APPENDIX C. VOLATILE COLLECTION SYSTEM STUDY REPORT

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1.0 PURPOSE

This report documents the design of an improved volatile collection system (VCS) for the Stirred Air Flow Test (SAFT). The prototype SAFT included a VCS which consisted of a copper coil condenser operated at ambient temperature. Data published for several binders during the development of the SAFT showed that the mass of volatiles collected was a factor of 10 lower than the mass change in the RTFOT (*1*). Several possible causes for this discrepancy were identified including:

1. Condensation of volatile compounds on the lid of the SAFT before they entered the air-cooled condenser.
2. Inefficiency of the air-cooled condenser allowing volatiles to pass completely through the VCS.
3. Production of fewer volatile compounds in the SAFT compared to the RTFOT due to the shorter duration of the SAFT conditioning procedure and the lower air-flow rate used in the SAFT.
4. Rapid saturation of the small air bubbles produced in the SAFT with volatiles so that they are not able to absorb additional volatiles as they move upward through the binder.
5. Suppression of volatilization caused by the build-up of air pressure in the SAFT.

The VCS Study consisted of a series of small experiments to evaluate these potential causes and to design a more effective VCS for the SAFT.

2.0 BACKGROUND

Concern with the VCS in the prototype SAFT, which consisted of a copper coil condenser operated at ambient temperature, was identified during Phase I of NCHRP Project 9-36. In the prototype SAFT the volatiles produced during the conditioning process are assumed to be completely trapped in the air-cooled condenser. They are removed by washing the condenser with solvent, and then they are weighed after the solvent evaporates. Figure 1 presents a comparison of the mass change from the RTFOT and the mass of volatile compounds collected

with the prototype SAFT *(1)*. As shown in Figure 1, the mass of volatile compounds collected with the VCS from the prototype SAFT does not correlate with the RTFOT mass change, but of more concern, the amount of volatiles changes very little among the nine binders. Since mass change during the RTFOT includes mass loss due to volatilization and mass gain due to oxidation, the RTFOT mass change was expected to be less than the mass of the volatiles collected with the SAFT. The developers of the SAFT also reported high variability for the VCS measurements (*1*). Coefficients of variation for multiple tests on the same asphalt were high, averaging approximately 35 percent. The developers of the SAFT dismissed the poor agreement between the RTFOT mass change and the mass collected in the VCS of the SAFT as being the result of systematic errors in the RTFOT mass change measurements. They also hypothesized that the high variability in the VCS measurements may be the result of condensation on the underside of the lid caused by temperature gradients over the height of the vessel. To address this hypothesis they recommended that the vessel be heated over its entire height to reduce the potential for the condensation of volatiles on the lid.

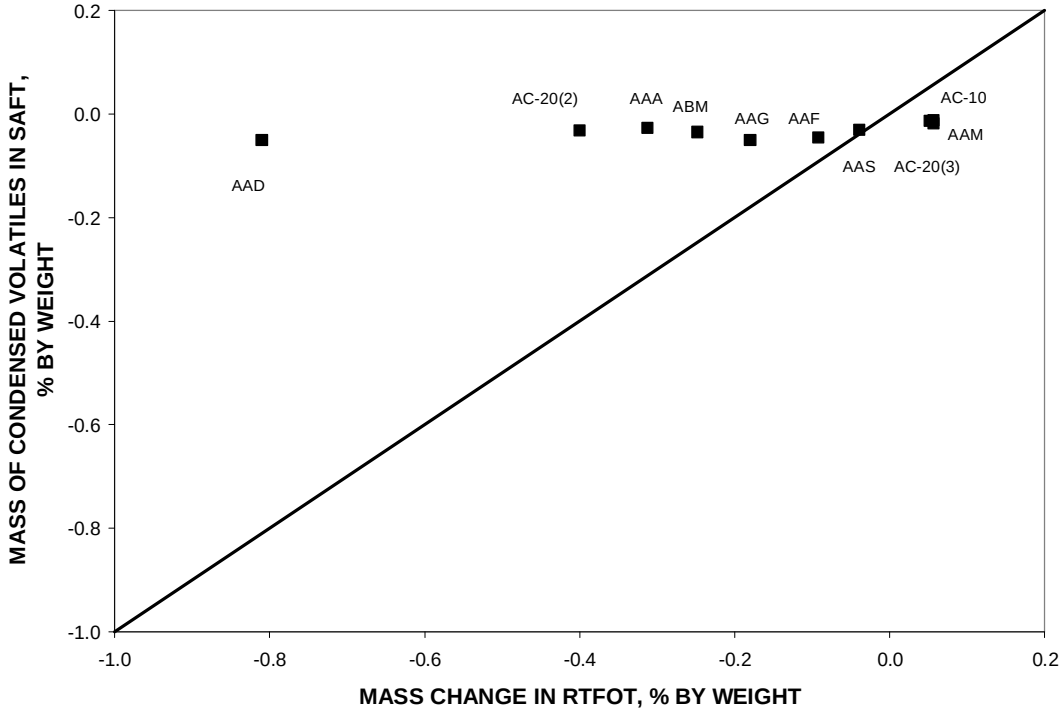


Figure 1. Comparison of Volatiles Collected During SAFT and Mass Change During RTFOT Conditioning (*1*).

In 2002, an interlaboratory study was conducted with the prototype SAFT to establish the variability in the SAFT procedure (*2*). One of the conclusions from this study was that the prototype SAFT VCS system worked very well and provided a significant improvement over the RTFOT mass change determinations. This conclusion regarding the VCS is suspect as the mass of the VCS volatiles was unexpectedly small, three of the laboratories could not provide valid volatile loss data, and the corresponding data for the RTFOT was not collected.

In addition to the hypothesized condensation problem identified during the development of the SAFT, two other possible causes for the discrepancy between SAFT VCS and RTFOT mass change measurements were identified by the NCHRP 9-36 research team. One suspected cause is that less volatile compounds are produced during the SAFT conditioning. The duration of the SAFT is significantly shorter than the RTFOT and the air flow rate is one-half of that in the RTFOT. Another suspected cause is that the small air bubbles produced in the SAFT become saturated with volatiles very quickly and are therefore not able to absorb additional volatiles as they move upward through the binder. A more plausible explanation is that the collection system was not properly designed; therefore, some of the volatile compounds produced in the SAFT pass completely through the VCS, a condition commonly referred to as blow through.

3.0 IDENTIFICATION OF CAUSES OF UNEXPECTEDLY LOW VOLATILE LOSS WITH THE PROTOTYPE SAFT VCS

Initial work on the SAFT VCS was performed to isolate the cause of the unexpectedly low mass of collected volatiles reported in the literature. This work was done while the research team was waiting for the delivery of the commercial SAFT device. In recognition of the localized heating issues caused by the heating mantle used in the prototype SAFT, the NCHRP 9-36 research team replaced the heating mantle with an oil bath. This modified version of the SAFT was used to evaluate the VCS using the operating parameters for the prototype SAFT:

- Flow rate of 2,000 ml/min
- Impeller speed of 700 rpm
- Conditioning time of 35 min

It should be noted that the oil bath avoided the "hot-spots" that likely occurred with the prototype SAFT and to this extent altered the thermal history during the heat-up and aging phases of the procedure.

A mass change experiment was conducted with the SAFT to identify the cause of the unexpectedly low volatile mass collected in the prototype VCS. The neat PG 58-28 binder that was included in the Selection Study, was aged in replicate under the following conditions:

1. Condition 1 - RTFOT using standard conditions,
2. Condition 2 - SAFT with the prototype VCS in place, air-flow rate 2000 ml/min,
3. Condition 3 - SAFT without the lid or prototype VCS, air flow rate 2000 ml/min, and
4. Condition 4 - SAFT without the lid or prototype VCS, air flow rate 4000 ml/min.

The mass of the volatiles was determined for Condition 2 by flushing the volatiles from the VCS with solvent and evaporating the solvent. In Conditions 2, 3, and 4 mass change was determined by weighing the vessel and its components before and after conditioning. DSR shear modulus and phase angle measurements were made at 58 °C and 10 rad/s. Table 1 summarizes the results of the testing.

Table 1. Summary of SAFT Mass Change Measurements.

Test and Test Parameters	Air Flow, ml/min	Mass Change, wt %[(a)]	Average Mass Change, wt %	Mass of Collected Volatiles, wt %	Average Mass of Collected Volatiles, wt %	G*/sinδ, kPa	Average G*/sinδ, kPa
RTFOT	4,000	-0.357 -0.349	-0.35	NA	NA	2.62 2.72	2.67
SAFT with lid and collection system	2,000	NA	NA	0.016 0.011	0.014	2.15 2.27	2.21
SAFT without lid and collection system	2,000	-0.108 -0.112	-0.11	NA	NA	2.22 2.21	2.22
SAFT without lid and collection system	4,000	-0.184 -0.176	-0.18	NA	NA	1.91 2.18	2.05

(a) Negative values in this table indicate a loss in mass.

This experiment provided important insight into the behavior of the prototype VCS. First, the SAFT without the lid and VCS produced mass losses that are less than the RTFOT, but a factor of 10 higher than the mass of the volatiles collected in the VCS. The mass of the volatiles collected in this experiment by weighing the SAFT components before and after aging is of the same size as those reported by the original developers of the SAFT, which ranged from 0.013 to 0.051 percent by weight (*1*). Thus, it appeared that only a small percentage of the volatiles that are produced by the SAFT were being collected by the VCS. At a flow rate of 2000 ml/min, the mass of the volatiles trapped in the collection system was only 0.013 percent by mass compared to a mass loss of 0.11 percent when the lid and collection system were removed. Three potential causes for this discrepancy were considered:

1. Volatile compounds condense on the lid of the vessel before being trapped in the condenser.
2. Volatile compounds are not condensed in the air-cooled condenser but instead pass completely through the system.
3. With the volatile compound collection system in place, sufficient pressure builds up in the SAFT vessel to suppress volatilization. The inlet and outlet piping are the same size, but the outlet piping has greater losses due to the presence of the condenser. These additional losses could possibly cause an increase in the pressure in the SAFT, which in turn may suppress the volatilization of some compounds.

The second important finding from the SAFT mass loss experiment was that the air flow rate in the SAFT significantly affects the mass loss. When the air-flow rate was doubled from 2000 ml/min to 4000 ml/min the mass loss increased from 0.11 percent to 0.18 percent. The mass change, which was not investigated during the development of the prototype SAFT, is significantly affected by the air-flow rate, increasing with increasing air-flow over the range investigated. This suggests that the air-flow rate can be further optimized to better reproduce the mass loss that occurs in the RTOFT without significantly changing the degree of stiffening that occurs.

The third important finding from the SAFT mass loss experiment was that the aging of the binder during the steady-state portion of the SAFT conditioning as measured by changes in $G^*/\sin\delta$ at 58 °C is significantly less than the RTFOT aging. For unaged conditions, $G^*/\sin\delta$ at 58 °C for the binder was 1.22 kPa. In the RTFOT it increased to 2.67 kPa, while the average for the SAFT residue for all three conditions was only 2.16 kPa. Work performed during the development of the prototype SAFT showed substantially better agreement between the SAFT and the RTFOT(*1*). Since the prototype version of the SAFT did not use an oil bath rather than a heating mantle it appears that the heating mantle contributes significantly to the degree of aging that occurs. During the heat-up phase, very large temperature gradients must occur in order to heat 250 g of binder from its initial temperature of approximately 93 °C to 163 °C in 15 minutes. This most likely exposes the binder to temperatures substantially above 163 °C at the vessel periphery resulting in increased aging.

Numerous scenarios were considered and test runs conducted in an effort to enhance the efficiency of the original VCS. Condensation of volatiles within the vessel and prior to reaching the condenser were quickly ruled out. The only place that volatiles can condense and not be detected is on the vessel lid; all of the remaining components of the SAFT were weighed before and after each run. At the end of the conditioning period the lid was weighed before and after cleaning with TCE and the results showed that only a small amount of material condenses on the lid. This confirmed the hypothesis that the problem was caused by material passing through the condenser and that condensation on the lid was not a major problem.

4.0 FIRST MODIFIED VCS, VCS-I

To better collect the volatiles that pass through the air-cooled condenser, a hydrocarbon trap (activated carbon filter) was added after the condenser. This modified VCS was called VCS-I. Initial testing of VCS-I showed the hydrocarbon trap collected a significant amount of material, but the amount collected was highly variable from one run to the next. It was hypothesized that the variability was caused by moisture and/or oil vapor in the air supply. A silica gel moisture trap, followed by the hydrocarbon trap, was subsequently added to the inlet of the SAFT vessel. The addition of these traps did not improve the variability of the material collected in the outlet

hydrocarbon trap. Information from outside experts on the efficiency of activated carbon filters indicated that the presence of moisture vapor significantly affects the efficiency of the activated carbon. Since one of the expected products of the oxidation reactions occurring in the SAFT is water, a silica gel moisture trap was added to the exhaust between the condenser and the hydrocarbon trap. This significantly increased the mass of the volatiles collected in the hydrocarbon trap and decreased the variability of the measurements. Figure 2 presents a schematic of VCS-I with the activated carbon and silica gel traps added to the outlet line. The following filters were used:

1. The disposable activated carbon hydrocarbon filter that is used to clean the incoming air and to collect hydrocarbon volatiles is produced by Koby (see Koby Junior at, http://www.kobyfilters.com/index.html?menu.htm&1 for details).

2. The disposable silica gel filter used to remove water from the air stream exiting the SAFT was supplied by Cole-Palmer as Part Number EW-02908-64 (see Http://www.coleparmer.com/catalog/product_view.asp?pfx=EW&sku=0290864&cat=1&sel =0290864 for details).

3. The rechargeable silica gel filter used to remove water from the in-flowing gas is produced by Agilent Technologies as part number MT 120-2S.

4.1 Pressure Effects

One of the hypotheses to explain the low volatile loss was that pressure inside the SAFT was suppressing the volatile loss. Several tests were run using the volatile compound collection system shown in Figure 2 to investigate the effect of pressure inside the SAFT on the amount of volatiles produced. All testing was performed with a PG 58-28 with an average RTFOT mass change of -0.343 percent. Triplicate 250 g samples were aged for 45 min at 163 °C using an air flow rate of 4000 ml/min. Three different conditions were used to produce the flow: slight positive pressure, vacuum with 90 kPa absolute pressure, and vacuum with 70 kPa absolute pressure. The sub-atmospheric pressures (70 kPa and 90 kPa absolute) were produced by applying a vacuum downstream, essentially sucking the air through the SAFT vessel.

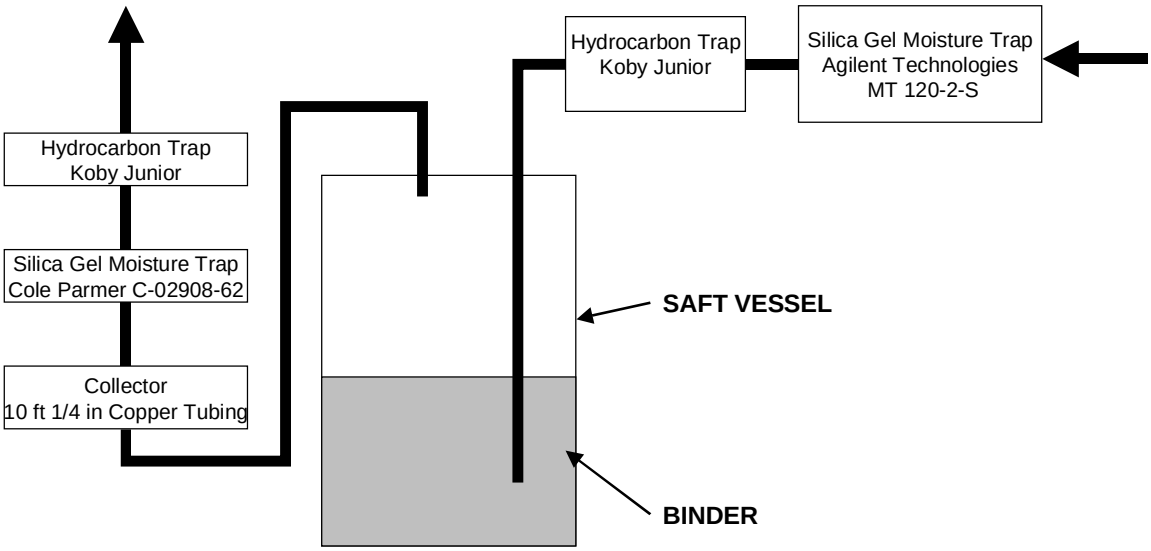


Figure 2. Schematic of VCS-I.

Table 2 presents the percent by mass of the volatiles (expressed as a percent of the initial binder mass) collected in the condenser, moisture trap, and hydrocarbon trap. Figure 3 is a bar chart presenting these results including 95 percent confidence intervals for each measurement. Also shown on the bar chart as horizontal lines are the RTFOT mass change (in this case with loss as a positive value) as well as the average mass loss reported earlier in Table 1 for the SAFT without the lid and VCS system.

The data shown in Table 2 indicate that significant mass is collected in each trap. Approximately 73 percent of the total is collected in the hydrocarbon trap, 17 percent in the moisture trap, and 10 percent in the condenser, Figure 4. The amount collected in the hydrocarbon trap exceeds the RTFOT mass change for this binder, which is reasonable considering the mass change measurement includes mass loss due to volatilization and mass gain due to oxidation. An analysis of variance was conducted on the data in Table 2. Only the mass collected in the condenser was significantly affected by the pressure in the aging vessel; however, the amount collected in the condenser is only approximately 10 percent of that collected in the hydrocarbon trap.

Table 2. Data Collected From VCS-I at Various Absolute Pressures.

Date	12/16/04	12/17/04	12/22/04	Average	Standard Deviation	Coefficient of Variation
Absolute Pressure, kPa	70	70	70			
Mass of AC, g	250.2	250.2	250.3			
Collector, wt %[(a)]	0.0687	0.0643	0.0723	0.0685	0.0040	5.83
Water Filter, wt %[(a)]	0.1079	0.0663	0.0451	0.0731	0.0319	43.66
Hydrocarbon Filter, wt %[(a)]	0.5016	0.4844	0.4539	0.4800	0.0242	5.04
Total[(a)]	0.6783	0.6151	0.5713	0.6216	0.0538	8.65

Date	12/23/04	12/27/04	1/4/05	Average	Std Deviation	Coefficient of Variation
Absolute Pressure, kPa	90	90	90			
Mass of AC, g	250.1	250.1	250.2			
Collector, wt %	0.0632	0.0560	0.0663	0.0618	0.0053	8.59
Water Filter, wt %	0.2043	0.1076	0.1079	0.1399	0.0558	39.85
Hydrocarbon Filter, wt %	0.4562	0.4294	0.5731	0.4863	0.0764	15.72
Total	0.7237	0.5930	0.7474	0.6880	0.0832	12.09

Date	1/5/05	1/6/05	1/7/05	Average	Std Deviation	Coefficient of Variation
Absolute Pressure, kPa	101	101	101			
Mass of AC, g	250.3	249.9	249.9			
Collector, wt %	0.0491	0.0536	0.0536	0.0521	0.0026	4.96
Water Filter, wt %	0.2082	0.1060	0.0500	0.1214	0.0802	66.04
Hydrocarbon Filter, wt %	0.4175	0.4650	0.4278	0.4368	0.0250	5.72
Total	0.6748	0.6246	0.5314	0.6103	0.0728	11.92

Average per run, All Runs	Run 1	Run 2	Run 3	Average
	0.060	0.058	0.064	
Collector, wt %	0.173	0.093	0.068	
Hydrocarbon Filter, wt %	0.458	0.460	0.485	
Total	0.692	0.611	0.617	

[(a)] Expressed as per cent of original asphalt binder by weight.

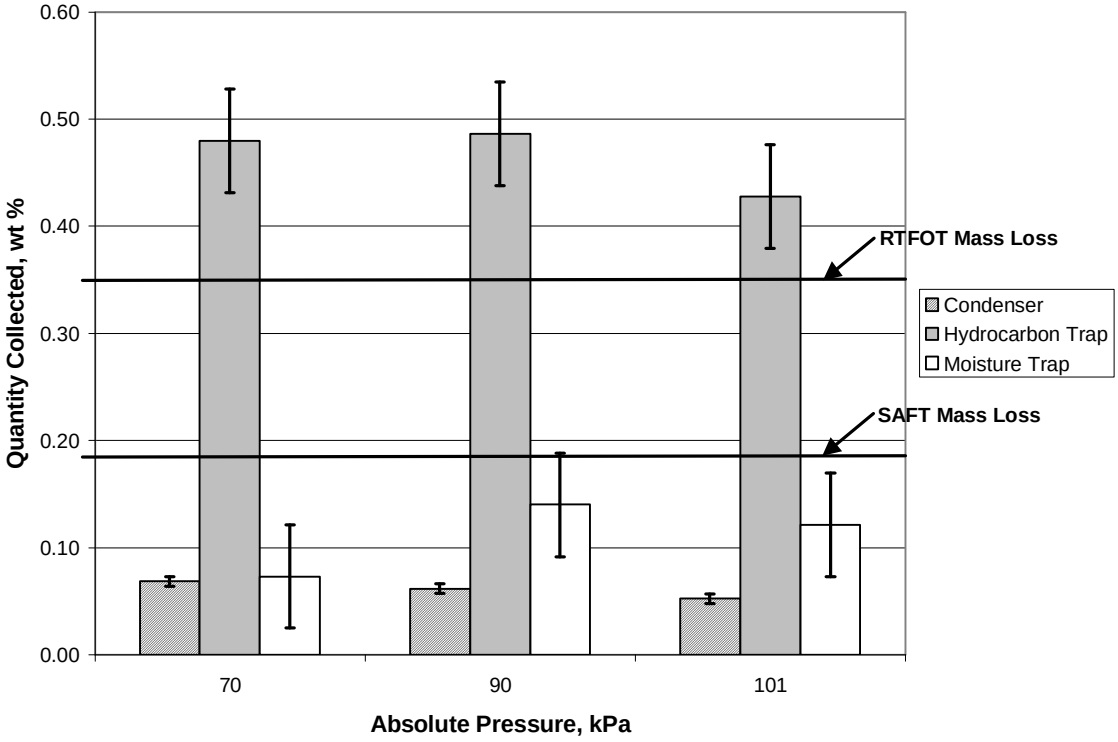


Figure 3. Mass of Material Collected in the Improved VCS, VCS-I.

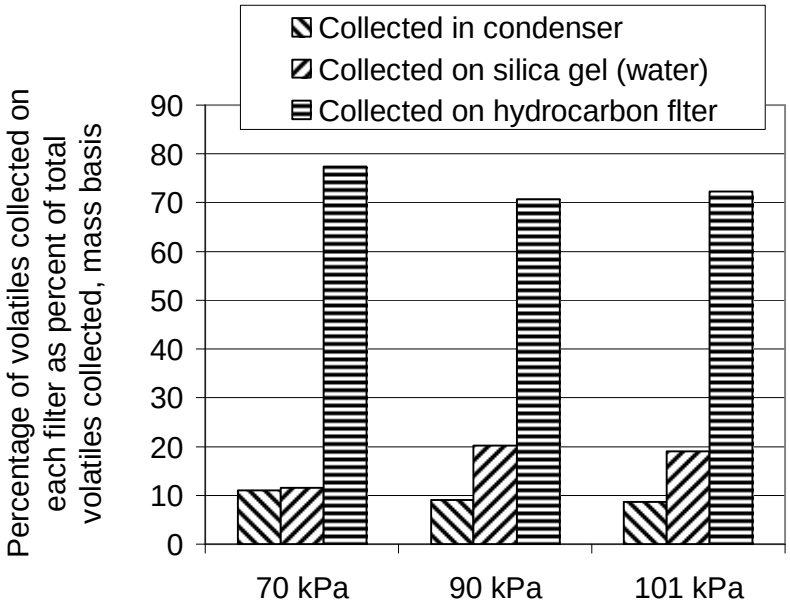


Figure 4. Volatiles Collected on Filters as Percentage of Total Volatiles Collected, VCS-I.

Since vessel pressure had little effect on the amount of collected volatiles a slight positive pressure was retained as the method for creating the air flow. No change in the procedure for circulating the air through the vessel was considered necessary. Considering that previous work with the SAFT conducted at TTI showed that for different binders there is little difference in the mass collected in the condenser (*1*), it appeared that the best measure of binder volatility was the mass collected in the hydrocarbon trap. The mass collected in the moisture filter was also considered significant as an indication of the degree of aging because water is an expected product of the oxidation reactions.

4.2 Volatiles Collected During Successive Runs

One component of the evaluation of VCS-I was to collect and analyze volatiles from different asphalt binders. This work was combined with the initial phase of the SAFT Optimization Study that was carried out on the commercial SAFT. It included multiple runs of three binders: AAD-2, AAM-1, and ABM-2. To collect volatiles for chemical analysis, dedicated condensers, silica gel filters, and activated hydrocarbon filters were used for each asphalt binder, and the components of the VCS were not cleaned or purged between successive runs. This allowed the volatiles from multiple runs to be combined. However the VCS-I mass change data obtained during the SAFT Optimization Study were very erratic and it was observed that the silica gel filter acquired a brownish color indicating that it was absorbing hydrocarbons as well as water. The mass collected in each component for each run, is shown in Figure 5. The mass collected in the silica gel decreases significantly from the first to the third run. Based on this observation and the brownish color acquired by the silica gel, it is appears that the silica gel adsorbs hydrocarbons as well as water. Further, the results show that the efficiency of the silica gel decreases with successive runs, most likely caused by interference from absorbed polar compounds. These observations prompted the need for a revised VCS design.

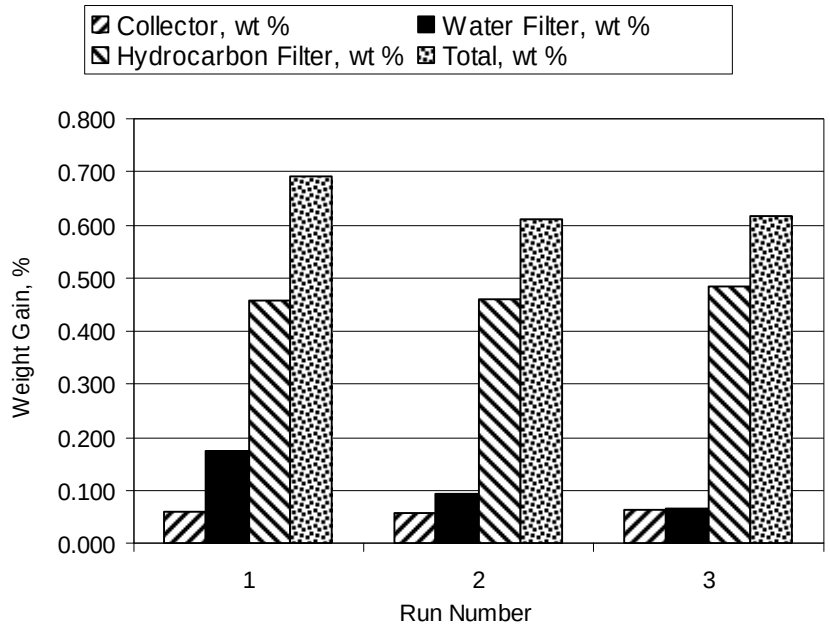


Figure 5. Average Amount of Volatiles Captured in Successive Runs.

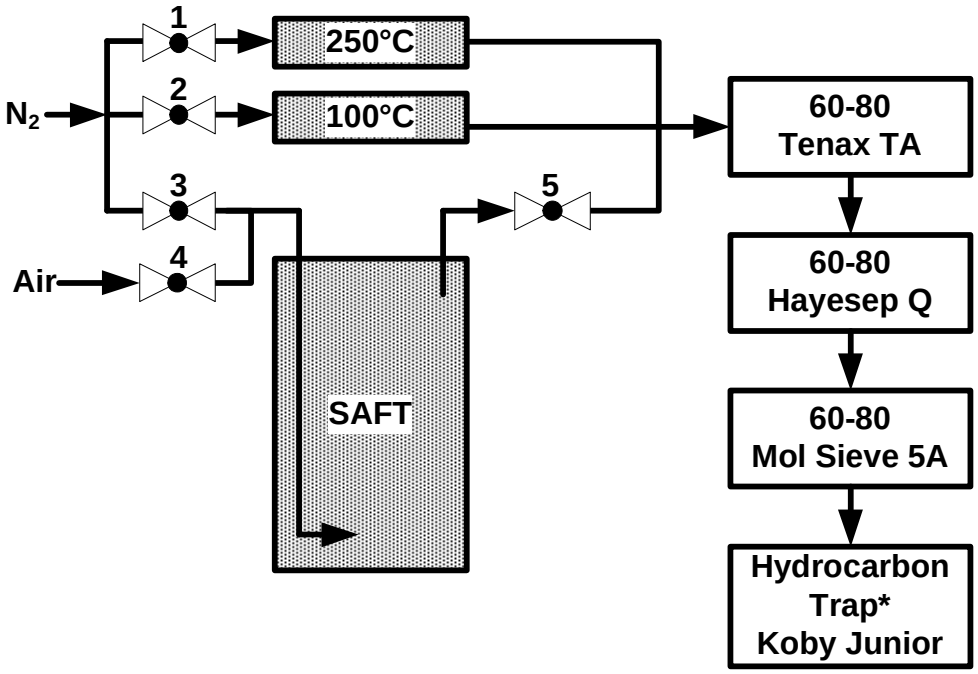
5.0 SECOND GENERATION COLLECTION SYSTEM, VCS-II

5.1 VCS-II Design

Based on the results presented above it became obvious that a major re-design of the VCS was needed. One alternative that was considered was to design a much larger condenser that would operate below room temperature. This approach was considered impractical from an implementation standpoint and instead, the researchers chose a volatile collection system based on chromatographic principles.

The new collection system was designed to use filters that are commonly used in chromatographic analyses. The resulting system, referred to as VCS-II is shown in Figure 6. Although not shown in Figure 6, the inlet silica gel and activated carbon filters from the VCS-I were retained to condition the incoming nitrogen and air. Like VCS-I, VCS-II was retrofitted to the commercial SAFT.

Process Step	Flow Path				
	1	2	3	4	5
1. Purge filter system	O	C	C	C	C
2. Preheat binder	C	C	O	C	O
3. Age binder	C	C	C	O	O
4. Flush H_2O at end of run	O	C	C	C	C



*Hydrocarbon trap may be redundant for this system.

Note: Flow diagram for descriptive purposes only and not to be used to lay out system. Air is pre-dried with a commercial drier and further cleaned by passing the air through a silica gel and charcoal filter before it is introduced into the SAFT.

Figure 6. VCS Based on Chromatographic Filters, VCS-II.

The presence of both hydrocarbons and water in the stream exiting the SAFT complicates the collection process. The two absorbent polymer resin filters, Tenax TA and HayeSep Q were selected to remove, respectively, the larger molecular weight polar materials (aromatics) and the remaining hydrocarbons, while the molecular sieve was selected to remove water. The activated carbon filter was included only to ensure the efficiency of the resin beads and molecular sieve. Nothing should be collected in the activated carbon filter if the system is properly designed. The

system shown in Figure 6 was not intended for routine use but instead was selected to provide an understanding of the nature of the volatiles that are being released and to form a basis for selecting a simplified system.

Each of the adsorbents are contained in a 7 in (150 mm) long 0.5 in (12.5 mm) diameter stainless steel tube and were connected with rubber tubing. A photograph of an assembled filter is shown in Figure 7. Approximately 50 grams of the absorbents are required to fill a filter bed 1.5 in (37 mm) in length. The filter beds can be reused by purging them of collected volatiles. Estimated life of the absorbents, as predicted by Supelco technical support staff, is in excess of 50 runs.

Figure 7. Photograph of Resin Bead Filter Used in VCS-II.

Some minor adjustments were required in the operation of the SAFT to accommodate the VCS-II. The operational sequence for the VCS-II consisted of four steps:

1. Purge the filters with nitrogen.
2. Heat the binder to the conditioning temperature with nitrogen flowing.

3. Condition the binder with air flowing (simulated aging).
4. Flush water from the resin beds to the molecular sieve.

The mass collected in each filter is obtained by weighing the filter before and after each run of the SAFT. Before the initial weight is obtained, the adsorbents must be challenged (purged of contaminants) by passing a stream of nitrogen gas heated to 250 °C through each of the tubes. For the VCS-II assembled in NCHRP 9-36, each tube must be challenged separately although in a commercial version of the VCS-II, it is expected that all of be absorbents would be contained in a single tube allowing all of the adsorbents to be challenged simultaneously. Based on the manufacturer's literature, the flow rate for the nitrogen gas during this step should be 2 l/min which gives a linear velocity of approximately 400 cm/min through the filter. Once the run is completed the Tenax TA and HayeSep Q filters should be flushed with nitrogen in order to ensure that any water trapped on the beads in these filters is transferred to the molecular sieve. The position of the various valves in the SAFT system during the four steps are indicated by a "C" (closed) or "O" (open) in Figure 6.

5.2 VCS-II Evaluation

A number of runs of the SAFT with the VCS-II were performed using the Citgo PG58-28 binder to gain experience with the VCS-II system, and to develop techniques for challenging the collectors. In these runs the nitrogen gas for challenging the collectors was heated by passing it through a copper coil placed in a heating mantle with an insulated cover. The temperature of the nitrogen gas when it enters the collectors is 250 ± 10°C and at the exit end of the collector is approximately 130°C. Data obtained by successively weighing the tubes with increasing flow times indicated that the challenging is complete within 15 minutes. Consequently the procedure developed for challenging the adsorbents is to purge them with nitrogen gas at 2 l/min at 250°C inlet temperature for 15 minutes. The efficacy of the current procedure is demonstrated in Table 3 where the change in the mass of the purged adsorbents and tubes is given after successive runs as compared to the initial masses before the first run.

Table 3. Weight of Adsorbents after Successive Runs.

Absorbent	Change in mass of adsorbents after run and purging compared to mass at beginning of first run, grams			
	After run 1	After run 2	After run 3	After run 4
Tenax TA	0.012	0.012	0.007	0.010
HayeSep Q	-0.008	-0.007	-0.003	-0.005
Mol Sieve 5A	-0.009	-0.006	0.001	-0.009

Once the run is complete the resin beads must be flushed with nitrogen in order to ensure that any water trapped on the beads is transferred to the molecular sieve. The effect of the nitrogen flush was investigated by obtaining the mass of the tubes with and without the nitrogen flush. The resulting data are shown in Table 4. These data show that very little mass is flushed from the Tenax TA and HayeSep Q collectors, and more material is flushed from the molecular sieve. Based on this data, the post-run nitrogen purge was eliminated.

Table 4. Effect of Nitrogen Flush at Completion of run, Citgo 58-28.

Absorbent	Mass remaining on absorbents after run, grams		
	W/o N_2 flush	With N_2 flush	Mass lost during N_2 flush
Tenax TA	0.063	0.059	0.004
HayeSep Q	0.064	0.057	0.007
Mol Sieve 5A	0.511	0.487	0.024

To obtain data on the magnitude and repeatability of the mass changes for each of the collectors, duplicate runs were made with four binders; Citgo PG 58-28, ABM-2, AAM-1, and AAD-2. The mass of the volatiles collected during replicate runs for four binders are shown in Table 5 for the SAFT with the VCS-II and the RTFOT. Surprisingly, the majority of the volatiles collected in the VCS-II are collected in the molecular sieve and not on the Tenax TA and HayeSep Q filter beds. For example, for the 58-28 binder 80% of the volatiles are collected on the molecular sieve while only 20% are collected on the Tenax TA and HayeSep Q with similar results for the other three binders. When the Tenax TA is challenged (purged) at the end

of the run considerable smoking was observed as the volatiles were released. The odor is acrid in nature, unlike the smell of asphalt binder. When the HayeSep Q is purged no smoke is observed but an asphalt-like odor is observed. The volatiles driven from the molecular sieve have a hydrocarbon odor somewhat similar to asphalt cement.

Table 5. Mass Change for RTFOT and SAFT With VCS-II.

Aging Device	Measured Value	Filter Media	CITGO 58-28	ABM-2	AAM-1	AAD-2
SAFT	Mass Change, percent of Initial Binder Mass	Tenax TA	0.025	0.020	0.007	0.034
		HayeSep	0.026	0.012	0.008	0.011
		Mol. Sieve	0.204	0.179	0.128	0.166
		Tenax + HayeSep	0.051	0.032	0.015	0.045
		Total	0.255	0.211	0.143	0.211
	Mass Change, percent of total volatiles collected	Tenax + HayeSep	20	15	10	21
		Mol. Sieve	80	85	90	79
RTFOT	Mass Change	None	-0.345	-0.348	0.122	-1.058

The total amount of volatiles collected in the VCS-II is compared to the mass change that occurs in the RTFOT is shown in Figure 8. The mass change numbers for the SAFT and RTFOT are now in much better agreement. Because they represent different processes, it is not expected that they will be the same. However, it is reassuring that they are now within the same order of magnitude. Interestingly, the amount of material collected in the copper coil of the original SAFT VCS is close in magnitude to the amount of material collected on the Tenax A resin. Apparently the prototype VCS did not collect the moisture produced during aging.

Material collected during the last run for binder AAD-2 was sent to Heritage Research Group to determine the composition of the volatiles collected in each filter. The procedure used by Heritage was to first sequentially elute each of the three tubes with hexane, methylene chloride, and methanol. Each eluent was analyzed by the gas chromatography with flame ionization detection (GC/FID) for quantification of the organic chromatographic material. Use of the three different solvents allowed the removal of compounds of varying polarities. Water present in each of the eluents was determined by Karl Fisher testing using a Mettler Toledo DL-38 unit. This analysis showed that essentially all of the water was collected in the molecular sieve. The Tenax TA filter collected 91.2 % of the organic material, the HayeSep filter collected 8.2 %, and

the molecular sieve collected the remaining 0.6%. The mass of organic material collected on each of the filters varied somewhat from the mass changes determined immediately after the SAFT runs at AAT. However, given the tendency to lose highly volatile components during handling and the nature of the GC measurements the results are considered compatible. The chromatograms were as expected, showing compounds similar to those obtained previously in the asphalt fume studies conducted by Heritage. Dr. Kreich also suggested that it may be possible to use only one of the filter materials. Given their relative costs eliminating the Tenax TA would be preferable.

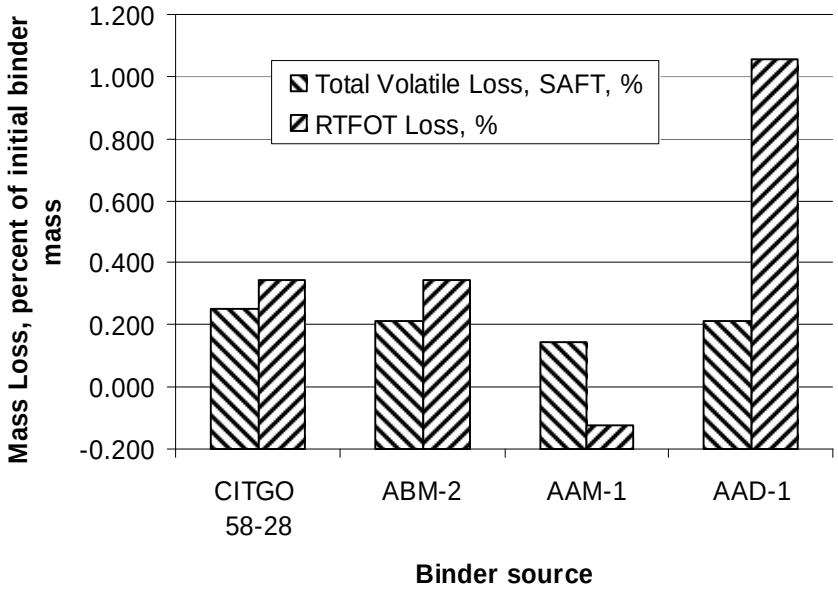


Figure 8. SAFT Volatile Loss and RTFOT Mass Change Compared.

6.0 FINAL VCS, VCS-III

6.1. VCS-III Design

The results of the VCS-II evaluation indicated that further refinements were warranted. The compositional analysis of the material collected in each filter indicated that some organic material was collected on the molecular sieve. This indicated that the length of the HayeSep Q was too short. As part of the VCS-III design study, an experiment was conducted to establish the length of HayeSep Q collector required to minimize breakthrough. This experiment was

performed using the Citgo 58-28 binder because it is refined from Venezuelan crude and has a relatively high mass change in the RTFOT. The length of the HayeSep Q collector was varied from 1.5 in (37 mm) to 4.5 in (111) mm by adding one or two 1.5 in (37 mm) lengths to the original 1.5 in (37 mm) length and the mass collected in each length was then weighed. The data are shown in Figure 9 where the percent of material captured on each of the filters is shown. The data are shown in three series, each with a different HayeSep Q filter bed length. The data are presented graphically and a slightly different format in Figure 10 where the total amount of volatiles captured in each bed are expressed as a percent of the total amount of volatiles captured. Very little difference is shown in the total amount captured when the HayeSep Q bed varies from 1.5 in (37 mm) to 4.5 (111 mm). Based on these results, the research team has concluded that breakthrough is minimal. A conservative HayeSep Q filter bed length of 3.9 in (100 mm) was selected for future work.

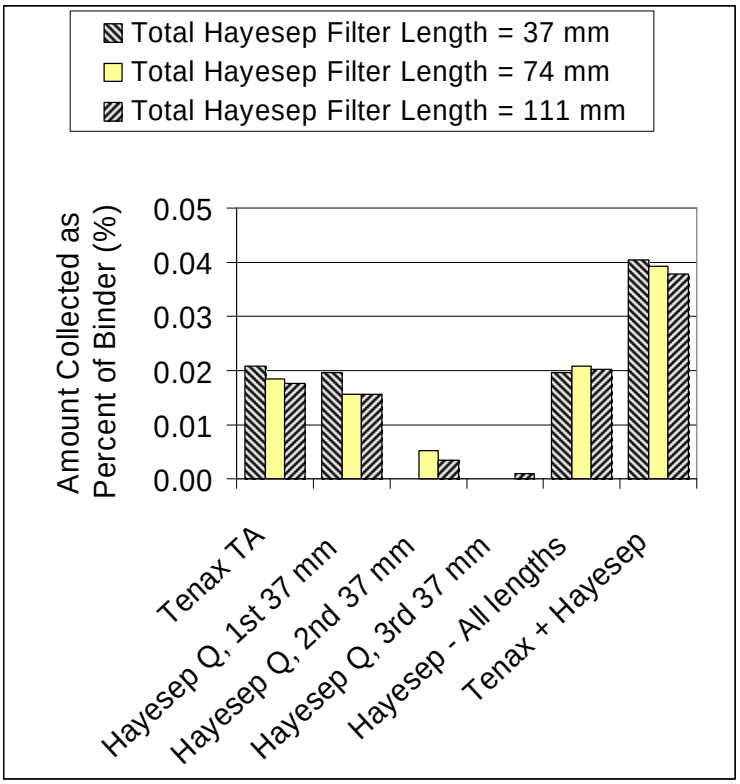


Figure 9. Material Collected with Varying HayeSep Bed Lengths, Citgo 58-28.

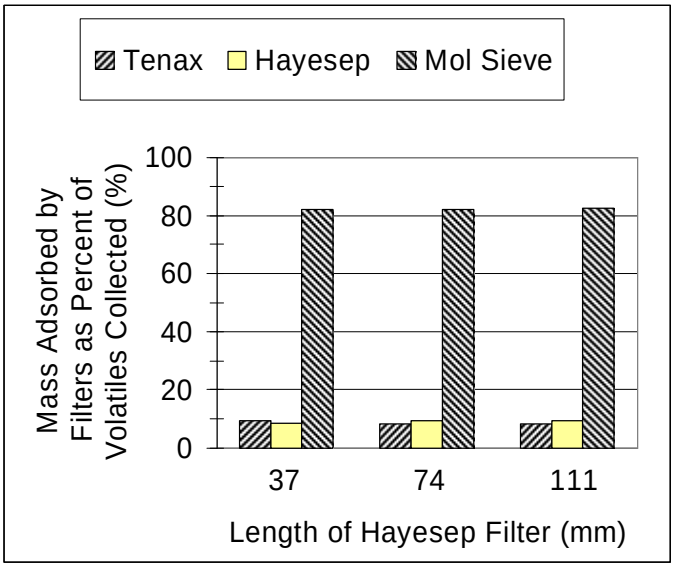


Figure 10. Volatile Mass Captured in Each Filter as a Percentage of Total Volatiles with Varying HayeSep Q Bed Length, Citgo 58-28.

Internal discussions as well as input from others outside the study suggested that the Tenax A filter could be removed from the system. Removing the Tenax A filter bed would simplify and reduce the cost of the VCS. Replicate SAFT runs were conducted with various lengths of HayeSep Q with and without the Tenax A. The results are shown in Figure 11. These results justify the removal of the Tenax A filter. The final configuration for the VCS-III is shown schematically in Figure 12. It consists of silica gel and activated carbon filters in the inlet gas stream. The outlet stream passes through a (3.9 in) 100 mm long HayeSep Q collector to collect hydrocarbons and a 5 A molecular sieve to collect water. The HayeSep Q collector and the molecular sieve are challenged prior to testing by passing nitrogen gas at 2 l/min and 250°C inlet temperature for 15 minutes.

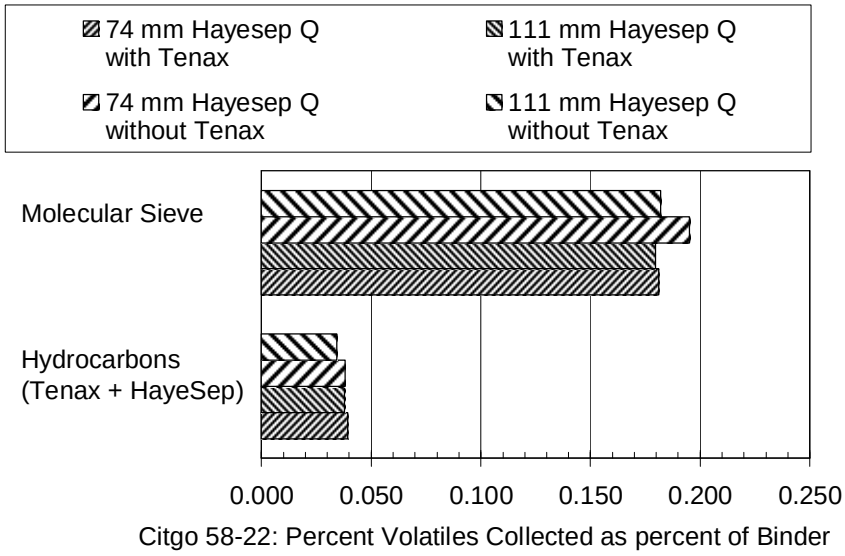


Figure 11. Volatiles Collected with and without Tenax A, VCS-3, and Citgo 58-28.

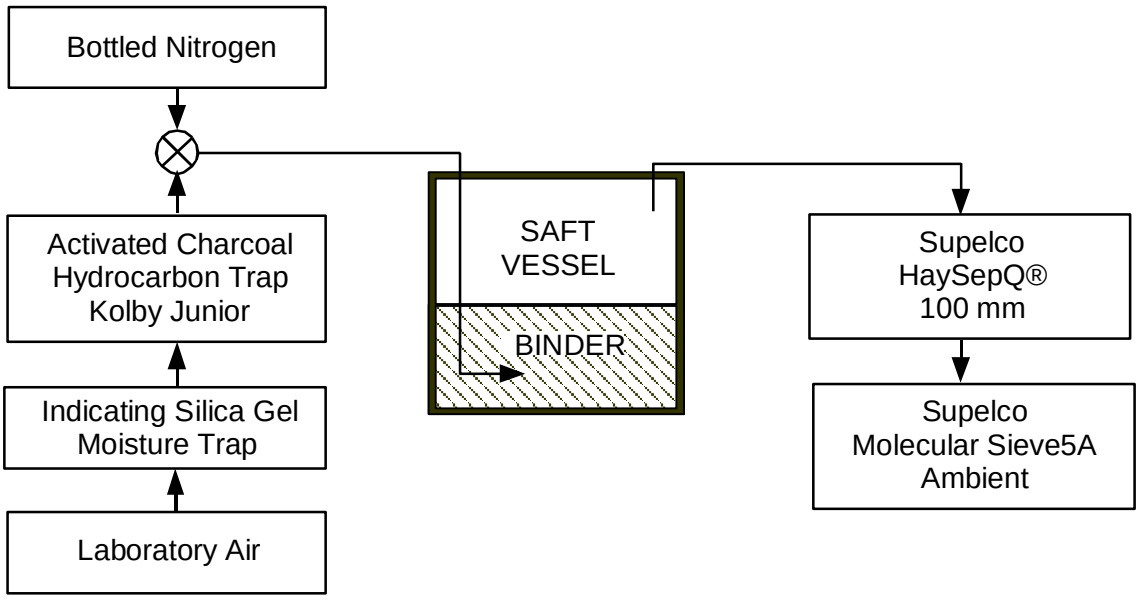


Figure 12. Final Version of VCS-III.

6.2 VCS-III Evaluation

The SAFT fitted with the VCS-III was used to condition the 12 binders used in the Verification Study. Three replicate samples of each binder were conditioned in the SAFT and the RTFOT. The amount of material collected on the HayeSep Q and the molecular sieve for each of the asphalt binders is shown in Table 6. Also shown in Table 6 is the negative value of the RTFOT mass change and the combined mass of the material collected on the HayeSep Q and the molecular sieve. The negative value of the RTFOT mass change is used so that a positive value for the absorbents and the RTFOT indicate material lost during the conditioning procedure.

Table 6. Mass Collected on VCS-III Filters and RTFOT Mass Change.

	Mass Collected on Filters, % of Original Mass			
Binder	HayeSep Q	Molecular Sieve	Combined HayeSep Q and Molecular Sieve	Negative of RTFOT Mass Loss, % of Original Mass
AAC-1	0.072	0.141	0.214	0.058
AAD-2	0.041	0.134	0.175	1.058
AAF-1	0.043	0.114	0.157	0.008
ABM-2	0.024	0.113	0.137	0.349
ABL-1	0.049	0.129	0.178	0.654
AAM-1	0.014	0.085	0.100	-0.122
Citgoflex	0.020	0.052	0.072	0.196
ALF 64-40	0.046	0.007	0.053	0.207
Air Blown	0.020	0.061	0.081	-0.031
Elvaloy	0.000	0.003	0.003	0.173
EVA	0.020	0.005	0.026	0.132
Novophalt	0.025	0.006	0.031	0.132

There is no apparent correlation between the mass lost during RTFOT conditioning and the mass collected on the individual or combined absorbents. This is illustrated graphically in Figure 13 where the mass collected on the absorbents is plotted versus the mass lost during the RTFOT conditioning. This is not surprising given that the RTFOT represents the balance between the oxygen consumed by oxidation, loss of hydrocarbon volatiles, and water resulting from oxidation or other chemical reactions. As shown in Figure 14, water accounts for 65% to 85% in seven of the binders and all of the unmodified binders. Hydrocarbons predominate in

three binders: the ALF 64-40, Novophalt, and EVA. Although not shown graphically, the ratio formed by dividing the percentage of water collected by the amount of hydrocarbons collected shows no relationship with the RTFOT mass change. No valid correlation was found between RTFOT mass change and the mass collected on the absorbents.

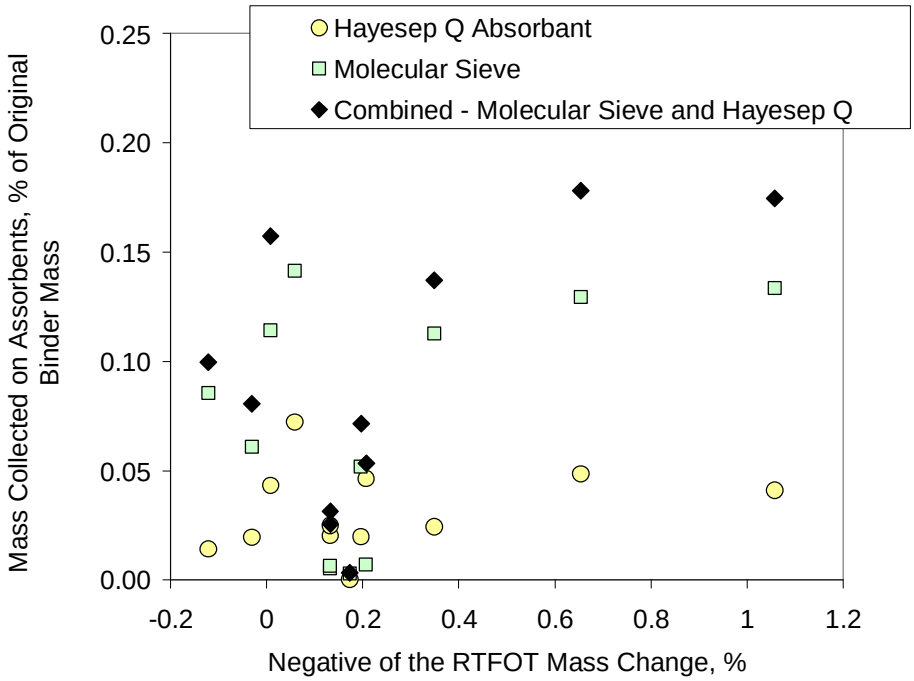


Figure 13. Material Collected on Molecular Sieve and HayeSep Q versus RTFOT Mass Change.

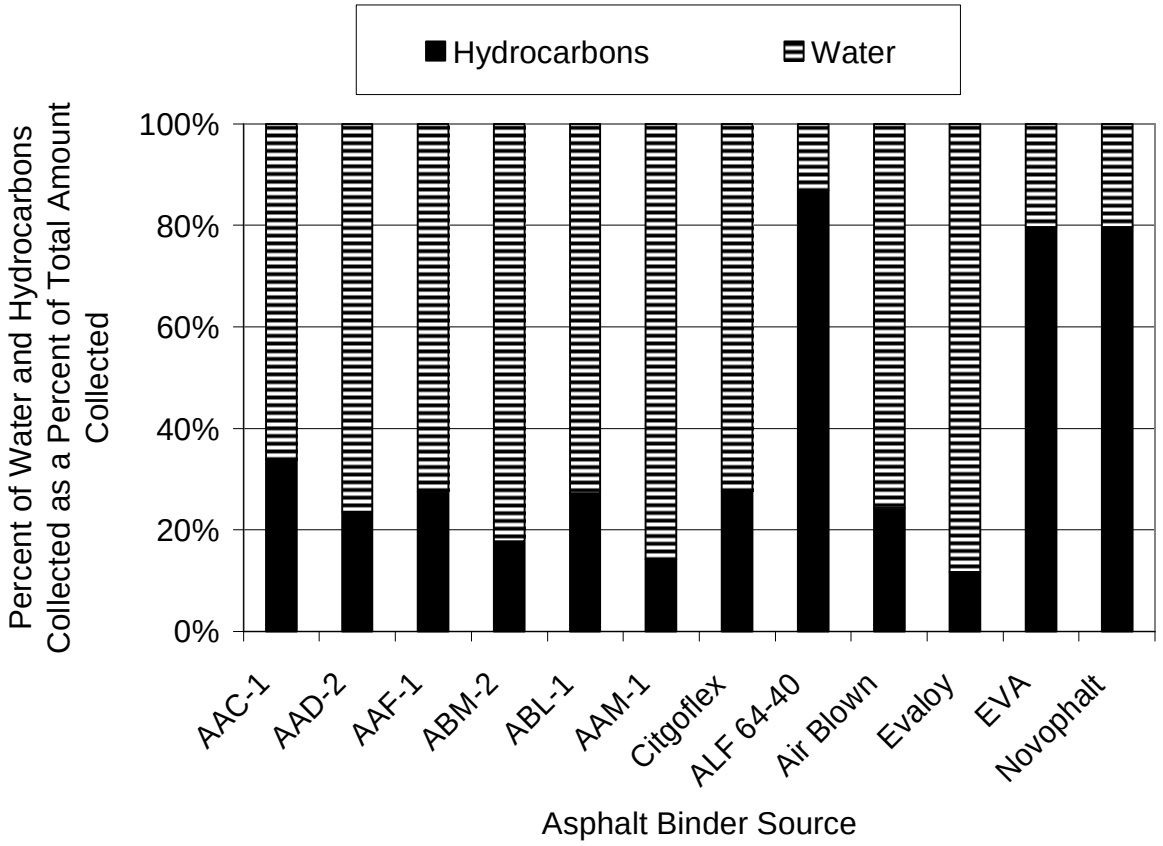


Figure 14. Relative Percent of Hydrocarbon and Water Collected on HayeSep Q and Molecular Sieve.

7.0 VCS STUDY FINDINGS

The VCS Study consisted of a series of experiments to evaluate potential causes of the unexpectedly low mass of volatiles collected the air-cooled condenser that served as the VCS in the prototype SAFT. The primary cause of this anomaly was attributed to the ineffectiveness of the air cooled condenser in collecting water vapor which allowed the water vapor to pass completely through the condenser. A redesigned VCS employing adsorbents used for chromatographic analyses was developed during the study. The final version of the redesigned uses two reusable filters, Supelco HayeSep Q resin beads and a 5 A molecular sieve, to separate and collect hydrocarbon volatiles and water from the exhaust stream of the SAFT.

For most of the binders tested in NCHRP 9-36, water was the primary component collected by the redesigned VCS. Comparisons of the mass of volatile compounds collected with the redesigned VCS and the mass loss from the RTFOT showed no correlation.

8.0 REFERENCES

1. Glover, Charles, J., Davison, Richard R., Vassiliev, Nikolai, Hausman, Todd, and Williamson, Shelly, A., "Development of a Stirred Air-Flow Test (SAFT) for Improved HMAC Plant Binder Aging Simulation and Studies of Asphalt Air Blowing," Report Number FHWA/TX-02/1742-4, Texas Transportation Institute, College Station Texas, September 2001, 80 pp.
2. Glover, Charles, J., Davison, Richard R., and Shah, Purveshkumar, V., "Pilot Implementation of New Binder Aging Simulation Equipment," Report Number FHAW/TX/02/1742-imp-S, Texas Transportation Institute, College Station Texas, July, 2002, 60 pp.