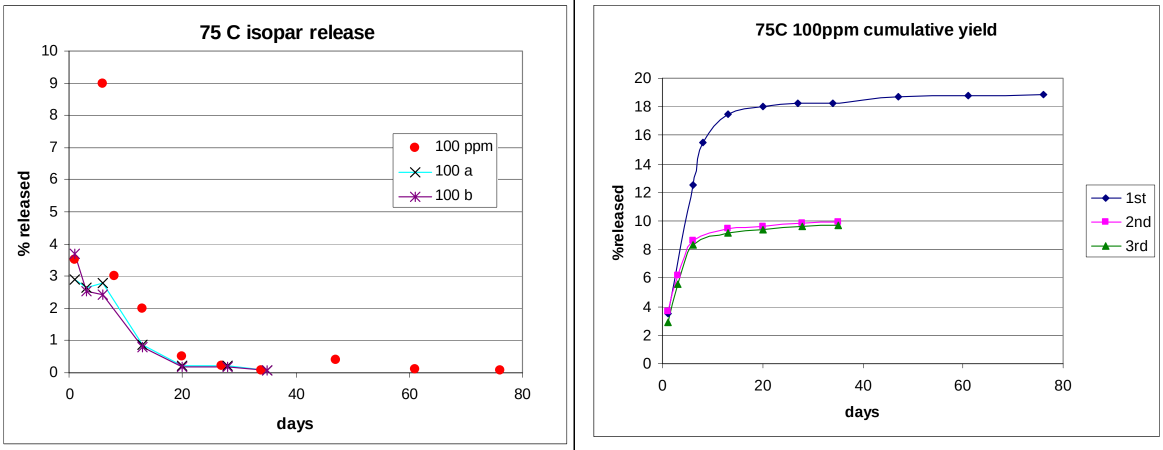


c) 95 °C 50 ppm Isopar® L release | f) 95 °C 50 ppm cumulative yield

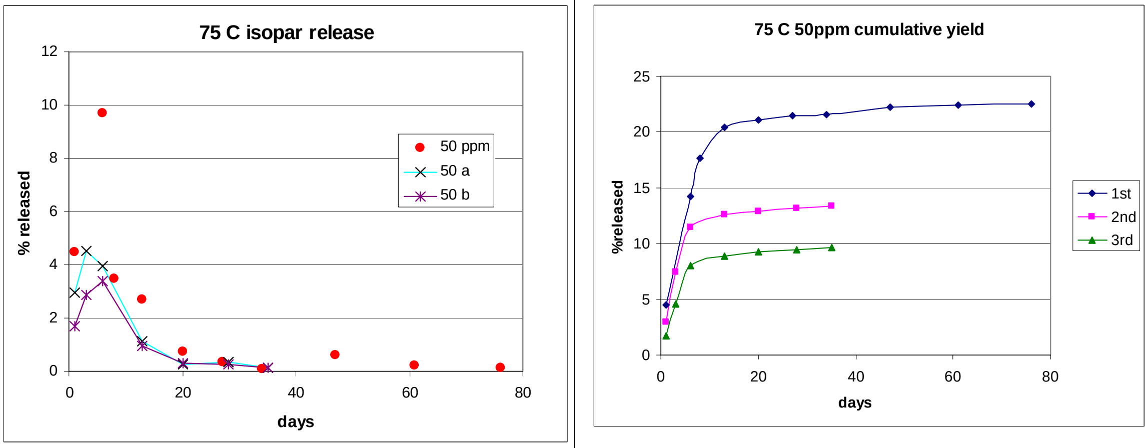
Figure 4-5. Plots of Isopar® L release, both yield (a-c) and cumulative yields (d-f), for 50 ppm, 100 ppm and 200 ppm concentrations of Isopar® L at 95 °C.



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

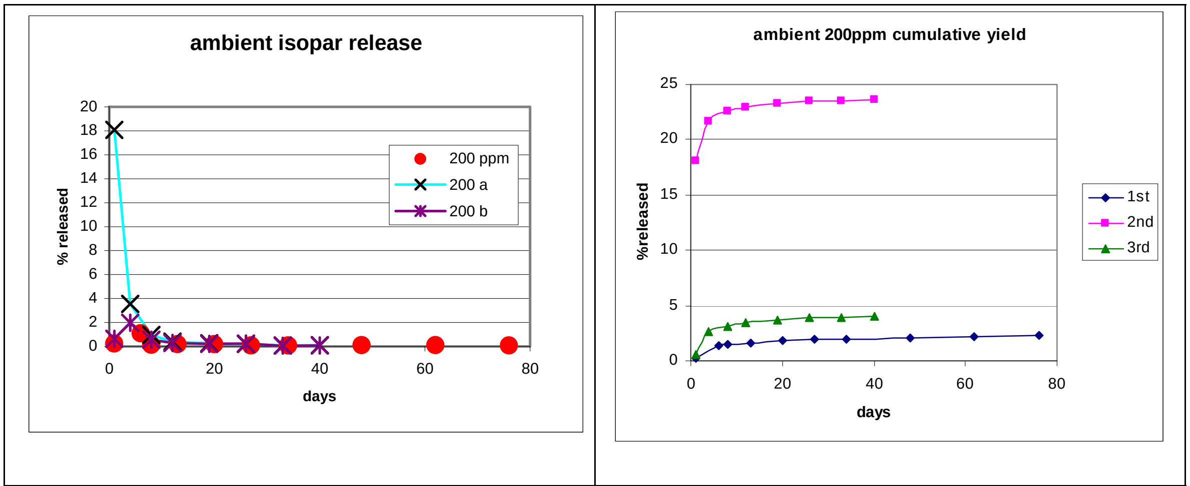


b) 75 °C 100 ppm Isopar® L release e) 75 °C 100 ppm cumulative yield

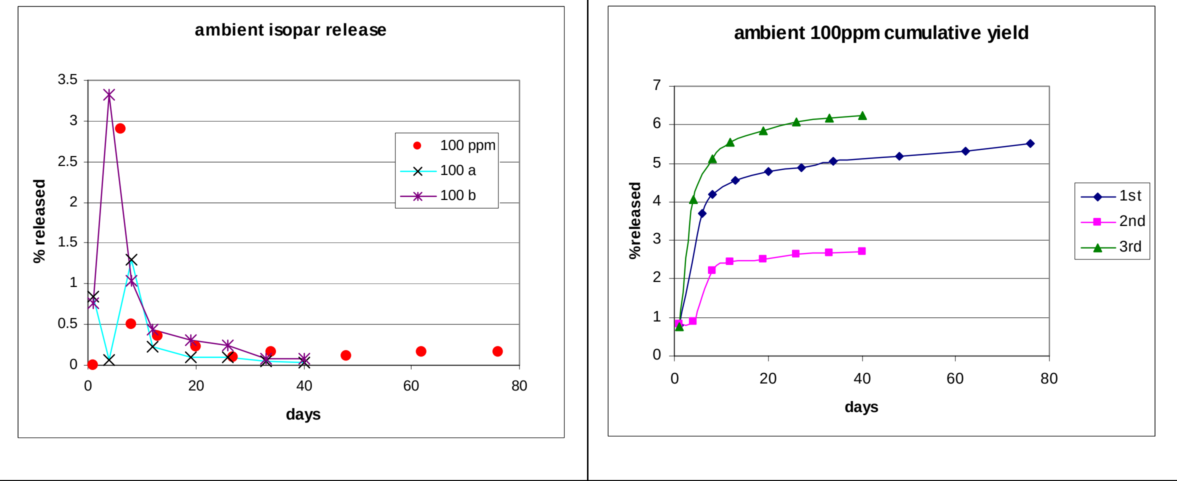


c) 75 °C 50 ppm Isopar® L release f) 75 °C 50 ppm cumulative yield

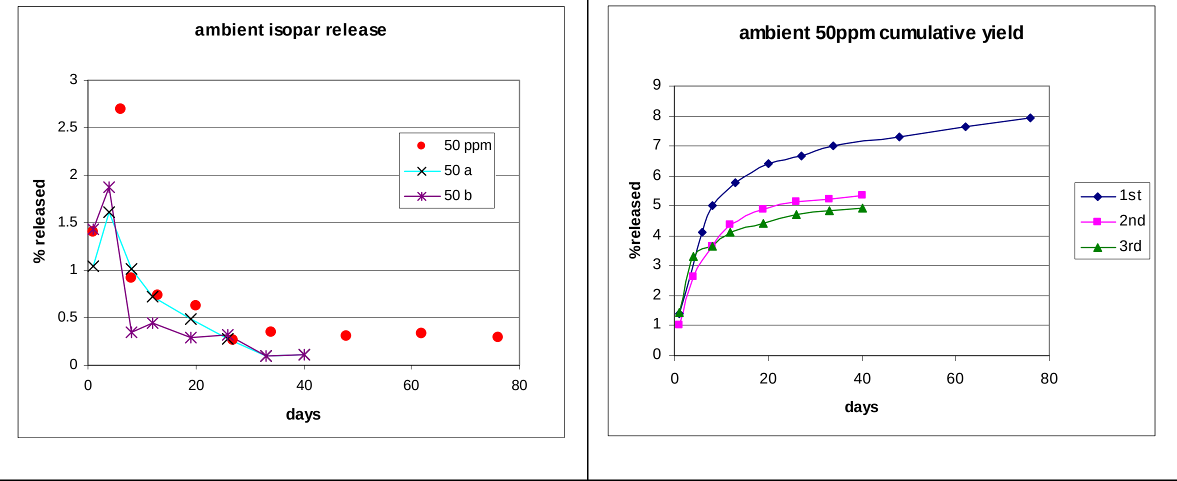
Figure 4-6. Plots of Isopar® L release, both yield (a-c) and cumulative yields (d-f), for 50 ppm, 100 ppm and 200 ppm concentrations of Isopar® L at 75 °C.



a) ambient 200 ppm Isopar® L release d) ambient 200 ppm cumulative yield

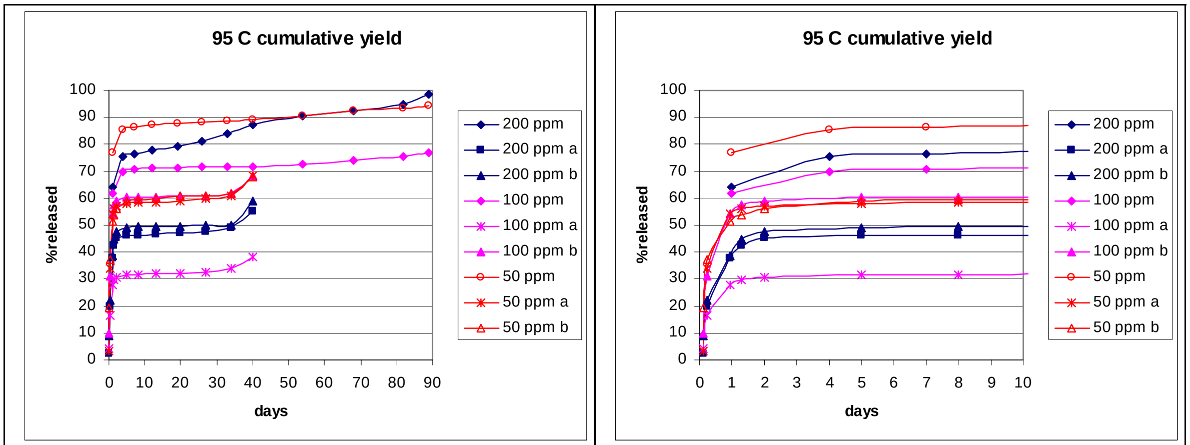


b) ambient 100 ppm Isopar® L release e) ambient 100 ppm cumulative yield

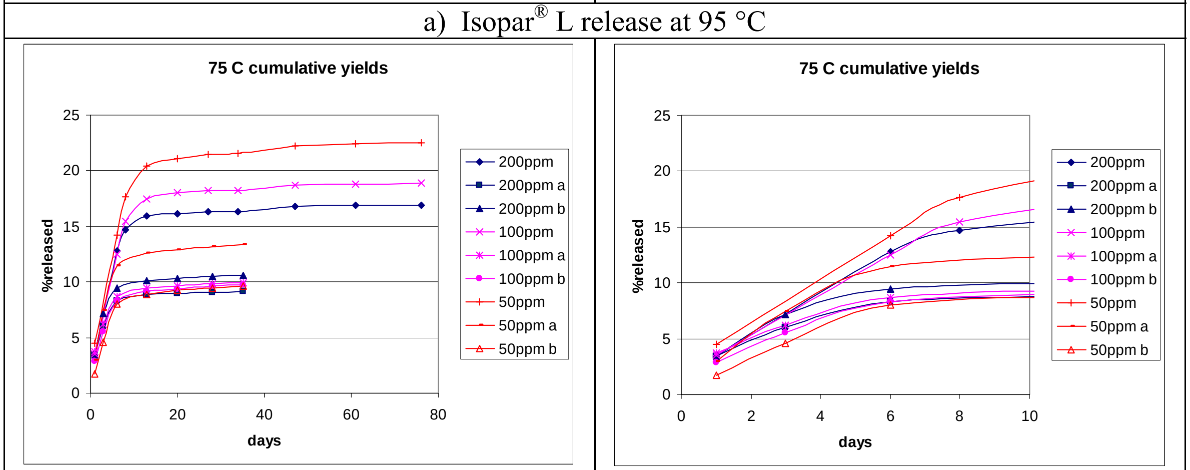


c) ambient 50 ppm Isopar® L release f) ambient 50 ppm cumulative yield

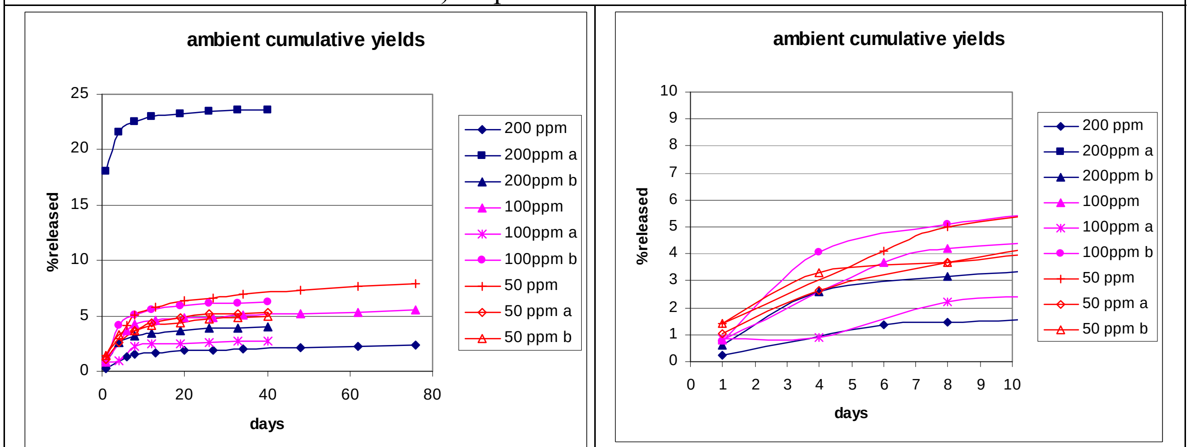
Figure 4-7. Plots of Isopar® L release, both yield (a-c) and cumulative yields (d-f), for 50 ppm, 100 ppm and 200 ppm concentrations of Isopar® L at ambient temperature.



a) Isopar® L release at 95 °C



b) Isopar® L release at 75 °C



c) Isopar® L release at ambient temperature

Figure 4-8. Cumulative yields of Isopar® L for all concentrations of Isopar® L at each temperature full and expanded scales.

Figure 4-5 shows the results of the 95 °C samples. Three differences in the 95 °C results can be seen. The first is that unlike the data for the 75 °C and ambient replicates, an upturn in the percent Isopar® L at forty days is seen. Although the amount is a bit higher than in the initial test, an increase is expected as it is an artifact of the experiment. The second is that all of the initial tests have a greater release. The replicates were spiked with the same amount of the Isopar® L/ TOA solution as the initial tests thus release would be expected to be the same unless some of the amount released initially was not captured. As the ports, when checked, were tightly sealed and the replicate tests consistently lost ~50%, it is unlikely that an amount of Isopar® L released initially was not captured. One possible explanation is that due to this being the first test run, more time was taken in spiking the empty vessel with the standard Isopar® L/TOA standard. The oven, in trying to maintain the temperature at 95 °C, may have overcompensated when the door was shut. The few samples in the oven may have increased in temperature beyond the 95 °C setpoint. Later standard spiking was quicker, and a larger number of saltstone samples at heat would minimize overcompensation. Unfortunately, the first week of the 95°C temperature logger data was lost during transfer, so the increase can not be quantified. The last difference in the data is more subtle. All of the third replicates give off a greater amount of Isopar® L than the second replicates. The difference is small for the 50 ppm and 200 ppm concentrations but considerable at 100 ppm.

The difference in the replicate results may be explained by the order in which the samples were made up and how long the saltstone sat before it reached temperature. Making the six replicates and placing them into the oven took 37 minutes. The first three saltstone samples were made in the order 100 ppm, 200 ppm, 50 ppm. The next three were made in the order 200 ppm, 100 ppm, and 50 ppm. The second set had considerably more time at ambient temperature for the saltstone to start to jell before the oven was turned back on than the third set did. Looking at the data one can see that the first set of replicates made (the second set) all had lower Isopar® L release than the second set of replicates made (the third set) at the two hour sampling. Even at the six hour sampling this is true. As for the large difference in the 100 ppm cumulative curves for the replicates, the time between making the 100 ppm samples was almost twice as long as the other two concentrations 31 minutes verses 17 minutes and 19 minutes for the 200 ppm and 50 ppm, respectively.

Figure 4-6 shows the results of the 75 °C samples. The main difference in the 75 °C results is that the replicate results are again lower than the initial sample results. On the 100 ppm and 50 ppm yield plots, the ~9% yield point seems considerably higher than the replicate ~3% yields. However, the replicates were measured on the third and the sixth day, so the sum of these results should equal the Isopar® L release for the initial sixth day point. The replicate three and six day sum of ~6% is still lower than the initial result. The greater release can be explained, as in the 95 °C case, by an increase in temperature during the initial setting of the saltstone. In the initial test, the oven was mistakenly set to 95 °C instead of 75 °C. Although caught quickly at the beginning of the experiment, the oven was above 75 °C for less than 15 minutes and reached 91 °C.

Differences in makeup time are less than in the 95 °C experiments so the variation due to the saltstone jelling would be small. Times for replicate sample preparation at each concentration are 19 min, 19 min, and 16 min for 200 ppm, 100 ppm, and 50 ppm, respectively. The difference between the replicate data is thus expected to be mainly due to sample or Isopar® L measurement.

To calculate the cumulative yields at 75 °C, the three datum that were missing were replaced with the average of the other experiments. The six day initial 200 ppm result was lost due to evaporation in the sample vial during measurements. An average (9.4% ± 0.5%) of the initial 100 ppm and 50 ppm results is used on the cumulative plots. Results from the first sampling of the 200 ppm replicate samples are absent and both have been replaced by the initial sample result of 3.4% for comparison.

Figure 4-7 shows the results of the ambient samples. Differences in the initial and replicate data are small except for the 200 ppm data. The initial ambient samples were made up at 27 °C and the replicates were made at 22 °C. Replicate data at 200 ppm would be expected to release less Isopar® L due to the lower temperature during preparation, but they are greater. The initial sample release is far less—approximately half of the lower replicate value. The simple explanation is that when the initial sample was made up a carbon tube slipped through the output port and remained in the saltstone with the open end just above the saltstone surface. The carbon in the tube adsorbed a portion of the Isopar® L released, thereby lowering the amount that was adsorbed on the carbon tube attached to the outlet port. This result is much like the addition of coal or clays to cement to reduce loss of organics. The first data point for the first 200 ppm replicate indicates an 18% release of Isopar® L. This 18% release is as yet unexplainable, but two possibilities exist. The first is that the saltstone was not mixed thoroughly when made; the second is that the sample partially evaporated prior to or while being measured, thus the solution was artificially concentrated in Isopar® L. As all of the saltstone samples were mixed by the same person in the same way the second explanation is far more plausible. Either way the initial 200 ppm data and the 18% point of the second replicate will not be used to determine the average cumulative yields.

Figure 4-8 shows the cumulative release data for all concentrations as a function of temperature for comparison. The results for the initial samples at 95 °C and 75 °C are definitely higher than the replicate results. However, looking at the variability in the replicate data, especially the 100 ppm 95 °C and the 50 ppm 75 °C data, the initial results may not be statistically different from the replicate data.

When looking at all the results, it appears that the release of Isopar® L is not a function of initial concentration at these low levels. If it were, the percent released would follow a pattern throughout such as 50 ppm release > 100 ppm release > 200 ppm release, which is not apparent in the results. Although, it does appear that as the temperature increases an increased spread between the results from the data at different concentrations occurs.

The slope of the cumulative yield distributions level out after a few days and remain relatively flat until day 30 when the saltstone samples drop in the vessels. A Ficks 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 expected in the pour schedules being looked at. Shorter term data are more important and are shown in the right half of Figure 4-8.

The most important aspect of the cumulative yields 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.

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.

4.3.2 Isopar® L average cumulative yields

The average cumulative yield was calculated by averaging all concentrations and samples of a single temperature. The reasoning for this is that the saltstone pour schedule being considered is short in duration, so the earlier Isopar® L release data is most important. The earlier data has a large variance between replicates at a concentration which encompasses the other concentrations at a given temperature. Although differences due to minor short-term temperature variations while setting can explain this, the averaging of the replicates and the initial samples was justified for two reasons. The first is that saltstone processing will not be able to control minor short-term temperature changes that well. The second is that the saltstone will be produced at elevated temperature, unlike in the experiments where the samples were prepared at ambient temperature and then brought up to the test temperature. Starting at temperature will likely increase the release of Isopar® L compared to the experiments, so the higher initial sample results can be included.

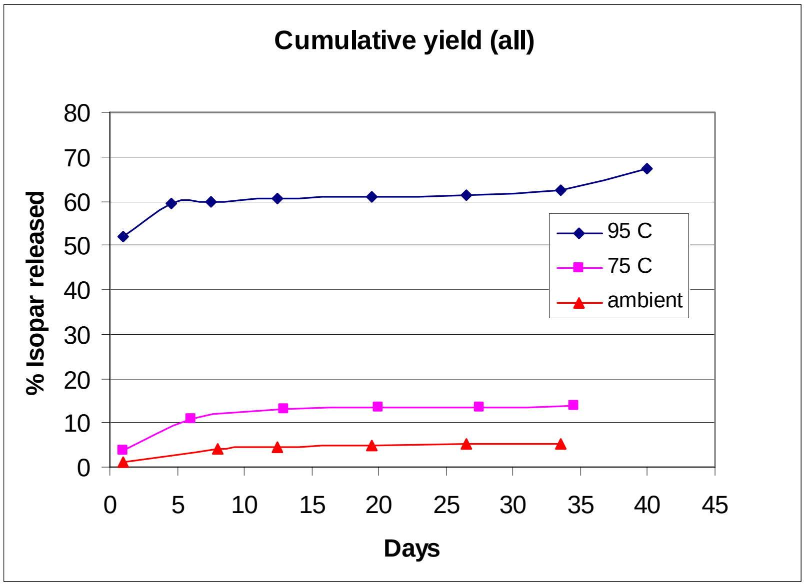


Figure 4-9. Average cumulative yield of Isopar® L

The average cumulative yield curves for Isopar® L release at 95 °C, 75 °C, and ambient temperature are shown in figure 4-9. They were calculated by averaging the cumulative yields at a specific time at one temperature over all initial sample concentrations. The ambient temperature data for the initial 200 ppm sample and the 18% release data point for the 200 ppm replicate a sample were not used as explained earlier. The first sampling of the 75 °C replicates also was estimated as previously described in section 4.3.1. Some of the averages are over time intervals that are different by a day and are plotted with an average time. As an example, the 95 °C initial samples were taken after 4 days and the replicate data were taken after 5 days.

These values were averaged and the average cumulative yields are shown at day 4.5. From this data it can be seen that the higher the temperature the higher the amount of Isopar® L is released and the quicker the plateau is reached.

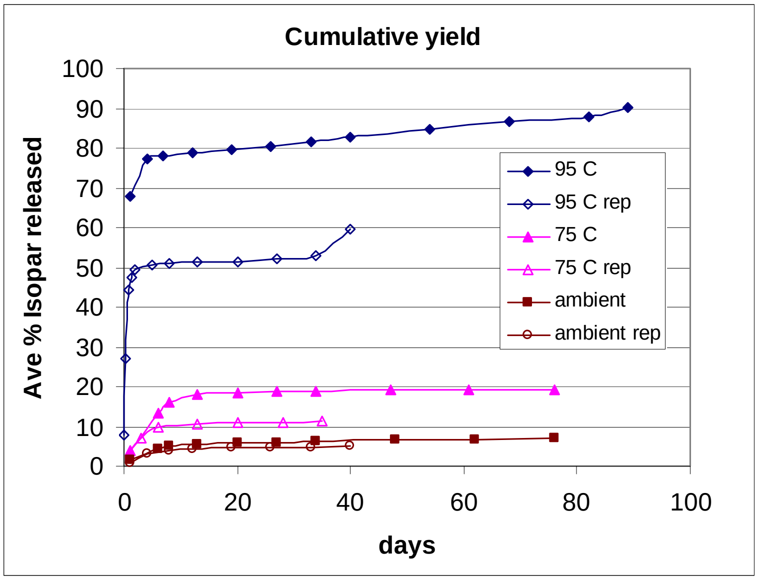


Figure 4-10. Average cumulative yield comparison for initial and replicate results.

As a check, the average cumulative yields of both the initial and replicate samples were calculated separately along with their standard deviations. The yield curves are shown in Figure 4-10, and the 6 day and 13 day average cumulative yields are given in Table 4-1. The resulting average yields appear to be quite different. However, to 2σ they are not statistically independent. Thus the average of all the data at a temperature will be used to report the average cumulative yield.

Table 4-1. Average cumulative yields of Isopar® L

Time & temp	Initial results % + 1σ	Replicate results (a, b) % + 1σ	All results % + 1σ
13 days at 95	79 ± 8.0 (12 d)	51 ± 11	60 ± 17 (12.5 d)
13 days at 75	18 ± 2.3	9.8 ± 1.3	13 ± 4.3
13 days at ambient	5.5 ± 0.42	4.3 ± 1.3 (12 d)	4.6 ± 1.2 (12.5 d)
6 days at 95	77 ± 7.8 (4 d)	51 ± 11 (5 d)	59 ± 16 (4.5 d)
6 days at 75	13 ± 2.0	9.0 ± 1.3	10 ± 2.3
6 days at ambient	4.2 ± 0.14	3.0 ± 1.3 (4 d)	3.3 ± 1.2 (6+4 d)

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 4-11. 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 4-11. After shaking, no blue fluorescence is seen when the UV lamp (380 nm) lamp was shone on the mixed sample as shown in Figure 4-12 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 4-11. The blue color becomes less intense closer to the bottom of the funnel hence 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 4-11. Dyed solvent on top of premix and salt solution, and dyed solvent after being mixed with salt solution with a contactor.

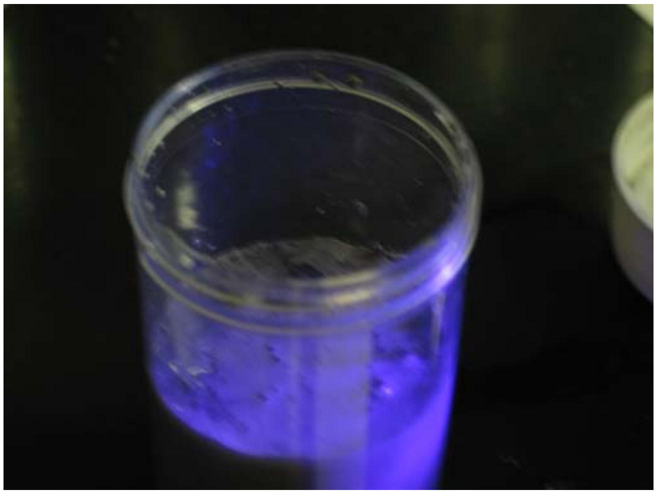


Figure 4-12. Dyed saltstone after mixing no fluorescence

No major difference was seen in the Isopar® L release at 95 °C due to the mixing method used with the full solvent. The results of the two mixing methods are shown in Figure 4-13 along with the average ng/µL Isopar® L released of the replicates. 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 stimulant, the spread of the data is too large to state this as fact. Additionally, the initial concentration of Isopar® L cannot be compared since results from the contactor DSS samples taken were compromised during analysis.

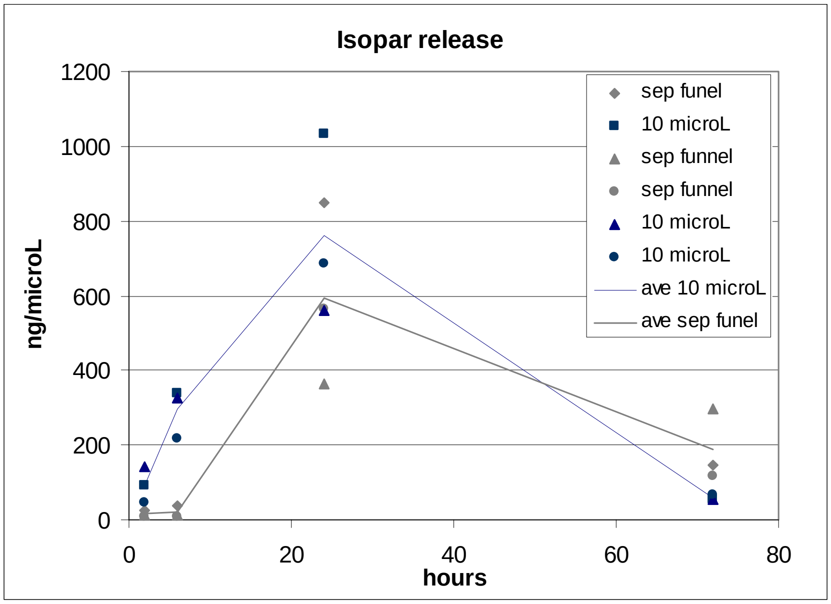


Figure 4-13. Isopar® L release at 95 °C from saltstone made with full solvent mixed by two methods.

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 be easily made due to sampling frequency. However, using the Isopar® L/TOA spike as a standard, the amounts of Isopar® L released after 3 days by the full solvent tests are 27%, 20%, and 19% for a cumulative average of 22% ± 5% (1 σ). The amounts released for the two results from the fifth day 50 ppm 95 °C replicates are 58.3% and 59.5%. Thus the amount released by the full solvent tests is at minimum ~37% lower than that released in the Isopar® L/TOA experiments. If one ignores the large standard deviation, the lowering of the Isopar® L release in the full solvent case is greater than the expected 17% due to the mole fraction of the modifier as has been seen in earlier studies.[14]

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 4-14 shows the Isopar® L release for both the immediate and one hour aging 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 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. The concentrations found were 66 mg/L and 58 mg/L for the DSS solution and 49 mg/L and 46 mg/L after an hour aging. 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.

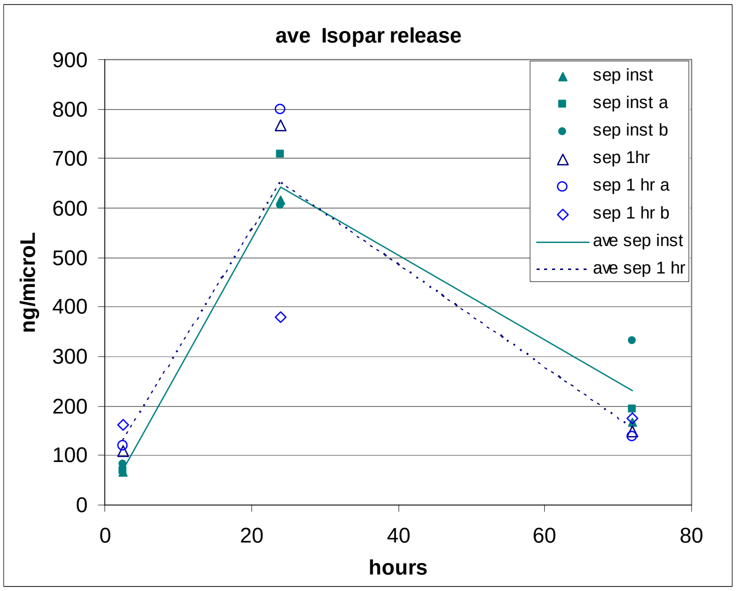


Figure 4-14. Isopar® L release from saltstone made with full solvent immediately and after one hour disengaging time.

Finally, the average Isopar$^{®}$ L release for all of the scoping tests is shown in Figure 4-15. The seemingly large difference between the 10 µL mixed sample and the contactor samples ng/µL 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.

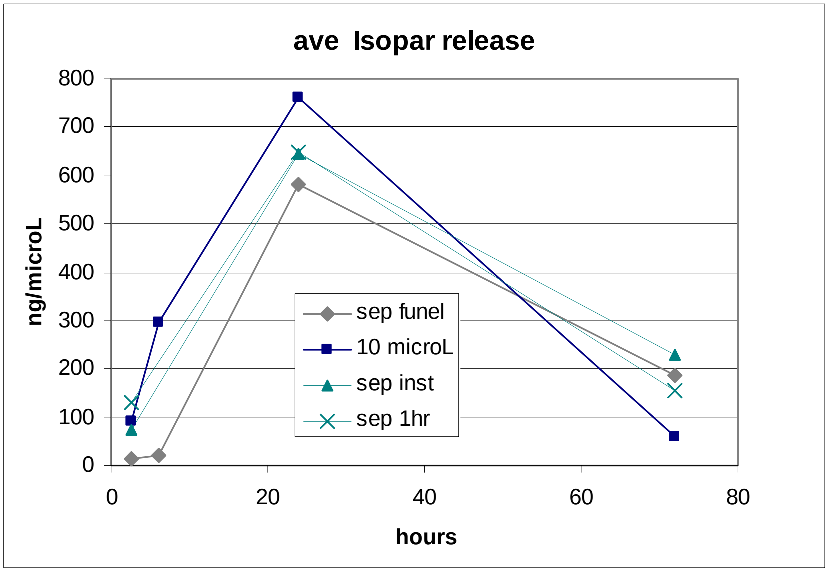


Figure 4-15. Average Isopar$^{®}$ L release for all scoping tests

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 higher temperature samples rose in their vessels due to a piston effect. After 30 days the bleed water would no longer separate the bottom gases from leaving the vessel. The increase of Isopar® L released due to this artifact of the experiment parallels the expected release from voids or cracks in the saltstone vaults.

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 Isopar® L yield results show that the majority of the Isopar® L was released in the first few days. The release begins immediately. 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 yield distributions showed that initial curing temperature was very important. Slight variations in temperature during the first few days affected the final Isopar® L amount released. A considerable, although not statistical, difference between the initial and replicate samples at 95 °C and 75 °C can be attributed to minor 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 that 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.

Finally, the average cumulative yield distributions were calculated for Isopar® L release at 95 °C, 75 °C, and ambient temperatures. From a SPF pouring perspective, a time period of a week or two is most important. The average percentage of Isopar® L released after 13 days from saltstone is to one sigma standard deviation; 60% ± 17% at 95 °C, 13% ± 4.3% at 75 °C, and 4.6% ± 1.2% at ambient temperatures.

6.0 REFERENCES

1. "Direct Grout Stabilization of High Cs Salt Waste: Salt Waste Alternative Phase III Feasibility Study(U)" WSRC-TR-98-00337, C. Langton, Sept. 1998.

2. "Characterization and Recovery of Solvent Entrained During the Use of Centrifugal Contractors" ANL-02/08, H.A. Arafat, M.C. Hash, A.S. Hebden, and R. A. Leonard, Oct. 2001.

3. "Recovery of Entrained CSSX Solvent from Caustic Aqueous Raffinate Using Coalescers", ANL-02-34, C. Pereira, H.A. Arafat, J.R. Falkenberg, M.C. Regalbuto, and G.F. Vandergrift, Nov. 2002.

4. "A Literature Review of Mixed Waste Components: Sensitivities and Effects Upon Solidification/Stabilization in Cement-Based Matrices", ORNL/TM-12656, C.H. Mattus and T.M. Gilliam, Mar. 1994.

5. "Literature Review of Stabilization/Solidification of Volatile Organic Compounds and the Implications for Handford Grouts" ORNL/TM-11824, R.D. Spence and C.S. Osborne, Sept. 1993.

6. "CSSX Solvent Limits at Saltstone", X-CLC-Z-00010 Rev. 0, P.D. d'Entremont, Feb. 2004.

7. "Examination of Organic Carry over from 2-cm Contactors to Support the Modular CSSX Unit" C.A. Nash et al., WSRC-TR-2005-00182, Rev. 0, 2005.

8. "Isopar® L Release Rates from Saltstone" WSRC-RP-2005-01581, A.D. Cozzi and M.G. Bronikowski May 2005.

9. "Measurements of Flammable Gas Generation from Saltstone Containing Simulated Tank 48H Waste (Interim Report)" WSRC-TR-2005-00180, Revision 0, A.D. Cozzi, et al., April 2005.

10. "NIOSH Method 1501 issue 3, Aromatic Hydrocarbons", NIOSH Manual of Analytical Methods (NIMAM), 4th edition Mar. 15, 2003.

11. "Determine Isopar L Release Rates from saltstone",SSF-TTR-2005-0004, Rev. 1, M. Naroto, 5/25/05.

12. "Caustic Side Solvent Extraction: Chemical and Physical Properties of the Optimized Solvent" ORNL/TM-2002/190 L.H Delmau et al., Oct. 2002.

13. "Formulation Development for Processing Tank 48H in Saltstone," WSRC-TR-2004-00477, Revision 0, A.D. Cozzi, 2004.

14. "Information on CSSX Solvent Properties", SPD-05-067, Letter to V.G. Dickert, Planning & Integration Technology, WSRC from C. Hansen DOE Asst. Mgr. Waste Disposition Project.

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APPENDIX

1. Calculation of the amount of Isopar® L used.

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;

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

23.4 mg Isopar® L ÷ 0.77mg /μL Isopar® L = 30.4 /μL Isopar® L needed

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

2. Relative Ratio Calculation.

$$\frac{\text{ng/μL Isopar® L sample}}{\text{ng/μL Isopar® L spike}} \text{ x 10λ (5λ) Isopar® L in spike = \#λ released by the sample}$$

$$\frac{\text{\#λ released by the sample}}{\text{initial λ (31,15.5,7.5) in sample}} \text{ x 100 = \% Isopar® L released by the sample}$$

3. 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 yields reported. Data not utilized, such as the 200 ppm ambient data are highlighted in yellow. Average data added for missing data to make cumulative yields as described in the text is given in red.

95°C 1st days	200	100	50	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	50a	50b	100a	100b	200a	200b	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	200	100	50	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	0.500	0.730	0.480	18.4	0.260
27	0.110	0.210	0.350	0.223	18.6	0.120
34	0.049	0.060	0.093	0.067	18.7	0.023
47	0.500	0.410	0.620	0.510	19.2	0.105
61	0.038	0.093	0.210	0.114	19.3	0.088
76	0.047	0.078	0.120	0.082	19.4	0.037

75°C replicates days	50a	50b	100a	100b	200a	200b	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	200	100	50	ave	cum ave	sdev
1	0.250	1.4	1.40	1.40	1.40	---
6	1.10	2.90	2.70	2.80	4.20	0.141
8	0.130	0.500	0.920	0.710	4.91	0.297
13	0.180	0.360	0.740	0.550	5.46	0.269
20	0.190	0.230	0.630	0.430	5.89	0.283
27	0.092	0.100	0.270	0.185	6.08	0.120
34	0.073	0.170	0.350	0.260	6.34	0.127
48	0.110	0.110	0.310	0.210	6.54	0.141
62	0.120	0.160	0.330	0.245	6.79	0.120
76	0.070	0.170	0.290	0.230	7.02	0.085

ambient days replicates	50a	50b	100a	100b	200a	200b	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

Distribution:

J.E.	Marra,	773-A
R.E.	Edwards,	773-A
D.A.	Crowley,	773-A
A.M.	Murray,	773-A

T.B.	Calloway,	999-W
C.C.	Herman,	773-42A
N.E.	Bibler,	773-A
J.R.	Harbour,	773-42A
C.M.	Jantzen,	773-A
G.G.	Wicks,	773-A
C.W.	Gardner,	773-A
M.A.	Heitkamp,	999-W

M.S.	Miller,	704-S
J.E.	Occhipinti,	704-S

C.J.	Berry	999-W
T.E.	Chandler,	704-Z
D.T.	Conrad,	766-H
P.D.	D`entremont,	766-H
J.M.	Duffey,	773-A
R.E.	Eibling,	999-W
S.D.	Fink,	773-A
J.C.	Griffin,	773-A
W.L.	Isom,	766-H
A.W.	Knox,	704-Z
C.A.	Langton,	773-43A
C.A.	Nash,	773-42A
M.A.	Norato,	773-A
S.J.	Robertson,	766-H
J.P.	Schwenker,	703-H
D.C.	Sherburne,	704-S
A.V.	Staub,	704-28S
P.C.	Suggs,	766-H
D.G.	Thompson,	704-Z
W.R.	Wilmarth,	773-42A
J.R.	Zamecnik,	999-W