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Use of Blends in Commercial Refrigeration Systems: Fractionation characteristics and material compatibility of R-448A

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ABSTRACT

The development of lower global warming potential (GWP) blends offers an alternative for the widely used high GWP fluids such as R-404A. Commercial refrigeration systems for supermarkets are a common example for such systems. These kinds of systems show relatively large refrigerant leakage rates of 15% to 20% per year. The newly developed R-404A lower GWP alternatives are zeotropic blends, meaning they show a temperature glide during phase change processes in the evaporator and condenser of the system. Because of the glide, there is a concern within end users that the blend components could separate, or fractionate, during a leak event. This paper will describe the results from tests carried out to determine the effect of refrigerant fractionation and particularly its effect on the performance of an actual refrigeration system subject to multiple leak events. The second part of this paper provides characteristics for the solubility and miscibility of R-448A with POE oil and results from a material compatibility study of R-448A with common materials used in refrigeration equipment.

1. FRACTIONATION

1.1 Literature review

Fractionation is the shift in refrigerant blend composition of zeotropic mixtures due to leakage. The potential issue of refrigerant mixture fractionation, and its effect on the system performance and blend composition has been of interest to users and developers for years. Kruse et al (1992) investigated the effect of leakage from the two-phase region on a large glide zeotropic blend (R23/R152a) in an automotive air conditioning system and in a supermarket refrigeration system using a near azeotropic blend (R125/R290/R22, 38/2/60). In both cases the composition was analyzed using a gas chromatograph. For the large glide blend it was reported that the concentration was not influenced until bubbles in the sight glass before the expansion valve were seen indicating low charge levels. In case of the near azeotropic blend only a small shift in composition was seen even after 50% of the mass had leaked out.

Extensive investigations were done by Biancardi et.al. (1996) who analyzed the influence of lubricant, the charging process, the influence of transients on the fractionation inside the system as well as leakage scenarios for a system using R407C. They determined that fractionation effects inside the system due to lubricant and transients had a minor influence on the system performance. Leakage was identified to have the strongest effect on system composition and performance. Biancardi et. al. (1996) furthermore showed that leaks during standstill cause the largest shift in composition whereas leakage during operation only has minor effect.

Stanbouly et al. (1996) tested a R22 3 ton heat pump system and used R407C as the drop-in refrigerant. They applied leaks from the vapor as well from the two phase region and topped the system off. They reported variations of the system performance parameters capacity and efficiency within ±5% typical experimental uncertainty. No analysis of the blend composition was performed.

The software package Refleak (Domanski, 2011) from NIST does theoretical simulations of leakage situations to model the effect of shifting composition on refrigerant mixtures. These simulations apply mainly to refrigerant cylinders and do not consider real system parameters such as the refrigerant interaction with oil or the effect of system components.

Yana Motta et al. (2012) investigated the effect of slow leakage of R407F from single vapor and two-phase locations from a walk-in cooler system. The leakage was done to simulate the worst case scenario which is when the system is not in operation. They reported no major shift in composition and variations of capacity and efficiency within typical measurement uncertainties.

1.2 Experimental set-up

In order to quantify the potential effect of fractionation of refrigeration systems using R-448A (R32/R125/R134a/R1234yf/R1234ze(E), 26/26/21/20/7) an experimental investigation was performed using the test set-up shown in Figure 1.

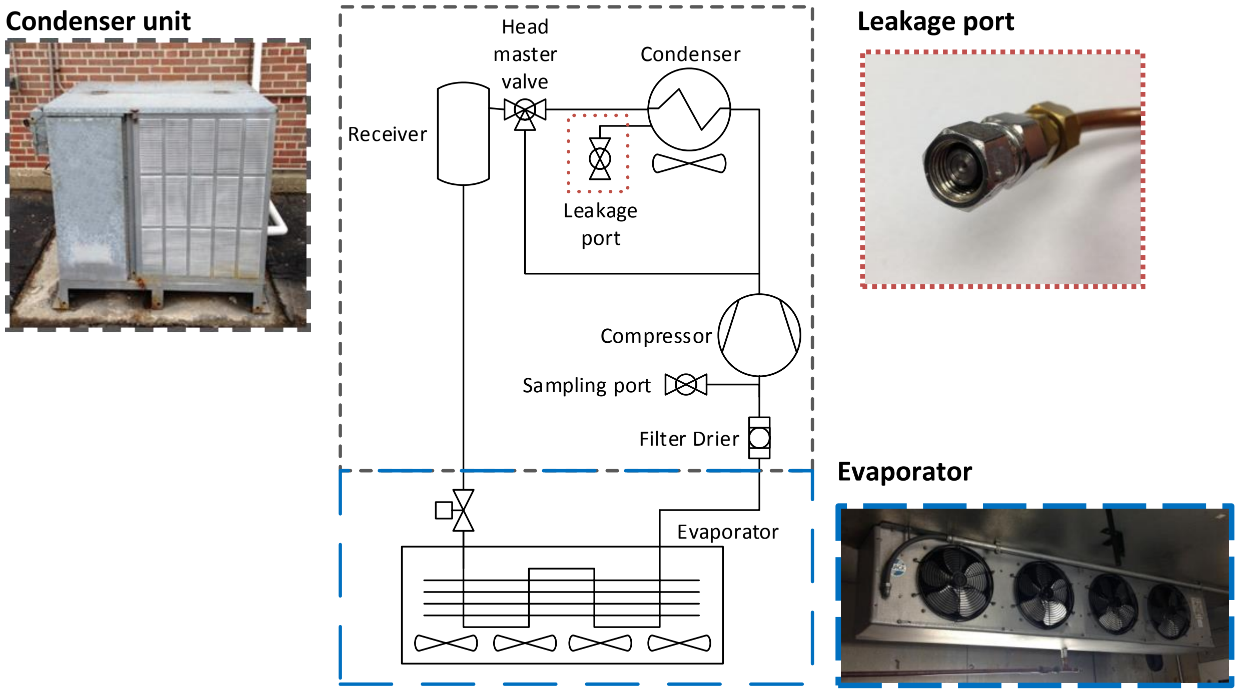

Figure 1. Experimental facility

A conventional walk-in cooler/ freezer with a nominal capacity of 1 ton designed for R-404A with a semi-hermetic reciprocating compressor, a liquid receiver, tube and fin heat exchangers and the refrigerant R-448A was used for the experimental analysis. The compressor was charged with 2200 ml of ISO32 POE oil and the system refrigerant charge was 9.1 kg. The system was providing cooling to a walk-in cooler with a chamber temperature set-point of -4°C. The ambient temperature providing cooling to the condensing unit varied between 10°C and 15°C during the tests. One leakage port was installed in a return bend in the middle of the condenser coil and another one was mounted in the suction line between the evaporator and the compressor. The leakage port consisted of an orifice with an internal diameter of 0.1mm simulating a small corrosion leak. This resembles a small leak representing a worst case scenario of a slow leak of refrigerant charge. For both scenarios the sampling to determine the circulating composition was taken from the compressor suction port when the system was in operation.

The refrigerant composition was sampled and analyzed before charging the system and at different times after each leakage step. Sample sizes were small (4g each) so they would not affect the outcome of the experiment. The samples were analyzed in a gas chromatograph to determine the sample composition. The performance for capacity and efficiency at the varying shifting compositions was determined using Refprop (Lemmon et. al., 2013) property data and thermodynamic simulations at the test conditions.

1.3 Results

Three leakage scenarios were investigated covering both single and two-phase leakage situations:

1. Refrigerant leak from the vapor side from the compressor suction line with the system shut off
2. Refrigerant leak from the two-phase side from the middle of the condenser with the system shut off
3. Refrigerant leak from the two-phase side from the middle of the condenser with the system in operation

The results of the three scenarios for composition and performance parameters are summarized in Table 1 to Table 3.

Table 1. Refrigerant leak from the vapor side from the compressor suction line with the system shut off

Description	Start	Sample 1	Sample 2	Top-off
Time [hours]	0.0	60.4	111.6	N/A
Charge [%]	100.0%	89.7%	81.0%	N/A
R32	25.6%	24.5%	23.7%	24.1%
R125	26.3%	25.9%	25.6%	25.7%
R134a	21.6%	22.3%	22.9%	22.5%
R1234yf	20.0%	20.4%	20.8%	20.6%
R1234ze(E)	6.6%	6.9%	7.1%	7.1%
Efficiency	100.0%	100.1%	100.2%	100.2%
Capacity	100.0%	98.6%	97.5%	98.1%

Table 1 shows the results of the first experiment simulating a vapor leak from the compressor suction line with the system shut off. This represents a very slow leak due to the lower density of the refrigerant vapor as can be seen in the duration between the sampling steps. Overall it can be noted that the efficiency and capacity of the blend remained within the experimental uncertainty of ±5% of the baseline values. The composition of the blend components shifted within 2.3% for R32 for a charge loss of 19% and was recovered to within typical refrigerant tolerances of 2% after the top-off step. This is similar to situations seen in supermarket refrigeration systems where a top-off is performed after a charge loss of 20%.

Table 2 summarizes the results for a leak from the two-phase region with the system shut off.

Table 2. Refrigerant leak from the two-phase side from the middle of the condenser with the system shut off

Description	Start	Sample 1	Sample 2	Top-off
Time [hours]	**0.0**	**5.7**	**11.5**	**N/A**
Charge [%]	100.0%	90.4%	80.6%	N/A
R32	25.7%	24.8%	24.0%	24.4%
R125	26.0%	26.2%	25.8%	25.8%
R134a	21.2%	21.5%	22.0%	21.8%
R1234yf	20.1%	20.3%	20.7%	20.5%
R1234ze(E)	7.1%	7.2%	7.5%	7.4%
Efficiency	100.0%	100.0%	100.1%	100.2%
Capacity	100.0%	99.1%	98.0%	97.4%

This is a leak with a larger leak rate causing a shorter overall test duration until short cycling of the compressor was reached. Even though this test has a larger potential for fractionation due to the nature of a leak from the two-phase region the overall trend is similar to the results seen in Table 1. The performance parameters for efficiency and capacity remain within ±5%. The composition shifts to about of 2% for R32 for a charge loss of 19.4% which is further recovered to 1.6% after the top-off step. After the typical service indicator of 20% charge loss R32 is still within 2% refrigerant tolerances.

Table 3 shows the results of a leak from the middle of the condenser with the system in operation.

Table 3. Refrigerant leak from the two-phase side from the middle of the condenser with the system in operation

Description	Start	Sample 1	Sample 2	Top-off
Time [hours]	0.0	4.2	9.3	N/A
Charge [%]	100.0%	84.4%	65.5%	N/A
R32	26.2%	26.1%	24.1%	24.7%
R125	26.2%	25.2%	25.2%	25.5%
R134a	20.8%	21.3%	22.2%	21.8%
R1234yf	19.8%	20.3%	20.8%	20.5%
R1234ze(E)	7.0%	7.2%	7.7%	7.4%
Efficiency	100.0%	100.0%	100.2%	100.1%
Capacity	100.0%	98.7%	96.4%	97.3%

This test scenario is the closest to actual systems operating in the field. The results for the performance parameters for capacity and efficiency remained again within typical measurement uncertainty of ±5%. The composition shift for R32 for a typical charge loss of 15.6% was 0.1%. For a charge loss of 34.5% the composition shifted for R32 was 1.9%. It has to be pointed out that a service call would likely occur in actual applications before this charge loss level is reached. Topping off at this low charge level recovered the composition to a difference of 1.3% compared to the design composition. All compositions were within 2% after the top-off step at the end of the test.

The described three leakage scenarios covered continuous leakage up to a low charge level that caused short cycling of the compressor. Another test was performed to simulate a leak from the middle of the condenser with the system in operation with a subsequent top-off situation which is typically seen in the field. This common situation can be seen in supermarket systems that show leakage rates of about 20% which routinely get topped-off with refrigerant during regular service intervals. For this experiment 20% of charge was leaked from the system and topped-off to obtain a full charge amount before repeating the procedure. In addition these experimental results were compared to calculations done using Refleak (Domanski, 2011) simulating the same leak/ top-off scenarios. The results are summarized in Table 4 and Figure 2.

Table 4. Comparison of experimental data and Refleak simulation for 20% leakage with subsequent top-off

Description	START		1st Step				2nd Step				3rd Step			
			20% Leak		TOP-OFF		20% Leak		TOP-OFF		20% Leak		TOP-OFF	
	Exp.	Refleak	Exp.	Refleak	Exp.	Refleak	Exp.	Refleak	Exp.	Refleak	Exp.	Refleak	Exp.	Refleak
R32	26.0%	26.0%	25.4%	23.4%	25.4%	24.0%	24.6%	21.9%	24.8%	22.8%	24.1%	20.7%	24.2%	21.8%
R125	26.1%	26.0%	25.9%	24.1%	26.1%	24.5%	25.8%	22.9%	26.0%	23.6%	25.7%	21.9%	26.0%	22.8%
R134a	20.9%	21.0%	21.3%	22.8%	21.2%	22.4%	21.7%	23.9%	21.5%	23.3%	22.0%	24.8%	21.8%	24.0%
R1234yf	20.0%	20.0%	20.2%	22.1%	20.2%	21.6%	20.5%	23.3%	20.4%	22.6%	20.7%	24.4%	20.5%	23.4%
R1234ze(E)	6.9%	7.0%	7.1%	7.6%	7.1%	7.5%	7.4%	8.0%	7.3%	7.8%	7.5%	8.4%	7.4%	8.1%
Efficiency	100.0%	100.0%	100.1%	100.3%	100.0%	100.2%	100.1%	100.5%	100.1%	100.4%	100.2%	100.6%	100.1%	100.5%
Capacity	100.0%	100.0%	99.3%	96.3%	99.3%	97.1%	98.3%	94.1%	98.6%	95.3%	97.6%	92.2%	97.9%	93.9%

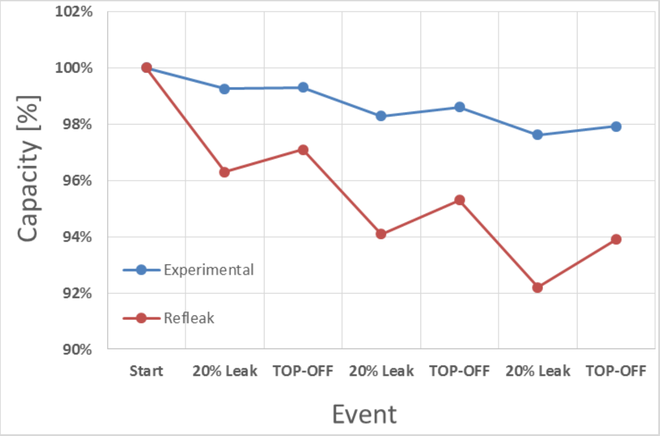

Figure 2. Capacity development during leak/ top-off events

It was shown that all experimental results for the blend composition stayed within 2% of the design composition over the three leakage and top-off steps. R32 having the highest vapor pressure showed the largest change, however also remained within 2% maximum difference. Both efficiency and capacity remained within 3%, lower than typical uncertainties of ±5%. The theoretical calculations (Refleak) show a more pronounced variation in composition and performance compared to the experimental data. Table 4 shows that for the final top-off the R32 concentration shift is larger (4.2%). The efficiency is relatively stable, however the capacity drops by 6.1%. Overall the results show that the actual shift in composition and performance cannot be predicted using theoretical models (Refleak). Effects such as refrigerant interaction with oil and the dynamic mixing of the refrigerant when the system is in operation are not considered in the theoretical models. Actual experimental studies show smaller shifts in composition.

2. MISCIBILITY, SOLUBILITY AND MATERIAL COMPATIBILITY PROPERTIES OF R-448A

2.1 Miscibility of R-448A and POE lubricant

Miscibility data was obtained for refrigerant/lubricant mixtures of R-404A/POE-32, R-448A/POE-32, and R-448A/POE-68. The test facility consists of a series of cells placed inside a temperature chamber with a window in front and lights behind to allow for visual inspection of the refrigerant/lubricant mixtures in each cell. The chamber temperature was controlled over the temperature range of –40 to 100°C and measured using a thermocouple inside an additional test cell containing lubricant. Results are presented in Figure 3, which shows for each refrigerant/lubricant pair, the line which divides the miscible region below and the immiscible region above. It is clear that R-448A is miscible with both viscosity grades of POE over a wider range of temperatures than R-404A. For an evaporator under typical refrigeration conditions (below 0°C) both R-448A and R-404A are miscible with the lubricants tested. For typical condenser conditions, (refrigerant concentrations greater than 95% at up to 50°C) R-404A would be at the limit of miscibility while R-448A would be miscible up to greater than 70°C.

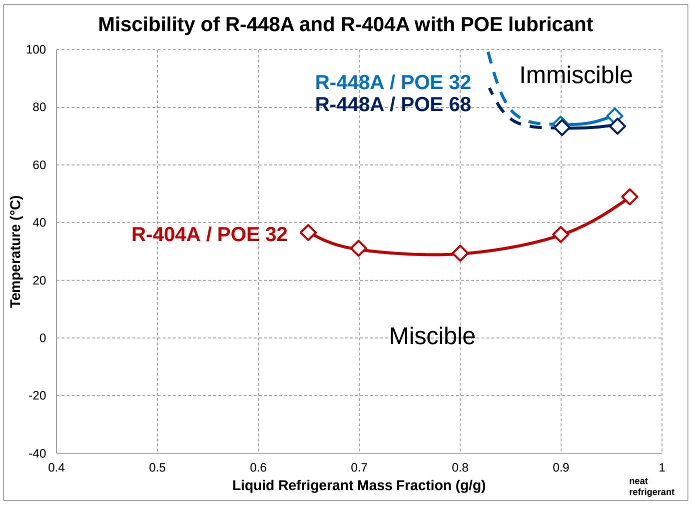

Figure 3. Miscibility of R-448A and R-404A with POE lubricants

2.2 Solubility of R-448A and POE lubricant

Beyond miscibility, further considerations for a candidate refrigerant/lubricant pair include concerns for the compressor, focusing primarily on the solubility of the refrigerant in the lubricant, and the effect this has on the viscosity of this working fluid (working viscosity) under various pressure and temperature conditions experienced during normal operation of the equipment.

Pressure data for working fluids consisting of either R-448A or R-404A in 5, 20, and 40 weight% compositions with POE 32 lubricant over a wide temperature range are presented in Figure 4. It should be noted that the pressure curves for pure R-448A and pure R-404A are essentially the same, so for clarity are shown with only the one curve on the graph. Figure 4 clearly indicates the different solubility between the HFC blend R-404A and the HFC/HFO blend R-448A, as the vapor pressures of similar refrigerant/lubricant compositions are compared. The R-448A blend exhibits lower pressures, and therefore slightly higher solubility as compared to R-404A.

Another parameter that was measured is the viscosity of various refrigerant/lubricant compositions as a function of temperature and pressure. The specialized equipment and method for obtaining this data has been previously described. (Seeton and Hrnjak 2009) This PVT data is presented in Daniel chart form in Figure 5, where the solid lines show the viscosity of various working fluid compositions at ambient pressure, and the dotted lines display the viscosity/temperature relationship at the indicated pressures. It can be noted that the working viscosity of a given composition of R-448A is slightly lower than the respective R-404A composition, in agreement with the solubility (pressure) data.

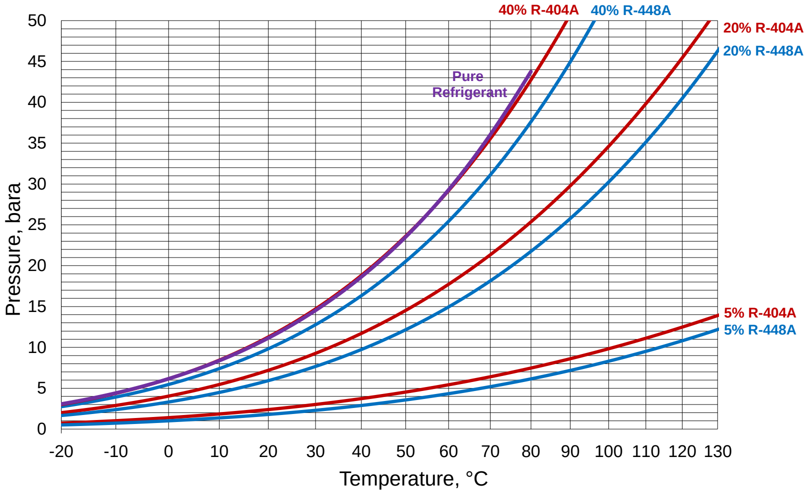

Figure 4. Solubility of R-448A and R-404A with POE 32 lubricant

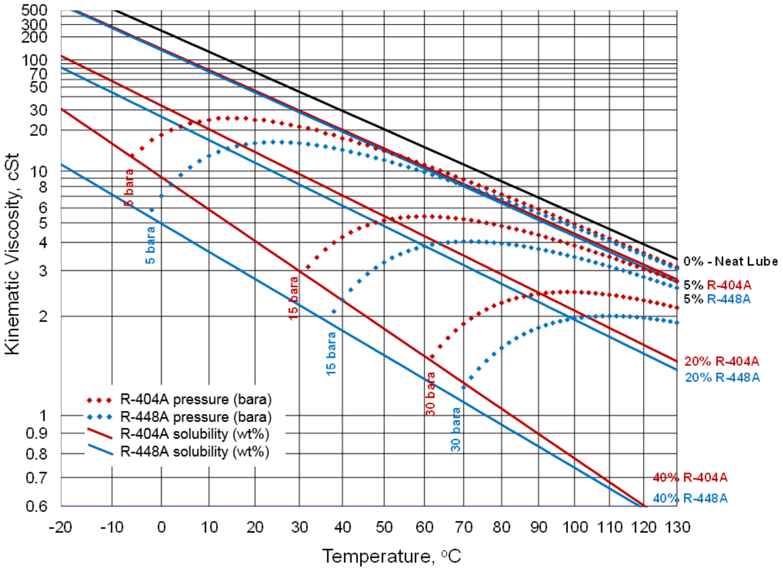

Figure 5. Pressure-Viscosity-Temperature curves for R-448A and R-404A with POE 32 lubricant

For example, consider a compressor discharge condition of 15 bar and 110°C: for R-404A (red curve) the solubility is 6% and the viscosity is 3.6 cSt while for R-448A (blue curve) the solubility is 8% and the viscosity is 3.1 cSt. Extensive compressor testing has been completed and R-448A has been qualified for several existing R-404A compressor designs and standard lubricants. (Pottker et. al., 2014).

2.3 Material Compatibility of R-448A

Another important consideration when assessing the suitability of a next-generation refrigerant for use with current HVAC&R systems is its compatibility with materials of construction. System materials must be compatible with not just the refrigerant, but the working fluid consisting of a mixture of the refrigerant and lubricant. In order to assess the compatibility of R-448A with various plastics and elastomers, material samples were placed in metal pressure vessels along with a working fluid composition of 10% POE 32 lubricant and 90% R-448A refrigerant by weight. Two material samples were placed in each test vessel to allow for a vapor and liquid exposure for each material. Vessels were placed in the oven for 14 days at 100°C for all materials except HDPE which was run at 75°C due to the low melting point of the material.

This work is meant only to give a broad indication of the appropriateness of a material with a working fluid, so only volume change and visual appearance results will be discussed. Before and after the exposures, all materials were weighed and density was determined in order to assess the changes in volume for each of these materials due to the exposure.

The volume change results for the plastics tested are shown in Figure 6. All exhibited volume changes were within approximately ± 3% with the exception of PVC which was approximately + 5%. The industry generally assesses a low-risk to plastic materials based on a volume change between –3 % and + 10 %, so all of these common materials appear to be good candidates.

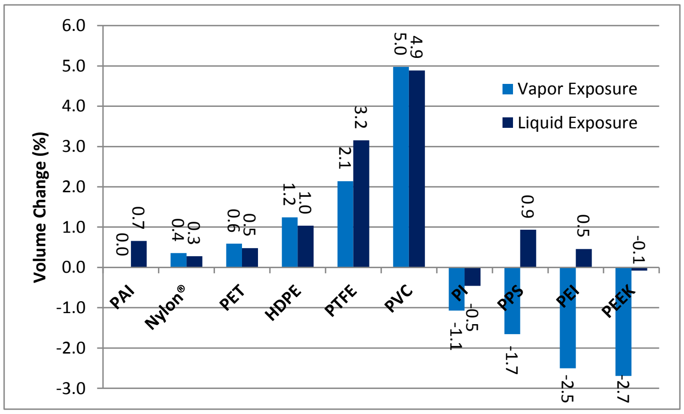

Figure 6. Volume changes for plastic materials exposed to R-448A and POE lubricant

The volume change results for the elastomers tested are shown in Figure 7. All increased in volume with the exception of the vapor Neoprene sample which showed a very small decrease. The largest increases in volume, greater than 30%, were observed for the non-standard materials Viton and SBR consistent with behavior seen with HFCs. The volume increases of less than 30% would place the rest of these elastomer materials in a lower risk category, which again indicates that they could be good candidate materials.

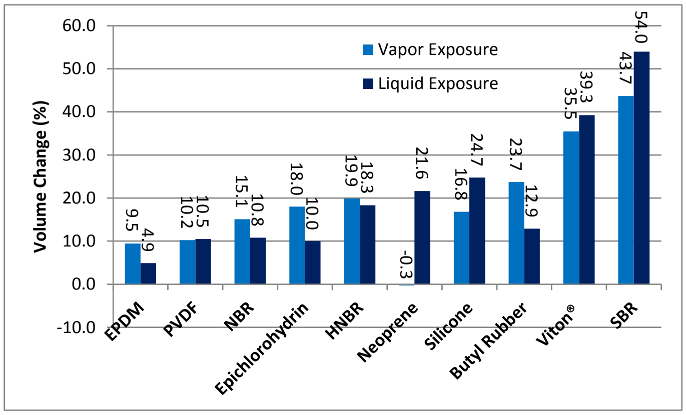

Figure 7. Volume changes for elastomer materials exposed to R-448A and POE lubricant

3. CONCLUSIONS

Fractionation investigations were performed for a walk-in cooler system using R-448A. Different test scenarios were considered for single phase and two-phase leaks with both the system in standstill as well as in operation. For all tests the composition shift of the blend components for a charge loss of 20% to 30% remained within typical refrigerant tolerances of 2% before the top-off was performed. After the top-off was completed the concentrations were brought even closer to the design composition. For all tests the performance parameters for capacity and efficiency remained within ±5%. Finally a leak top-off test was performed to simulate a situation commonly seen in the field and the results were compared to software simulations. The results that were obtained were less severe than predicted by the software simulation. The composition remained within 2% and the performance parameters efficiency and capacity within 3%. Overall the leak tests showed no significant effect on the composition shift as well as on the performance of the system. It is also shown that theoretical calculations cannot predict the fractionation in real systems.

Furthermore miscibility and solubility data for R-448A with POE and material compatibility data for R-448A with common materials were presented. It was shown that R-448A has improved miscibility compared to R-404A and shows miscible behavior up to 70°C compared to 50°C for R-404A. A comparison of the solubility of R-404A and R-448A showed slightly greater solubility for the latter. In consistency with that R-448A showed a slightly lower viscosity compared to R-404A. In consideration of this, compressor qualifications by leading OEMs were performed and R-448A was qualified for several R-404A compressor designs and lubricants.

The material compatibility study results indicate a low-risk to plastic materials based on a volume change. All tested commonly used elastomer materials are also considered low risk and therefore are good candidates for materials to be used with R-448A.

NOMENCLATURE

ASHRAE	American society of heating, refrigerating and air conditioning engineers	PEEK	Polyether ether ketone
EPDM	Ethylene propylene diene rubber	PEI	Polyetherimide
GWP	Global warming potential	PET	Polyethylene terephthalate
HDPE	High density polyethylene	PI	Polyimide
HFC	Hydrofluorocarbon	POE	Polyolester
HFO	Hydrofluoroolefin	PTFE	Polytetrafluoroethylene
HNBR	Hydrogenated nitrile butadiene rubber	PVC	Polyvinyl chloride
NBR	Nitrile butadiene rubber	PVDF	Polyvinylidene difluoride
PAI	Polyamide-imide	SBR	Styrene butadiene rubber

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