Evaluation of Solvents for Extraction of Residual Asphalt from Aggregates

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When highway cores and hot mixes are extracted, several percent of the asphalt frequently remains on the aggregate. A variety of solvents were evaluated for their ability to remove this material. They were compared using several aggregates that had been extracted by three procedures. The effectiveness of alcohols as a solvent additive was investigated. Finally a direct comparison of trichloroethylene and toluene containing 15 pecent ethanol using an old road-core material was made. In general, trichloroethylene containing 15 percent ethanol was the best solvent tested. Pyridine is similar but objectionable for other reasons. The residual unextracted material is difficult to remove even with the best solvents.

To study the changes occurring in asphalt as it hardens in the hot-mix plant or roadway and to determine the asphalt content of cores and mixes, asphalt must be extracted from the aggregate. This is done almost exclusively today by either the centrifuge or reflux procedure, usually as specified in ASTM D2172, Methods A and B.

A number of solvents have been used to extract the asphalt. In early years, carbon disulfide was widely used but was largely replaced by benzene. In the 1950s and 1960s, chlorinated solvents became popular. The most common were trichloroethylene, 1,1,1-trichloroethane, and methylene chloride. Abson and Burton (1, ASTM D2172-81) tested several of these and found trichloroethylene to be as effective as benzene. Addition of about 10 percent ethanol or methanol to benzene was shown to remove more asphalt from the aggregate (2). This has become popular among many researchers. Because benzene has been proven carcinogenic, its use has been phased out and trichloroethylene has been the primary replacement. Pyridine and tetrahydrofuran are used on rare occasions for specialized extractions (3,4).

Either Method A or B with a variety of solvents is satisfactory for determining the percent asphalt. Round-robin tests of various procedures show no difference in results (5). Actually, none of these procedures removes all the asphalt, but the quantity remaining is within the variance of the methods. This does not guarantee that results will be satisfactory when the properties of the recovered asphalt are studied, however.

INADEQUATE EXTRACTION AND RECOVERY METHODS

Evidence is strong that the present extraction and recovery methods are either inadequate or being performed improperly

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in the laboratories nationwide. AASHTO conducts interlaboratory proficiency tests periodically to determine the precision of the methods. It sends identical pavement samples to 50 to 100 laboratories. The laboratories extract and recover the asphalt, perform various tests, and send the results to AASHTO. In a February 1989 report, the coefficients of variance on recovered viscosities were about 25 percent. In earlier years, it has been as high as 42 percent (6).

In the extraction-recovery discussions, there appear to be three main areas from which errors are likely to stem:

1. The solvent has some hardening effect on the asphalt, which increases with temperature and time of exposure.
2. Solvent is often not completely removed from the asphalt during recovery. This results in viscosities that are lower than the true value.
3. Asphalt is not completely removed from the aggregate. The strongly adsorbed material left on the aggregate has a significantly different composition than the bulk asphalt.

Solvent Hardening

Solvent hardening of asphalt is particularly severe at higher temperatures such as exist in the reflux method. Though ASTM D1856 specifies that ASTM D2172 Method B is not to be used when asphalt properties will be determined, a survey of the literature indicates this has been ignored as often as followed. Even when using low-temperature extraction, it has been shown that some solvent hardening usually occurs (7). Incomplete solvent removal has been studied in detail by Burr et al. (8).

Incomplete Extraction

It is evident that the percentage of total asphalt removed during extraction could also be significant in determining a method's effectiveness. Traxler (2) has found that additional asphalt can be removed by adding 10 percent ethanol to benzene. Pyridine has also been used to extract additional asphalt (9). Petersen et al. (10,11) have published several papers that state that up to 4 percent—but usually 2 percent—of the asphalt remains on the aggregate after benzene or trichloroethylene extractions. The asphalt seems to be more strongly adsorbed in old cores than in laboratory mixes.

The strongly adsorbed material is also of a different nature than the bulk asphalt. Glover et al. (12) has shown this ma-

terial to be highly oxidized. Petersen (13) analyzed this material and found concentrations of carboxylic acids were higher by 12 to 63 times, anhydrides 4 to 32 times, ketones 1 to 6 times, sulfoxides 1 to 4 times, and 2-quinoline types 3 to 10 times in the strongly adsorbed material. Relative affinities of functionalities to the aggregate with respect to the bulk are carboxylic acids > dicarboxylic anhydrides > 2-quinoline types > sulfoxides > other nitrogen groups > ketones. Ketones and sulfoxides can account for 90 percent of the polar compounds in the strongly adsorbed material (9). The amount of strongly adsorbed material is a function of the aggregate surface area and not as dependent on aggregate composition (9). Apparently, no work has been done to determine the effect on physical properties of adding the strongly adsorbed material back to the bulk asphalt. It is not even clear whether the strongly adsorbed material should be considered part of the asphalt binder. Because of its strong interaction with the aggregate, it may play a stronger role as an aggregate substituent.

Most solvents that have been used for extracting asphalt from aggregates remove the bulk of the asphalt rather quickly but leave some material that is not removed even after repeated or lengthy contacting. The choice of solvent or solvent mixtures, then, should be based on efficiency removing the hard-to-remove material. Pyridine has been indicated to be particularly effective as a single solvent for removing this material. Methanol and ethanol have been shown in this laboratory and in others to improve the ability of commonly used solvents to remove this material with about 15 percent ethanol in trichloroethylene being optimum.

In this work, a number of solvents and mixtures with alcohols are quantitatively compared with respect to their ability to remove the hard-to-remove material from a variety of previously extracted (recovered) aggregates. Because of some objection to chlorinated solvents, direct comparisons between trichloroethylene, toluene, and cyclohexane were made with various alcohol contents.

PROCEDURES

Pavement cores or hot mixes extracted using ASTM D2172 Method A or Method B or a method using trichloroethylene/ethanol previously recommended by this laboratory (modified Method A) were used. The resulting recovered aggregate material was subsequently contacted by solvents to test their ability to remove any strongly adsorbed residual asphalt material.

The recovered aggregates used in this study were limestone from several sources and were obtained in several ways. First, three recovered aggregates, simply identified by their state of origin—New York (NY), Georgia (GA), and California (CA)—were used. These had all been pavement cores extracted by Method B using trichloroethylene. Second, a composite core (CC) recovered aggregate was formed from a large amount of diverse discarded core material. The core material was divided into three portions, each of which was extracted by a different method—ASTM D2172 Method A using trichloroethylene, Method B using trichloroethylene, and the recommended modified procedure using trichloroethylene/ethanol—to give three more recovered aggregate materials.

Third, the recovered aggregate from an Ampet AC-20 hot mix was obtained by an ASTM D2172 Method B extraction and was used in several experiments. In one experiment, this hot-mix recovered aggregate was extracted with pyridine by repeated contacts in a beaker until additional asphalt removal was not evident, and another, a Method B−extracted core, was preextracted with trichloroethylene before the experiment. Finally, a few experiments were made with unidentified Method B−extracted core material. Clean limestone aggregate with no previous contact with asphalt was used as a blank.

To obtain a measure of the relative extraction power of the different solvents or solvent systems, 100- or 150-mesh fines were obtained from each of the recovered aggregates and the blank, and these were used in subsequent extraction experiments with a variety of solvents and conditions. Ten grams of fines were weighed into vials, and 10 mL of the solvent were added. The fines were allowed to soak for 24 hr and then they were filtered. At 650 nm the absorbance was found to vary linearly with whole asphalt content, and this was assumed to be true for all asphalt fractions. Furthermore, in each case the absorbance (650 nm) was normalized by the amount of aggregate contacted to obtain absorbance per gram of aggregate contacted. This provided a basis for comparing the various extracted fine samples. The absorbance measurements were not further converted to an amount of asphalt extracted, however, because of the assumptions that would be required to justify such conversions, that a calibration made with a given whole asphalt would be valid for the hard-to-remove material.

In modified Method A, 15 percent ethanol is added to the solvent and the hot-mix or core material is stirred after each solvent addition. In a final experiment, this procedure was used in a direct comparision of trichloroethylene and toluene.

In all, the following eight sets of experiments were performed:

1. Fines from a Method B−extracted core were equilibrated with 12 solvents to compare their relative abilities to remove the residual hard-to-remove material.
2. Fines from the same Method B−extracted core were further extracted using two successive room-temperature washes, each with 200 mL trichloroethylene, in an Erlenmeyer flask. The fines were then equilibrated with the same 12 solvents as Experiment 1 to compare their relative abilities to remove the residual material.
3. Fines resulting from the different extraction methods or from the different aggregate sources equilibrated with 10 solvents to compare the different methods and sources in their amounts of residual material and to compare the effectiveness of the solvents in removing the residual material.
4. Method B−extracted CC fines containing incremental quantities of water were equilibrated with trichloroethylene and trichloroethylene/15 percent ethanol to evaluate the effect of moisture on these solvents' abilities to remove the residual asphalt material.
5. Method B−extracted hot-mix fines were equilibrated with toluene and cyclohexane containing incremental amounts of methanol and ethanol to evaluate these solvent systems.
6. Method B−extracted hot-mix fines were equilibrated with trichloroethylene and toluene containing incremental amounts

of ethanol and propanol to evaluate the relative abilities of these alcohols to enhance removal of the residual material.

7. Three fines loadings of Method A–extracted CC material were equilibrated with trichloroethylene containing incremental amounts of ethanol to assess the optimum trichloroethylene/ethanol ratio.

8. Both hot-mix and CC aggregate materials were extracted by modified Method A using 15 percent ethanol in either toluene or trichloroethylene. These recovered aggregate materials were then equilibrated in pyridine for several days, and the amount of asphalt thus dissolved in the pyridine was determined gravimetrically so as to establish the fraction of the original asphalt left behind by the extraction method for a solvent.

In Experiments 1 and 2, the fines loading in the equilibrating solvent was 2 g of 150-mesh material to 10 mL of solvent. In Experiments 3–6, 5 g of 100-mesh fines were used per 10 mL of solvent. In Experiment 7, incremental amounts of 100-mesh fines were used. In Experiment 8, the entire recovered aggregate from a hot-mix or core extraction (approximately 1000 g) was equilibrated with 1 L of pyridine.

RESULTS

The results of Experiments 1 and 2 are given in Figure 1. The extractability index is defined to be the 650 nm absorbance of that solvent's equilibrated solution relative to the absorbance of the trichloroethylene solution obtained from Experiment 1. In Experiment 2, the same fines were further extracted with trichloroethylene before the 24-hr experiment. As can be seen, trichloroethylene/15 percent ethanol and pyridine are very nearly equal and give the best results in each instance, particularly as more material is removed.

Results for various recovered-aggregate/solvent combinations are given in Table 1 (Experiment 3). Figure 2 compares the solvents on the New York, Georgia, and California Method
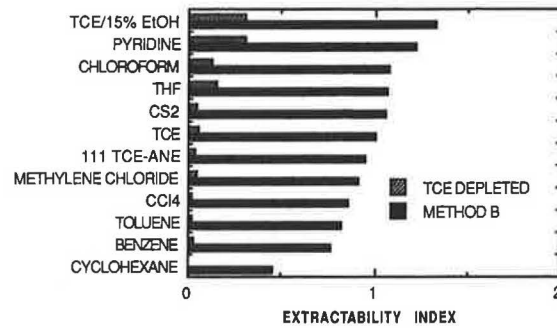

FIGURE 1 Comparison of solvents for extraction of hard-to-remove material from aggregate.

B–recovered aggregates. Pyridine and trichloroethylene/ethanol are generally best (yield the highest 650 nm absorbance). All absorbance levels were lower for the California aggregate, indicating that it had been much more completely extracted previously.

Figure 3 compares the solvents relative to the method used to preextract the composite recovered aggregate. As can be seen, the modified Method A using trichloroethylene/ethanol was always superior, providing the least amount of asphalt subsequently removed by a solvent wash, followed by Method A, which in turn is superior to Method B. Comparing the solvent systems, trichloroethylene/ethanol is best, extracting the most of the hard-to-remove residual asphalt, except on the material that was preextracted with trichloroethylene/ethanol (modified Method A) on which pyridine was marginally best. On the hot-mix aggregate preextracted with pyridine, however, trichloroethylene/ethanol was clearly superior (Figure 4). It appears that each solvent may selectively remove certain materials.

Six experiments were performed to assess the effect of water on extractability (Experiment 4). Recovered aggregate (CC material, Method B extraction) was used with trichloroethylene and trichloroethylene/15 percent ethanol (absolute). The

TABLE 1   650 nm ABSORBANCES OF SOLVENTS CONTACTED WITH VARIOUS RECOVERED AGGREGATES

| Solvents	650 nm Absorbance per gm of Recovered Aggregate					Composite Core		
	Blank	N Y	GA	CA	Pyridine	Modified A	Method A	Method B
Trichlor/Ethanol	0.0000	0.0251	0.0437	0.0078	0.0374	0.0268	0.0768	0.2371
Pyridine	0.0026	0.0307	0.0448	0.0170	0.0128	0.0302	0.0722	0.2291
Chloroform	0.0000	0.0252	0.0264	0.0012	0.0056	0.0074	0.0330	0.1339
Tetrahydrofuran	0.0006	0.0108	0.0276	0.0010	0.0052	0.0074	0.0370	0.1431
Carbon disulfide	0.0038	0.0204	0.0200	0.0048	0.0064	0.0094	0.0250	0.1092
Trichloroethylene	0.0058	0.0212	0.0192	0.0064	0.0078	0.0052	0.0176	0.0923
111-Trichloroethane	0.0036	0.0192	0.0176	0.0056	0.0076	0.0094	0.0244	0.0934
Methylene Chloride	0.0044	0.0186	0.0232	0.0048	0.0042	0.0090	0.0154	0.0931
Carbon Tetrachloride	0.0032	0.0132	0.0122	0.0018	0.0014	0.0024	0.0100	0.0679
Benzene	0.0018	0.0122	0.0094	0.0018	0.0042	0.0050	0.0116	0.0769
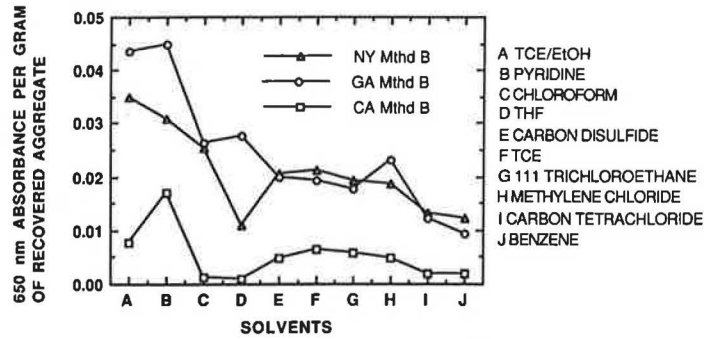
FIGURE 2 Comparison of solvent systems' abilities to extract hard-to-remove asphalt material remaining on aggregate after ASTM D2172 Method B extraction using trichloroethylene (three sources of pavement core were used).
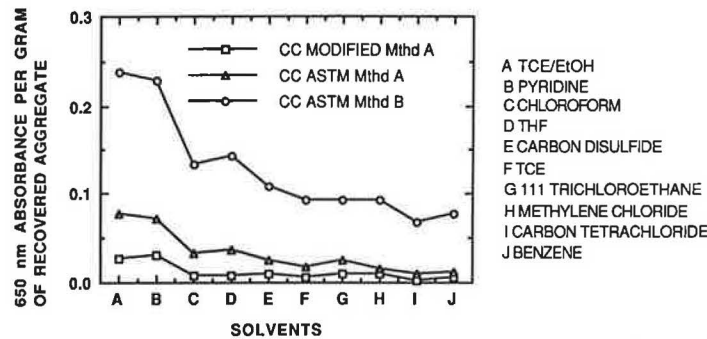

FIGURE 3 Comparison of solvent systems' abilities to extract hard-to-remove asphalt material and of amount of hard-to-remove material left by three extraction procedures.
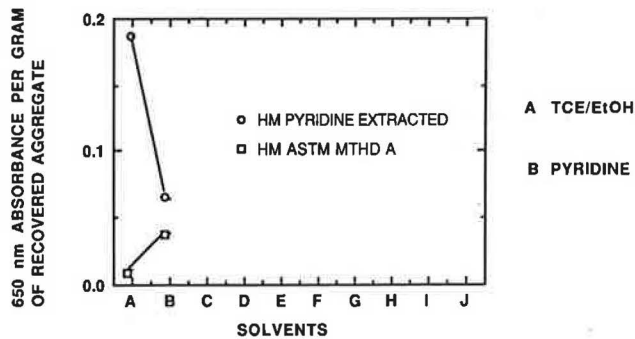

FIGURE 4 Ability of pyridine to remove material left behind by trichloroethylene/ethanol extraction procedure and vice versa.

TABLE 2 EFFECT OF WATER ON EXTRACTABILITY FROM THE METHOD B-EXTRACTED CC AGGREGATE

% Water in Solvent	650 nm Absorbance per gm of Recovered Aggregate	
	TCE	TCE/Ethanol
0	0.011	0.027
2	0.012	0.032
5	0.007	0.025

results in Table 2 suggest that the effect of added moisture to the solvent probably is not significant. This does not, however, assess the effect of prolonged soaking of a pavement core in water (i.e., weathering) on asphalt extraction.

To study the effect of alcohol on the extraction power of nonchlorinated solvents, recovered aggregate (hot-mix material, Method B extraction) was treated with incremental quantities of methanol and ethanol in cyclohexane and toluene (Experiment 5). The results in Table 3 indicate that methanol is relatively ineffective as an additive and that toluene/ethanol is much superior to cyclohexane/ethanol, although inferior to trichloroethylene/ethanol.

Because ethanol was so superior to methanol, it was decided to investigate propanol as an additive in both trichloroethylene and toluene (Experiment 6). New samples of the same recovered aggregate were used. The results are shown in Table 4 and Figure 5. Propanol is seen to be less effective than ethanol, and toluene less effective than trichloroethylene.

Using a different recovered aggregate (CC material, Method A extraction) additional data were obtained to reconfirm the optimum ethanol level in trichloroethylene. This was done at three different recovered aggregate-to-solvent loadings (Experiment 7). The results are shown in Figure 6 and indicate that the alcohol content should be at least 15 percent but that little is gained beyond that.

This multiple testing indicated that for probably any aggregate and at any solvent-to-aggregate ratio, trichloroethylene with 15 percent ethanol was equal or superior to any

TABLE 3 EFFECT OF METHANOL AND ETHANOL ON EXTRACTABILITY OF TOLUENE AND CYCLOHEXANE FOR METHOD B–EXTRACTED HOT-MIX RECOVERED AGGREGATE

% Alcohol Added	650 nm Absorbance per gram of Recovered Aggregate			
	Toluene		Cyclohexane	
	Methanol	Ethanol	Methanol	Ethanol
0	0.003	0.001	0.003	0.000
5	0.004	0.016	0.001	0.008
10	0.003	0.019	0.002	0.007
15	0.003	0.026	0.001	0.009
20	0.003	0.025	0.009	0.013
25	0.003	0.024	0.005	0.010

TABLE 4 EFFECT OF ETHANOL AND PROPANOL CONCENTRATIONS ON EXTRACTABILITY FOR METHOD B–EXTRACTED HOT-MIX RECOVERED AGGREGATE

% Alcohol	650 nm Absorbance Per Gm of Recovered Aggregate			
	Trichloroethylene		Toluene	
	Ethanol	n-Propanol	Ethanol	n- Propanol
5	.0548	.0465	.0324	.0244
10	.0756	.0535	.0429	.0286
15	.0799	.0586	.0478	.0312
20	.0871	.0619	.0542	.0352
25	.0862	.0598	.0687	.0389
30	.0753	.0597	.0554	.0413

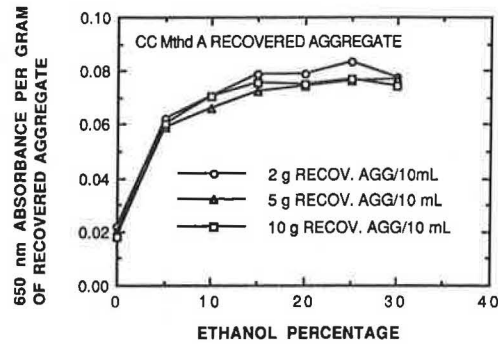FIGURE 5 Comparison of ethanol and propanol as additives for improving asphalt extraction.

FIGURE 6 Effectiveness of ethanol in improving asphalt extraction at different alcohol concentrations.

extraction). The results shown in Figure 7 were obtained by soaking the recovered aggregate in pyridine for several days and quantitatively determining the asphalt material dissolved in the filtered solution by evaporating aliquots to dryness and weighing the residual asphalt. Determinations were made at 1, 3, and 9 days of soaking; the data in Figure 7 are the 9-day determinations. Two separate determinations were made for each (solvent system)/(asphalt core or mix) combination to give the eight data points shown in Figure 7.

The results show estimates of the percentage of the original asphalt that remained after extraction using the modified Method A procedure. The amounts of solvent used on the eight tests vary because of the way in which the procedure is carried out. Solvent contact is continued until the solvent comes out straw-colored, independent of the solvent system used. The data indicate the trichloroethylene/ethanol system more efficiently removes the hard-to-remove material from the recovered aggregate than does the toluene/ethanol system when this variation of solvent volume is taken into account (Figure 7). When the same amount of solvent is used for the two solvent systems, as was the case for the hot-mix material, the trichloroethylene system removes significantly more or leaves significantly less of the hard-to-remove material than does the toluene system. But when the same amount of residual material was left by the extraction procedure by the two solvent systems, the trichloroethylene system achieved its level by using significantly less solvent than the toluene

other solvent tested. It also indicated that the modified Method A using trichloroethylene/15 percent ethanol with increased agitation removed more material than Method A or B.

The final experiment (Experiment 8) was a direct comparison of toluene/15 percent ethanol and trichloroethylene/15 percent ethanol using modified Method A (which included stirring of the solvent and mix before soaking for improved
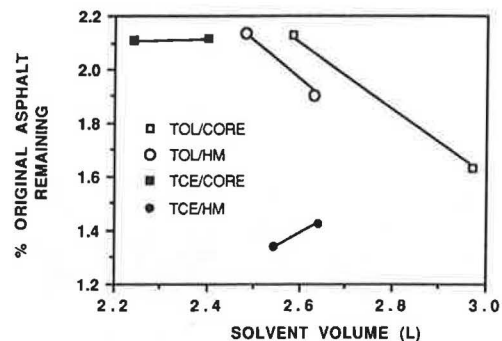

FIGURE 7 The unextracted material remaining following extraction with trichloroethylene/ethanol and toluene ethanol as a function of the solvent volume used.

system used. The one toluene extraction on the core material that resulted in the lowest amount of residual asphalt remaining required 50 percent more solvent than the trichloroethylene extractions.

From the pyridine soakings of the eight recovered aggregate samples of Experiment 8 made at the 1-, 3-, and 9-day soak times (Figure 8), it is evident that contact time also plays a significant role in the recovery of this residual material. The total contact time in modified Method A is 2.5 to 3 hr spread over six or seven contacts. The pyridine—which, based on the experiments described earlier, is a considerably better solvent—still extracted additional material after 9 days. Obviously, the trichloroethylene and toluene systems after only 2.5 to 3 hr would have benefited from additional contact time as well.

Finally, it should be recalled that Figure 3 indicates that modified Method A is superior to Method A, but that the increased agitation in the modified method might account for most of the superiority rather than the different solvent systems (trichloroethylene/ethanol versus trichloroethylene).

The data clearly show that no method removes all the asphalt; to take full advantage of the better solvents for hard-to-remove material, more agitation and longer contact is required, but does it matter? Material that is so hard to remove probably affects adhesion but not bulk properties. It might be that the property of only the relatively easily removed material is a better predictor of cracking. Certainly the easily extracted and hard-to-remove material can be extracted and studied separately. Regardless, it is desirable to have an extraction procedure that at least can remove all the material.

CONCLUSIONS

1. Trichloroethylene with 15 percent ethanol is a superior solvent.

2. Trichloroethylene/ethanol and pyridine are comparable in solvent power for a hard-to-remove material but appear to remove different material preferentially.

3. If only removing the bulk of the material is required, then many solvents and methods will suffice although there are some differences.

4. To recover more than 99 percent of the asphalt material will require the development of better contacting methods.
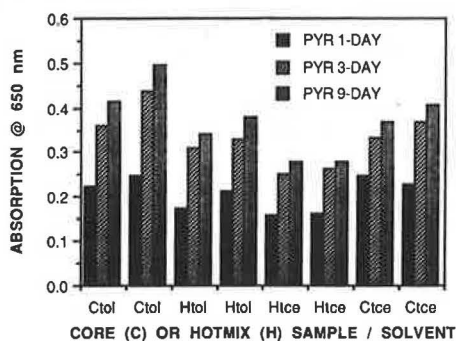

FIGURE 8 Time required for pyridine to remove hard-to-remove material from extracted core aggregate.

5. Extraction and recovery procedures also must be designed to minimize solvent hardening and ensure complete solvent removal.

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