SD94-03-F

SD Department of Transportation
Office of Research

INVESTIGATION OF ANOMALOUS ASPHALT CONCRETE ON US212

Study SD94-03
Final Report

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May, 1995

DISCLAIMER

ACKNOWLEDGEMENTS

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TECHNICAL REPORT STANDARD TITLE PAGE

1. Report No.
SD94-03-F

2. Government Accession No.

3. Recipient's Catalogue No.

4. Title and Subtitle
Investigation of Anomalous Asphalt Concrete on US212

5. Report Date
March 31, 1995

6. Performing Organization Code

7. Author(s)
Elaine Thompson, PhD

8. Performing Organization Report No.

9. Performing Organization Name and Address
Technical Research, Investigations and Development (TRIAD) Ltd.
787 Haney Street
Winnipeg, Manitoba, Canada R3R 0Y7

10. Work Unit No.

11. Contract or Grant No.
310307

12. Sponsoring Agency Name and Address
South Dakota Department of Transportation
Office of Research
700 East Broadway Avenue
Pierre, SD 57501-2586

13. Type of Report and Period Covered
Final;May 94-June 95

14. Sponsoring Agency Code

15. Supplementary Notes
A 2-page executive summary is included with the report

16. Abstract

An investigation into a recycled asphalt pavement built in 1989 on US212 between La Plante and the Missouri River which had prematurely failed revealed an unusually high concentration of metals in the asphalt cement. These metals, capable of promoting the oxidation of asphalt, could not be attributed entirely to either the fines or the stones in the asphalt mix. The types of metals found (by inductively coupled plasma emission spectroscopy, ICP) plus the nature of the organic compounds identified (by gas chromatography and mass spectrometry, GC/MS) in the asphalt cement suggest that either used lubricant or a residue of waste oil may have contaminated the asphalt used in the construction of the pavement built between LaPlante and the Missouri River.

17. Keyword
asphalt, pavement, failure, cracking, metals, oxidation, waste oil

18. Distribution Statement
No restrictions. This document is available to the public from the sponsoring agency.

19. Security Classification (of this report)
Unclassified

20. Security Classification (of this page)
Unclassified

21. No. of Pages
57

22. Price
$ 32,847.50

INVESTIGATION OF ANOMALOUS ASPHALT CONCRETE ON US212 - SD94-03

EXECUTIVE SUMMARY

Premature failure of US212 project F0212(56)187 constructed in the summer of 1989 led to an investigation into the cause of severe heaving at transverse cracks. As a part of that study, extractions of asphalt cement were carried out using reflux-type extraction equipment and 1,1,1-trichloroethane as the solvent. Fourteen cores had been removed from this and five other pavements built in the same general vicinity within a year or two of this project. Four cores from project F0212(56)187 were the last to be extracted. During the extraction of these cores, severe corrosion of the copper condensers was noted and the asphalt residue appeared curdled. That anomalous behaviour stimulated further investigation into the nature of possible contamination of the asphalt mix at that project.

In this investigation, extractions were carried out on twelve cores from four different projects. Ten cores were extracted by trichloroethane in the absence of heat. Two cores were extracted using a large glass soxhlet extraction apparatus, which subjected the sample to reflux conditions. Both cores were from the project F0212(56)187, taken from sites where cores had been removed for the first study (MRM 204.2 and MRM 188). Noxious fumes which formed during the extraction of the first core (from MRM 204.2) were collected in a water trap and were found to contain chlorides and nitrates/nitrites. The extracted asphalt had a curdled appearance. Prior to extracting the second core (from MRM 188), the yellow colored solvent was filtered to remove rust particles, then distilled. Fumes were not noticeable in the extraction of the second core, but the water trap still contained chlorides and nitrates/nitrites as well as sulfates. Nitrates/nitrites and sulfates are combustion products of diesel engines; the chloride appears to have come from the thermal decomposition of trichloroethane to hydrogen chloride - a reaction that is catalyzed by metals and metal oxides.

The asphalt cement from the core at MRM 188 was found to contain an unusually high concentration of ash, silica, aluminum, calcium, iron, magnesium, phosphorus, silicon and

zinc when compared with the asphalt cement from a core obtained from another paving project - F0073(14)146 - carried out the same summer by the same contractor using the same grade of asphalt from the same supplier. The asphalt cement from the original pavement - located in the bottom lift of Project F0212(65)205 at MRM 206 - contained elevated quantities of the same elements as well as of copper, lead and manganese.

Examination by x-ray diffraction and scanning electron microscopy of the inorganic materials of the asphalt cement extracted from MRM 188 revealed the presence of both mineral and metallic particles.

Comparing the organic compounds found in asphalt cements from US212 MRM 188 and US73 MRM 147 by gas chromatography/mass spectrometry revealed that most of the compounds identified in both asphalt cements are what one would normally expect to find in an asphalt. However, several compounds in the asphalt from US212 MRM 188 are also products of incomplete combustion of diesel fuel or decomposition products of lubricants. The presence of N-butyl benzenesulfonamide in the asphalt of MRM 188 could not be readily explained.

When the stones, fines and the asphalt cement extracted from cores obtained from US73 and US212 were compared chemically, it became apparent that the inorganic composition of the fines was not similar to that of the stones in the mix and that the inorganic composition of the asphalt cements could not be attributed solely to the fines in the mix.

The contaminant responsible for the anomalous behaviour of US212 between LaPlante and the Missouri River appears to be a high concentration of metals such as one might find in used oil or in waste lubricating oil distillation bottoms or processing sludges.

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1. INTRODUCTION

Premature failure of US212 project F0212(56)187 constructed in the summer of 1989 led to an investigation into the cause of severe heaving at transverse cracks [1]. Part of that study involved extractions of asphalt cement from asphalt concrete cores with the solvent 1,1,1-trichloroethane in reflux-type extraction equipment. Fourteen cores removed from this and five other pavements built in the same general vicinity within a year or two of the 1989 project had been extracted. Four cores from project F0212(56)187 - at MRM 188, 189.7, 198.4 and 204.2 - were the last of fourteen cores to be extracted. During the extraction of these four cores, severe corrosion of the copper condensers was noted and the asphalt residue appeared curdled. That anomalous behaviour prompted a request for research proposal (SD94-03) for further investigation into the nature of possible contamination of the asphalt mix.

1.1 Research Objectives

The Request for Research Proposal for Problem Number SD94-03 listed the following research objectives:

1) Identify the presence of any detrimental material present in the asphalt concrete.
2) Identify test methods that would detect of limit any extraneous materials in the asphalt.
3) Develop recommendations on implementation of test methods, policies and procedures to identify and limit any extraneous materials in the asphalt.

1.2 Research Tasks

The Request for Research Proposal for Problem Number SD94-03 listed that following research tasks:

1) Meet with the Technical Panel to review the work and scheduling.
2) Review and summarize relevant literature concerning asphalt concretes exhibiting high crack frequencies and asphalt that may contain foreign substances and exhibit anomalous extraction properties.

3) Review project documentation and interview appropriate departmental personnel.

4) Conduct appropriate physical and chemical analyses on the pavement materials in question to determine what may have contributed to excess cracking in the asphalt from LaPlant to the Missouri River on US212.

5) Provide comparative testing on two nearby projects fromt he previous research "Heaves at Transverse Cracks in Asphalt Concrete Pavement" SD92-11.

6) Based on the results of the physical and chemical analyses recommend test procedures that will identify asphalt exhibiting similar properties to those on US212 LaPlant to the Missouri River. The test procedures should include but not be limited to the SHRP test equipment and procedures.

7) Prepare a final report and executive summary of the literature review, research methodology, findings, conclusions and recommendations.

8) Make an executive presentation to the SDDOT Research Review Board at conclusion of the project.

2. BACKGROUND

An examination of the literature reveals a myriad of materials that have been added to asphalts - sometimes in an attempt to improve the properties of the asphalt cement and other times as a means of disposing of waste materials.

2.1 Salvage Asphalt Material

In recent years, one of the most common waste materials introduced into asphalt mixes has been salvage material from aged pavements. This is a practice that is encouraged by highway agencies as it provides a means of re-using the non-renewable resources contained in those pavements. While asphalt mixing technology has developed means of introducing salvage asphalt into new pavements in an environmentally acceptable manner, the binder in the resulting product is often much harder (having higher viscosity and lower penetration values) than an agency would normally accept in a pavement in the same climate with the same level of traffic if one were using new aggregate and asphalt only. Such a recycled pavement that has not been sufficiently rejuvenated by the new materials added to it should not be expected to have the same performance life as a new pavement made with virgin materials only. Many recycled pavements are still aged pavements.

2.2 Organic Wastes

Organic wastes are carbon-containing compounds that would typically be added to the asphalt cement prior to its use in an asphalt mix. While their effects on the properties of asphalt cement may be beneficial when they are used at certain concentrations, these organic wastes could have a detrimental effect on asphalt cements at higher levels. While the most common organic wastes added to asphalts would be materials like vulcanized rubber from scrap tires [2] and other polymeric wastes [3], there are other organic waste materials that either have been or could be incorporated into asphalts. These include processed waste oil [4], waste oil distillation bottoms [5], lignin from gasohol plants [6], petroleum-based solvents from inadvertent contamination [7], chlorinated solvents from dry-cleaning plants or laboratories, alkylamine distillation residues [8], fatty acid distillation residues [9], residues from the fractionation of synthetic aromatic substances [10], coal tars from metallurgical plants [11], pulping liquor waste [12], aromatic sulfonate wastes [13], petroleum distillation residues [14], shale oil distillation residues [15], carbon black wastes from coke-oven gas purification [16], plastics [17], pyrolysis products of cellulosic and polymeric wastes [18], waste coal [19] and waste roofing products [20].

2.3 Inorganic Wastes

Inorganic wastes may be incorporated either as part of the asphalt binder (if the particle size is small) or with the mineral aggregate (if particle size is larger). As with the organic wastes, the beneficial effects of inorganic waste materials may occur at some optimal range of concentrations, but excessive amounts would have a detrimental effect on the asphalt cement or the asphalt mixture. The most common inorganic materials placed into asphalt mixes are limestone (calcium carbonate) [21], lime (calcium oxide) [22] or hydrated lime (calcium hydroxide) [23]. Other inorganic waste materials introduced into asphalt mixes include sulfur [24], asbestos fibres [25], waste foundry sand [26], blasting sand [27], steel slag [28], baghouse fines [29], crusher waste dust [30], phosphate mining waste [31], ashes of various products [32], electroplating sludges [33], crushed porcelain toilets [34], contaminated soils [35] and glass [36].

Most of the inorganic wastes likely to be introduced into an asphalt binder or asphalt mix have the capability to stiffen the mix (as most fines do, by adsorbing the lighter ends of the asphalt) or to catalyze the oxidation of an asphalt cement in a mix (as multivalent metals like copper [37], manganese [38], iron [39], cobalt [40] and vanadium [41] do). Lime, however, has been found to reduce age-hardening [42].

2.4 Construction Problems

While the Class G asphalt mix (all virgin materials, lab designed for 6.3% AC-5) put down on Highway 73 in Project F0073(14)146 (also built in the summer of 1989) had been soft, had suffered tracking from the rollers and had to be redesigned several times [43], no such problems had been encountered for the recycled pavement built on Highway 212 earlier that summer. Project F0212(56)187 used 3.5 to 4.1% AC 120-150 in the HR mix [44] which was made up of a blend of salvage material (49%) and virgin asphalt cement and mineral aggregate (51%).

Problems that did occur in Project F0212(56)187 included the following:

- the pyrometer in the plant not working (June 2, July 18-20)
- pavement mat being "very crooked" (June 1-14) and rough (June 6)
- accidental spilling of 14 tons of "MC-70 prime oil" into a tank containing 64 tons of AC-5 (June 8 - contaminated AC was not used)
- tears in the mat from chunks coming out behind the paver (June 13) and
- the roller not being able to keep up with the asphalt plant (June 30, July 5-7).

Had the AC-5 contaminated with MC-70 prime oil been inadvertently used on June 8th or 9th, the sections paved on those days were STA 411-561 (MRM 194.4 to 197.1) eastbound lane and STA 425-553 (MRM 194.7 to 197.0) westbound lane. None of the cores obtained from Highway 212 came from either of those two sections. Except for low pavement densities resulting from insufficient rolling at the proper temperature, none of these problems appear to be related to the subsequent premature failure of the asphalt pavement. According to the construction diary, the sections of the project paved when rollers couldn't keep up to the plant were in the eastbound lane between Stations 491 and 641 (corresponding to MRMs 195.8 and 198.5), between eastbound Stations 200 to 491 (between MRM 190.6 and MRM 195.8 eastbound lane) and between Stations 316 to 452 westbound (between MRM 192.7 and MRM 195.1 westbound lane) [5]. No cores had been obtained from any of those pavement sections.

3. APPROACH

In connection with the present study, an examination of some of the records available at the Pierre office of the South Dakota Department of Transportation (SDDOT) led to a decision to obtain a total of 48 cores from between the wheel paths as summarized in Table 1. There were 28 from Project F0212(56)187 between LaPlant and the Missouri River, four cores from Project F0212(65)205 (the bottom lift of which contained the original pavement built in 1958), four cores from Project F0212(72)166 (recycled pavement built in 1990) and 12 cores from Project F0073(14)146 (the bottom lift of which contained AC-5 in a virgin mix). The sites of the cores are shown on a map in Figure 1.

Table 1 - Asphalt Cores obtained in Study

Sites of Cores	# of cores	Analyses	Comments
Hwy 212 MRM 176, WBL	4	1 - asphalt content (ASTM method)	West of LaPlante, **not** part of the problem pavement
Hwy 212 MRM 188, EBL	4	1 - asphalt content (ASTM method); asphalt properties; fines content in aggregate; inorganic composition of asphalt cement, fines & stones by ICP; organic content by GC/MS 1 - asphalt extraction (soxhlet method); off-gases trapped and analyzed; asphalt properties	Site of cores taken during previous (Preber) study
Hwy 212, MRM 190+398 (190.08) WBL	4		Part of the problem pavement
Hwy 212, MRM 192-111, (191.98) EBL	4		Part of the problem pavement
Hwy 212, MRM 194+1110 (194.2), WBL	4		Part of the problem pavement
Hwy 212, MRM 198+3976 (198.75), EBL	4		Part of the problem pavement
Hwy 212, MRM 202-370, (201.93), WBL	4		Part of the problem pavement
Hwy 212, MRM 204+1234 (204.2), WBL	4	1 - asphalt content (ASTM method); asphalt properties 1 - Soxhlet extraction; analysis of trapped off-gases	Site of cores in previous (Preber) study
Hwy 212, MRM 206, EBL	4	4 - asphalt content (ASTM method) and properties of bottom lift	Bottom lift represents original pavement of 1958
Hwy 73, MRM 146, SBL	4		
Hwy 73, MRM 147-2640, (146.5), SBL	4		
Hwy 73, MRM 147, SBL	4	1 - asphalt content (ASTM method) and properties; ash content of asphalt; inorganic composition of asphalt, fines and stones by ICP; organic content by GC/MS	Only the bottom lift was examined; Paved in late summer 1989 by same contractor as US212 project F0212(56)187

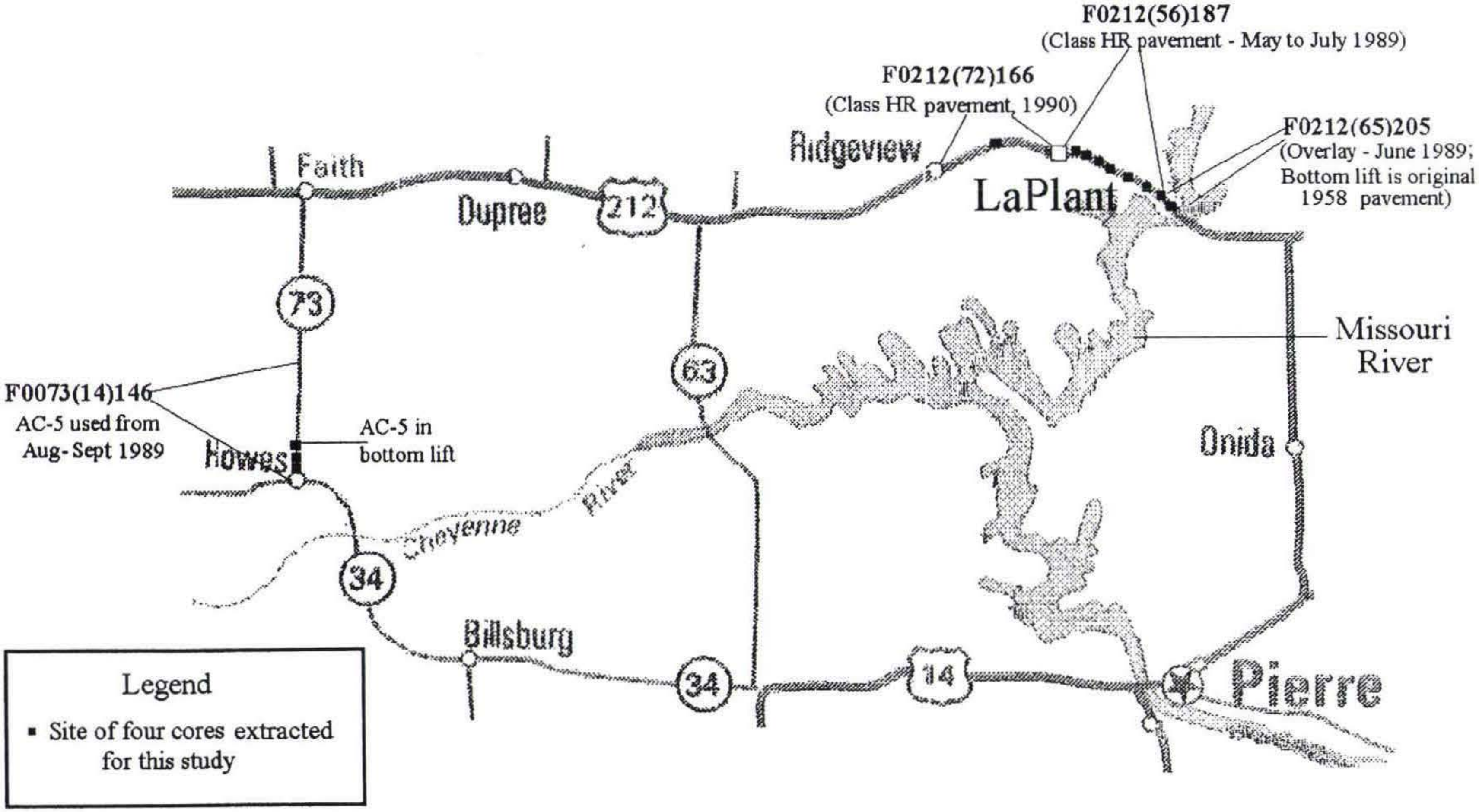

Figure 1 - Locations of the Pavements Cored

3.1 Rationale for the Core Sites

The bottom lift of Project F0212(65)205 contained the original pavement which was presumed to be identical with the aged pavement milled off Highway 212 between MRM 187 and MRM 205 then used as salvage material constituting 49% of the recycled mix put down as the pavement for the project F0212(56)187. The cores from both F0212(72)166 and F0212(56)187 were presumed to contain salvage material similar to that found in the bottom lift of Project F0212(65)205. Hence four cores were obtained from Highway 212 MRM 206 because their bottom lifts provided an indication of what the recycled pavements west to LaPlante and Ridgeview were like in terms of asphalt properties and fines content prior to recycling. Cores from Highway 212 between La Plante and Ridgeview (Project F0212(72)166) provided a comparison of a pavement that was purportedly similar in materials to that between LaPlant and the Missouri River (Project F0212(56)187), except that it was paved by a different contractor one year later.

Projects F0212(56)187 and F0073(14)146 had both been paved by the same contractor during the summer of 1989 using the same grade of asphalt cement (for the bottom lift only in the latter case) from the same supplier. The bottom lift of the cored section of Highway 73 had been paved between August 31st and October 16, 1989 by Heavy Constructors Ltd. of Sioux Falls and Rapid City [45] using an AC-5 (120-150 penetration asphalt) supplied by Little America refinery of Sinclair Oil Corporation. The top lift on Highway 73 was paved with AC-10 starting on September 28 as a result of persistent pavement softness during construction with AC-5 [2][46]. Built in the same summer, both pavements had been subjected to the same severely cold temperatures of the winter of 1989-90. The pavement at F0073(14)146 had less cracking than Hwy 212 between LaPlant and the Missouri River. The bottom lift of cores from Highway 73 would provide AC-5 that had only been subjected to aging during mixing and laydown, since its exposure to the elements was brief prior to being covered by the second lift. Hence the AC-5 from Highway 73 cores should provide an indication of the asphalt added to the recycled mix on Highway 212 between LaPlant and the Missouri River.

3.2 Cores Extracted

Of the 48 cores obtained from the various pavements, the following asphalt cores were extracted with 1,1,1-trichloroethane, the same solvent used in the 1992-93 study [1]:

i) One core from US212, MRM 176, westbound lane

> *The whole core was extracted. This pavement was paved in the summer of 1990 with an HR mix by Border States Paving using an AC-5 supplied by Little America refinery [47]. Located west of the problem stretch of US212.*

ii) Two cores from US212, MRM 188, eastbound lane (Project 0212(56)187, near Station 56, paved July 14th and 18th, 1989)

> *One core was extraced by the ASTM method and the second core was subjected to soxhlet extraction. This stretch of pavement between LaPlante and the Missouri River used AC-5 supplied by Little America Refinery for both the base course and the surface course. This was the site of cores removed for the Preber study [1]. Located within the problem area of US212.*

iii) Two cores from US212, MRM 204.2, westbound lane (near the eastern end of Project F0212(56)187, around Station 956, paved June 20 and June 23, 1989)

> *One whole core was extracted by the ASTM method and the second core was subjected to soxhlet extraction. AC-5 supplied by Little America refinery had been used for both lifts. This was another site where cores had been obtained for the Preber study. Located within the problem area of US212.*

iv) Four cores from US212, MRM 206, eastbound lane (near Station 56 of Project F0212(65)205, paved over on June 21, 1989)

> *The bottom lift of two sets of two cores was extracted by the ASTM method, as it contained the original pavement first put down in 1958. Similar material made up 49% of the Class HR paving mixture used to pave US212 MRM 187 to MRM 205 (Project F0212(56)187) between LaPlante and the Missouri River. Located just east of the problem area of US212.*

v) Two cores from US73, MRM 147, southbound lane (near Howes Corner, the southern end of Project F0073(14)146, around Station 48, base course paved September 12-13, 1989)

The bottom lifts of the two cores were combined prior to extraction by the ASTM method. The bottom lift corresponds to the pavement containing AC-5 supplied by Little America refinery. Located in Meade County.

3.3 Methods Used

3.3.1 Asphalt Extractions

The method used for the extraction of twelve of the fourteen cores was ASTM D2172, "Quantitative Extraction of Bitumen from Bituminous Mixtures" Method A. This involved soaking the mix in the solvent then centrifuging the asphalt-containing extract from the aggregate - all done at room temperature. The asphalt cement was recovered using ASTM Method D1856, "Recovery of Asphalt from Solution by Abson Method". The solvent used was 1,1,1-trichlorethane.

Two of the cores (those removed from F0212(56)187, MRM 188 and 204.2) were extracted with 1,1,1- trichloroethane using a large glass soxhlet extractor, the top of which was connected to plastic tubing leading to a water trap. The set-up for this extraction is shown in Figure 2. After the extraction was completed, the water in the trap was analyzed for the presence of ions using ion chromatography.

3.3.2 Asphalt Cement Characterization

Asphalt Cement Extracted from Cores

Asphalt content was determined by differences in weight of the dried asphalt mix before and after extraction; there was no correction for fines content.

Penetration (ASTM D5 "Penetration of Bituminous Materials") and kinematic viscosity (ASTM D2170 "Kinematic Viscosity of Asphalts") of the recovered asphalts were determined.

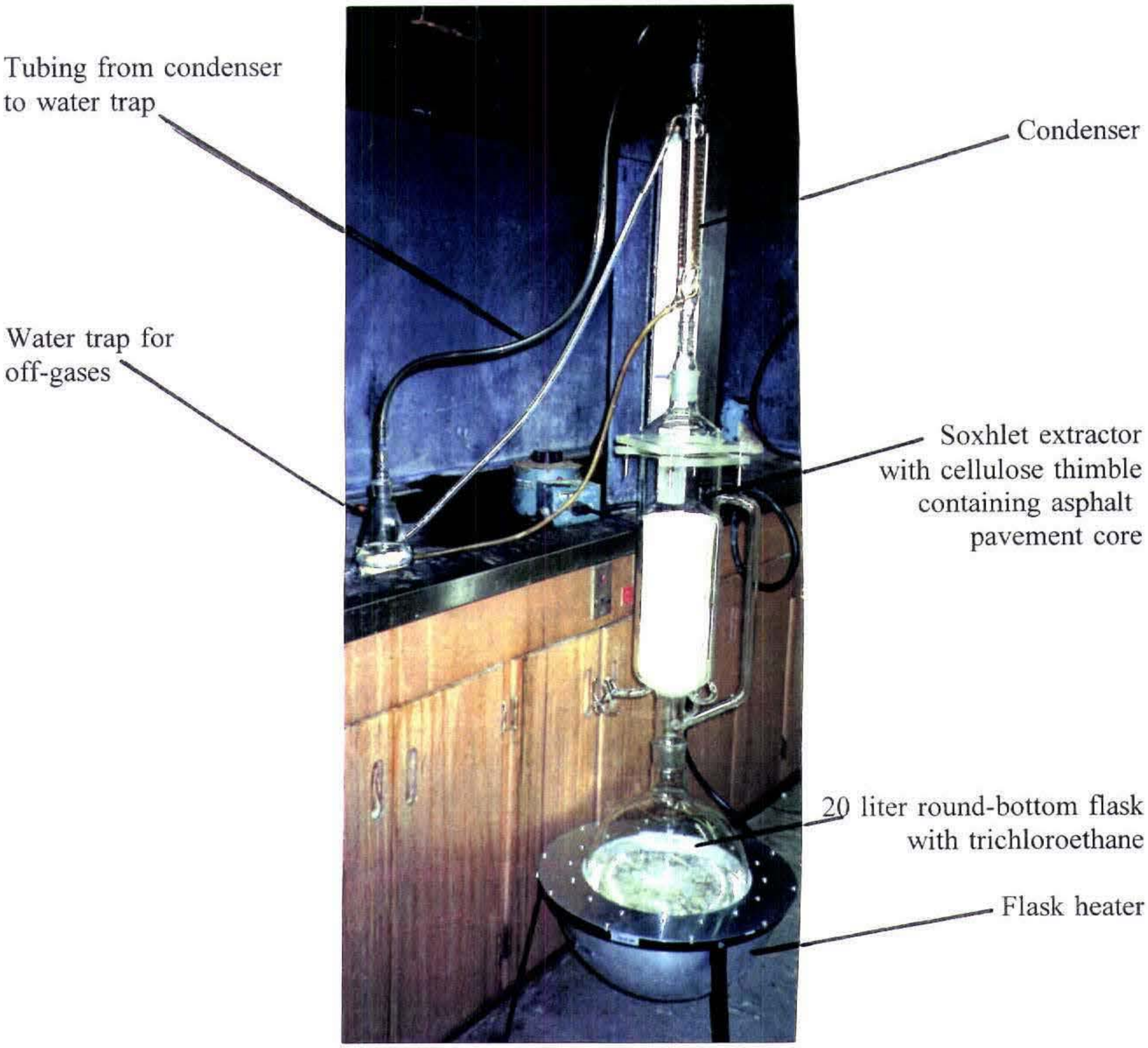

Figure 2 - Soxhlet Extraction Apparatus used to Collect Off-gases during Extraction of Asphalt Cores using Trichloroethane

Additionally, the asphalt cements obtained from the extraction of cores from US212 MRM 188 and US73 MRM 147 (bottom lift only) were examined for ash and silica content, for organic contaminants using gas chromatography coupled with mass spectrometry (GC/MS)and for inorganic compounds using inductively coupled plasma (ICP) emission spectrometry. The fines in the asphalt cement extracted from a core taken from US212 MRM 188 were examined further by X-ray diffraction (XRD) and a combination of scanning electron microscopy and X-ray energy spectrometry (SEM/XES).

Asphalt Cement from the Delivery Trucks

For comparison, several asphalt cement samples obtained from the delivery truck during construction of the paving projects F0212(56)187, F0212(72)166 and F0073(14)146 were also analyzed for inorganic content by inductively coupled plasma emission spectroscopy.

The procedure for determining the inorganic content of the asphalt cements involved ashing of the asphalt, followed by acid digestion of the ash, where all the materials except silica would be dissolved. The acid solution was then analyzed for 24 inorganic elements by ICP emission spectroscopy.

3.3.3 Aggregate Examination

The fines content of cores from both the original pavement (Project F0212(65)205, bottom lift of core from MRM 206) and of the recycled pavement (Project F0212(56)187, core at MRM 188) was determined by carrying out ASTM C117 "Material Finer than 75µm (No. 200) Sieve in Mineral Aggregates by Washing" on the aggregate remaining after asphalt extraction.

To determine if the fines (material passing 75 micron or 200 mesh sieves) in the mineral aggregate were responsible for the high inorganic composition found in the asphalt cements extracted from cores at both US212 MRM 188 and US73 MRM 147, the inorganic composition of the fines was obtained using ICP emission spectroscopy.

To determine if the inorganic composition of either the asphalt cement or the fines can be attributed to abrasion products of stones in the mix, the inorganic composition of the larger aggregate was also determined. The procedure used was to divide repeatedly the aggregate obtained from the extracted core to obtain a representative sample. That sample was sieved to remove the -200 material. The larger stones (retained on #4 seive) were then hand picked from the material retained on the 200 sieve, including a variety of aggregates of different sizes, shapes and colors. The stones were washed with dilute acid to remove any fines from the surface, then crushed and dissolved in acid for inorganic analysis by ICP emission spectroscopy. Tables 2, 3, 4 and 5 summarize the analyses carried out on all the samples.

Table 2 - Analysis Summary of Extracted Cores from F0212(65)205

Project F0212(65)205 Cores at MRM 206, bottom lift only		
Material isolated (method used)	Aggregate	Asphalt Cement (ASTM D2172 and D1856)
Tests/Analyses on the isolated material (method used)	Fines Content (ASTM C117)	asphalt content (difference) kinematic viscosity (ASTM D2170) penetration (ASTM D5) ash content (loss on ignition) silica content (acid digestion) inorganic element content (ICP)

Table 3 - Analysis Summary of Extracted Core from F0212(72)166

Project F0212(72)166 Core at MRM 176		
Material isolated (method used)	Aggregate (ASTM D2172)	Asphalt Cement (ASTM D2172 and D1856)
Tests/Analyses on the isolated material (method used)	none	asphalt content (difference) kinematic viscosity (ASTM D2170) penetration (ASTM D5)

Table 4 - Analysis Summary of Extracted Cores from F0073(14)146

Project F0073(14)146 Cores at MRM 147, bottom lift only			
Material isolated (method used)	Aggregate		Asphalt Cement (ASTM D2172 and D1856)
	Stones (+#4 sieve)	Fines (-#200 sieve)	
Tests/Analyses on the isolated material (method used)	silica content (acid digestion) and inorganic elements (ICP)	ash content (loss on ignition), silica content (acid digestion) & inorganic elements(ICP)	asphalt content (difference) kinematic viscosity (ASTM D2170) penetration (ASTM D5) ash content (loss on ignition) silica content (acid digestion) inorganic element content (ICP) organic compounds (GC/MS)

Table 5 - Analysis Summary of Extracted Cores from F0212(56)187

Project F0212(56)187, Core at MRM 188						
Material isolated (method used)	Aggregate (ASTM D2172)		Aggregate (Soxhlet Extraction)	Off-gases (Soxhlet Extraction)	Asphalt Cement (ASTM D2172 and D1856)	Asphalt Cement (Soxhlet Extraction)
Tests/Analyses on the isolated material (method used)	fines content (ASTM C117)		none	Chlorides, sulfates, nitrates (colorimetrically)	asphalt content (difference) kinematic viscosity (ASTM D2170) penetration (ASTM D5) ash content (loss on ignition) silica content (acid digestion) inorganic element content (ICP) organic compounds (GC/MS)	asphalt content (difference) kinematic viscosity (ASTM D2170) and penetration (ASTM D5)
	Stones - silica content (acid digestion) inorganic elements (ICP)	Fines - ash content (loss on ignition) silica content (acid digestion) inorganic elements (ICP)				

Project F0212(56)187, Core at MRM 204.2						
Material isolated (method used)	Aggregate (ASTM D2172)		Asphalt Cement (ASTM D2172 and D1856)	Off-gases (Soxhlet Extraction)	Aggregate (Soxhlet Extraction)	Curdled Asphalt Cement (Soxhlet Extraction)
Tests/Analyses on the isolated material (method used)	Stones - silica content (acid digestion) inorganic elements (ICP)	Fines - ash content (loss on ignition) silica content (acid digestion) inorganic elements (ICP)	asphalt content (difference) kinematic viscosity (ASTM D2170) penetration (ASTM D5)	Chlorides, sulfates, nitrates (colorimetrically)	none	none

4. RESULTS

4.1 Extracted Asphalt Physical Properties

The extracted asphalts were characterized by the usual asphalt tests (asphalt content, penetration and viscosity). These results are shown in Table 6.

Table 6 - Properties of Asphalt Extracted from Pavement Cores

Location	Asphalt Content, % by weight	Kinematic Viscosity @ 135°C, cSt	Penetration @ 25°C, 100 g, 5 s
US212 MRM 176 (1 whole core)	6.31	691	46
US212 MRM 188 (1 whole core)	6.26	815	33
US212 MRM 188 (1 whole core)	5.14*	536*	44*
US212 MRM 204.2 (1 whole core)	6.93	806	33
US212 MRM 206 (bottom lifts of two cores combined)	7.30	1329.2	21
US212 MRM 206 (bottom lifts of two cores combined)	6.93	1881.0	14
US73 MRM 147 (bottom lifts of two cores combined)	7.30	327	88

* Obtained by Soxhlet extraction of a pavement core in a cellulose thimble

4.2 Analysis of Extraction Off-Gases

The water used to trap gases given off during the soxhlet extraction was analyzed for a number of organic and inorganic ions. The results are shown in Table 7.

Table 7 - Trapped Ions from the Extraction of Asphalt Cores with 1,1,1-Trichloroethane

Ionic Species	**Concentration, mg/L**	
	US212 MRM 204.2	US212 MRM 188
Chloride	3.6	2.3
Nitrate/Nitrite	0.79	0.55
Sulfate	<0.3	1.1
Acetate	< 1.00	< 1.00
Butyrate	< 10.0	< 10.0
Formate	< 0.10	< 0.10
Propionate	< 5.00	< 5.00

4.3 Analysis of Asphalt Cements for Inorganic Materials

After Abson recovery and determination of penetration and viscosity, the extracted asphalts were examined for their inorganic content. These results are shown in Table 8. Inorganic analytical results of asphalt cements sampled from the delivery trucks during construction in 1989/90 and kept in penetration cans since then are shown in Table 9.

Table 8 - Inorganic Composition of Asphalt Cements from Cores

Inorganic Materials	**Concentration, mg/kg (or ppm)**			
	US73 MRM 147	US212 MRM 206 (Cores 1 & 2)	US212 MRM 206 (Cores 3 & 4)	US212 MRM 188
Ash @ 550°C	396	5600	5700	9750
Silica	none	*	2100	4050
Aluminum	4.38	158	184	234
Barium	34.5	6.37	7.05	33.5
Beryllium	1.47	1.23	1.22	1.56
Boron	< 0.5	2.97	1.27	1.53
Cadmium	< 0.2	0.14	< 0.1	< 0.2
Calcium	29.9	471	442	490
Chromium	0.60	1.18	1.21	0.80
Cobalt	1.64	0.28	0.23	2.10
Copper	2.87	54.4	17.3	1.02
Iron	13.2	478	488	988
Lanthanum	< 0.5	0.34	0.33	< 0.5
Lead	< 0.6	1.36	1.18	< 0.6
Lithium	<0.3	0.21	0.21	<0.3
Magnesium	4.34	58.3	60.1	101
Manganese	1.18	56.7	52.9	1.12
Molybdenum	< 0.3	< 0.2	< 0.2	< 0.3
Nickel	38.1	35.4	35.0	41.0
Phosphorus	2.18	11.7	13.3	26.0
Silicon	< 1	19.8	12.1	20.8
Sodium	*	17.6	18.0	*
Strontium	0.2	2.53	2.59	3.06
Tellurium	< 3	< 3	< 3	< 3
Titanium	< 0.4	2.44	2.51	< 0.4
Vanadium	133	127	125	149
Zinc	0.71	2.65	3.22	3.39

* not determined

Table 9 - Inorganic Composition of Asphalt Cements from Sample Cans

Project -	F0073(14)146		F0212(72)166		F0212(56)187	
Date Sampled - Sample # -	89/09/25 (#12)	89/09/25 (#13)	90/07/19 (#3)	90/07/23 (#5)	89/06/30 (#21)	89/07/13 (#27)
Inorganic Materials	**Concentration, mg/kg (or parts per million, ppm)**					
Ash @ 550°C	600	600	1200	800	900	700
Silica	none	none	none	none	none	none
Aluminum	8.68	4.90	8.40	5.61	8.96	4.42
Barium	1.25	1.24	1.35	0.86	1.18	0.80
Beryllium	1.08	1.21	1.47	1.37	1.04	1.66
Boron	< 0.3	< 0.3	0.45	< 0.3	< 0.3	0.51
Cadmium	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Calcium	31.8	18.3	20.2	15.4	35.4	9.50
Chromium	1.60	0.71	0.57	0.46	0.57	0.72
Cobalt	0.17	0.14	< 0.1	< 0.1	< 0.1	< 0.1
Copper	1.30	1.51	3.68	1.83	2.18	1.63
Iron	72.0	60.3	48.2	45.6	60.2	36.7
Lanthanum	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Lead	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Lithium	0.21	0.38	0.67	0.63	0.22	< 0.2
Magnesium	4.42	2.57	2.67	2.29	2.43	2.05
Manganese	0.74	0.35	0.27	0.24	0.32	0.21
Molybdenum	0.35	0.25	0.45	0.43	0.23	0.38
Nickel	36.0	38.1	46.9	44.5	32.8	49.8
Phosphorus	< 3	< 3	3.53	< 3	< 3	< 3
Silicon	18.1	12.5	18.1	12.5	19.8	12.1
Sodium	36.3	27.4	38.1	27.4	17.8	17.8
Strontium	0.57	0.45	0.52	0.50	0.59	0.34
Tellurium	< 3	< 3	< 3	< 3	< 3	< 3
Titanium	0.48	< 0.3	< 0.3	< 0.3	0.44	< 0.3
Vanadium	111	125	150	142	105	176
Zinc	2.11	2.65	1.64	1.12	2.80	1.59

4.3.1 Fines in the Extracted Asphalt Cement

Since the ASTM asphalt extraction procedure does not remove fines from the extract prior to Abson recovery of the asphalt cement, the fines in the asphalt cement extracted from US212 MRM 188 were collected by dissolving the asphalt cement in toluene then centrifuging the resulting solution. The fines collected were examined by x-ray spectroscopy and scanning electron microscopy. Appendix A contains the report provided on this examination of fines. Appendix B provides a second look at the information obtained from a metallurgist's perspective.

4.4 Examination of Mineral Aggregate from Extracted Cores

4.4.1 Fines Content

In Table 10 the fines content of the aggregate obtained after asphalt extraction of two cores are shown. Both cores had been extracted by Method A of ASTM 2172.

Table 10 - Fines Content of Aggregate from Pavement Cores

AGGREGATE SOURCE	FINES CONTENT (-200, passing 75μm sieve) ASTM C117
Extracted bottom lift from US212 MRM 206 (i.e. original 1958 pavement)	7.5%
Extracted core from US212 MRM 188 (i.e. 49% original 1958 pavement)	9.9%

4.4.2 Inorganic Composition of the Fines

Table 11 shows the inorganic composition of the mineral fines (material passing 75 micron or 200 mesh sieves) derived from both US212 MRM 188 and US73 MRM 147 after the asphalt had been extracted by the ASTM method.

4.4.3 Inorganic Composition of the Larger Aggregate

Table 11 records the inorganic composition not only of the fines but also of the larger stones (those retained on the 4.76 mm / 0.187 inch / #4 sieve) present in the mineral aggregate remaining from cores at US73 MRM 147 (bottom lift) and US212 MRM 187 after asphalt had been removed by the ASTM method. Minerals in both the fines and the stones that did not dissolve in the acid digestion step were identified separately as silica. The analysis for all the elements listed after silica in Table 11 is for materials that had dissolved in the acid digestion step.

4.5 Analysis of Asphalt for Organic Compounds

Two asphalts were examined by capillary GC/MS in the molecular weight range of 106 to 338 (C8 to C24). The capillary column was 25 m long with a 0.2 mm inside diameter which was coated with HP-5 (a cross-linked methyl silicone) as the stationary phase. Helium was the carrier gas. The column oven temperature was raised from 80° to 305°C at a rate of 5°C per minute during the chromatography run. The injection inlet temperature was kept at 310°C. Injection volume was 1 µl of sample, representing 10 µg of asphalt. The mass spectrometer, maintained at a temperature of 300°C, acted as the detector for the gas chromatograph. There were numerous unresolved peaks in the sample. Table 12 lists the compounds that had been resolved and identified. Detection limit was 0.01 parts per million (ppm).

Table 11 - Inorganic Composition of Mineral Aggregate from Pavement Cores

Inorganic Materials	US73 MRM 147			US212 MRM 188		
	Concentration, mg/kg (ppm)		**Ratio of inorganics concentration in fines to concentration in stones**	**Concentration, mg/kg (ppm)**		**Ratio of inorganics concentration in fines to concentration in stones**
	Fines (-200 sieve)	Stones(+#4) (washed)		Fines (-200 sieve)	Stones(+#4) (washed)	
Ash @ 550°C	961,300	*		925,800	*	
Silica	63.5	41.4	1.53	54.3	46.9	1.16
Aluminum	12,400	41,100	0.30	13,100	9,160	1.43
Barium	933	1,420	0.24	697	566	1.23
Beryllium	<1	<1	-	<1	<1	-
Boron	34.6	19.0	1.82	87.9	141	0.62
Cadmium	<2	<2	-	<2	<2	-
Calcium	60,900	197,000	0.31	55,900	106,000	0.53
Chromium	16.4	6.08	2.70	18.6	17.0	1.09
Cobalt	<10	<10	-	13.3	<10	-
Copper	18.7	9.13	2.05	25.6	27.1	0.94
Iron	19,300	11,600	1.67	48,900	78,500	0.62
Lanthanum	23.5	18.6	1.31	17.5	6.64	2.64
Lead	<20	<20	-	27.9	<20	-
Lithium	10.4	6.9	1.50	16.3	9.70	1.68
Magnesium	7,020	2,190	3.21	11,600	30,900	0.38
Manganese	1,020	248	4.11	4,700	6,860	0.69
Molybdenum	<20	<20	-	<20	<20	-
Nickel	16.6	6.72	2.47	44.2	32.3	1.37
Phosphorus	630	883	0.71	1,200	902	1.33
Silicon	1,160	362	3.20	1,530	779	1.96
Strontium	144	252	0.57	140	173	0.81
Tellurium	<60	<60	-	<60	<60	-
Titanium	372	94.4	3.94	260	294	0.88
Vanadium	31.9	24.4	1.31	46.8	58.2	0.80
Zinc	53.1	38.8	1.37	68.6	46.4	1.48

* not determined

Table 12 - Organic Compounds Identified by GC/MS in two asphalts

COMPOUNDS IDENTIFIED IN ASPHALT CEMENT FROM CORES AT	
US73 MRM 147 (bottom lift)	**US212 MRM 188**
1-Limonene	1-Limonene
Dodecane	Dodecane
Tetradecane	Tetradecane
1,6-Dimethyl naphthalene	1,6-Dimethyl naphthalene
2,7-Dimethyl naphthalene	2,7-Dimethyl naphthalene
2,4,6-Trimethyl azulene	2,4,6-Trimethyl azulene
1,4,6-Trimethyl naphthalene	1,4,6-Trimethyl naphthalene
Hexadecane	Hexadecane
Heptadecane	Heptadecane
Octadecane	Octadecane
Phenanthrene	Phenanthrene
Eicosane	Eicosane
2,5-Dimethyl phenanthrene	2,5-Dimethyl phenanthrene
2,3,5-Trimethyl phenanthrene	2,3,5-Trimethyl phenanthrene
1,2-Dimethyl benzene	1,8-Dimethyl naphthalene
1,2,3 - Trimethyl benzene	1,5-Dimethyl naphthalene
Undecane	Heneicosane
Tridecane	2-(1-Methylethyl) naphthalene
1,2,3,4-Tetrahydro-5-methyl naphthalene	1,6,7-Trimethyl naphthalene
1-Methyl naphthalene	Octacosane
2,6,10,15-Tetramethyl heptadecane	2-Methyl-1-propyl naphthalene
1,7-Dimethyl naphthtalene	2,6,10,14-Tetramethyl pentadecane
1,3-Dimethyl naphthalene	**N-butyl benzenesulfonamide**
1,2-Dimethyl naphthalene	3-Methyl dibenzothiophene
2,6-Dimethyl naphthalene	9-Methyl phenanthrene
Pentadecane	2-Methyl anthracene
1,3,6-Trimethyl naphthalene	9-Methyl anthracene
2,6,10,15,19,23-Hexamethyl tetracosane or 2,6,10,14-Tetramethyl pentadecane	**Nonahexacontanoic acid, hexadecanedioic acid or cyclopentadecanone**
Hexatriacontane or 5-ethyl-5-propyl undecane	**4,9-Dimethyl naphthothiophene**
9-Methyl phenanthrene	2,7-Dimethyl phenanthrene
2-Methyl phenanthrene	1,4-Dimethyl anthracene
3,6-Dimethyl phenanthrene	Pyrene
2,6,10,15-Tetramethyl heptadecane	1-Methyl pyrene
Docosane	2,4,5,7-Tetramethyl phenanthrene
2-Methyl pyrene	2,5-Diphenyl thiophene
11-Decyl docosane or nonadecane	**1-Ethenyloxy hexadecane**
1,3-Dimethyl pyrene	2,6-Dimethyl dibenzothiophene
2-Methyl-3-phenyl indole	
3-Methyl phenanthrene	

5. OBSERVATIONS AND DISCUSSION

5.1 Asphalt Core Extractions

5.1.1 Extraction by ASTM D2172, Method A

Technicians carrying out the asphalt extractions by ASTM D2172, Method A (which involves solvent at room temperature being forced through the sample by centrifugal force) noted that while a normal extraction for an asphalt mix is completed within 40 minutes, extraction of the cores from Highways 212 and 73 required 90 minutes for completion (not including the initial 15 minutes soaking time).

The technicians also observed, "The high iron content of the aggregate is visible on the surface of the core samples." Aggregates of the "Agency" facies of the "DeGrey" member of shale in the Pierre area of the Missouri River Valley are described as a light gray siliceous shale that weathers to a dark rusty brown color. It's possible that the aggregates obtained from the Lamb pit for this project contained some of this shale material. A chemical analysis of claystone from DeGrey member of Pierre shale in one location [48] gave the following results: silica 69.04%, alumina 12.37%, ferric oxide 2.92%, ferrous oxide ~1.20% (uncertain because of organic material in shale), magnesium oxide 1.7% and calcium oxide 0.76%.

Converting the elements aluminum to zinc in Table 8 to their respective oxides, recalculating their concentration on the basis of oxides, then normalizing the results, the composition for the fines from US73 MRM 147 would be silica 1.67%, alumina 15.37%, iron oxide 16.29%, magnesium oxide 7.64% and calcium oxide 55.92%. If the same were done for the results for the fines obtained from US212 MRM 188, the composition would be silica 1.67%, alumina 12.44%, iron oxide 31.62%, magnesium oxide 9.67% and calcium oxide 39.31%. This indicates that fines extracted from US212 MRM 188 are considerably richer in iron oxides than both the shales from that area and the fines extracted from US73 MRM 147.

5.1.2 Soxhlet extractions

The first soxhlet extraction carried out was that of the asphalt core from US212 MRM 204.2. This extraction was terminated after 18¾ hours because of the evolution of acrid, pungent, fuming gases from the extraction apparatus into the laboratory. When the trichloroethane had been removed from the asphalt partially extracted from the US212 MRM 204.2 core, the asphalt was found to have a curdled appearance. Dr. Preber's report indicated that when corrosion of the copper condensers had occurred during the extraction tests on US212 from LaPlante to the Missouri River, "the asphalt residue formed curd like particles" [1].

Before the second asphalt core (from US212 MRM 188) was extracted in the same apparatus, the remaining trichloroethane (which had been observed to have a yellowish color when it should have been clear) was filtered and distilled. The material collected when the trichloroethane was filtered looked like rust. The inside of the empty five gallon pail containing the trichloroethane was rusty. The second soxhlet extraction was not accompanied by the evolution of acrid gases and was carried out to completion (52½ hours). Thus it appears that rust may have been responsible for the rapid evolution of noxious fumes during the extraction of the first core. Since the role of the rust (and other metals and metal oxides) in 1,1,1-trichloroethane decomposition is catalytic [51,52], the presence of even a small amount (with no visible change in solvent color) would be expected to produce solvent decomposition.

5.2 Asphalt Cement Properties

Cores from US212 MRM 188 had been extracted with trichloroethane using two different methods - ASTM D2172, Method A (which does not include removal of all fines), and soxhlet extraction, wherein the fines are retained with the mineral aggregate by the cellulose thimble containing the core. It is interesting to observe the difference that the presence of fines makes on the values obtained for % asphalt, kinematic viscosity (an increase of 52%) and penetration (a decrease of 25%), even though the extended period of extraction (52½ hours) would have been expected to harden the asphalt cement.

Examining the results in Table 6, one observes that the asphalt cement extracted from the bottom lift of cores from US212 MRM 206 (an aged pavement built in 1958) is noticeably harder than the asphalt cement obtained from the recycled mixes put down in 1989 (US212 MRM 188 and 204.2) which is harder than the asphalt cement extracted from the recycled mix put down in 1990 (US212 MRM 176) which in turn is harder than the asphalt extracted from the bottom lift of a pavement where only virgin materials were used (US73 MRM 147). This is what one would expect. Thus, ignoring the values obtained from the 52½ hour soxhlet extraction, the progression of asphalt penetration and viscosity values makes sense.

5.3 Off-Gases

From Table 7, one sees that the water trapped significant quantities of chloride and nitrate/nitrite ions during the brief extraction period for the core from US212 MRM 204.2. For the second extraction, (US212 MRM 188), the water contained sulfate ions in addition to chloride and nitrate/nitrite ions. It's interesting to note that the chloride ion content of the water in the trap for the first extraction, which was terminated after only 18¾ hours, was more than 50% higher than for the water in the trap of the second (52½ hour) extraction.

The solvent 1,1,1-trichloroethane is known to corrode metals in the presence of moisture [49]. Also called methylchloroform and chloroethene [50], it is known to undergo decomposition to form mainly hydrogen chloride (and a small amount of phosgene) when heated in the presence of metals [51] and metal oxides [52].

Dr. Preber had observed corrosion of the copper condenser when asphalt was being extracted from the last four cores, which happened to be from the project F0212(56)187. Given the nature of the gas that was given off during the soxhlet extraction of the core from US212 MRM 204.2 plus the high concentration of chloride ions in the water trap, it appears that large quantities of hydrogen chloride were being formed in the soxhlet extraction apparatus due to the catalyzed thermal decomposition of 1,1,1-trichloroethane. It is also quite likely that it was hydrogen chloride that had corroded the copper condenser in Dr. Preber's reflux extraction apparatus. If the trichloroethane used by Dr. Preber had been stored in a metal pail or drum, rust would have also quite likely been present in the solvent by the time the last few samples were being extracted.

Nitrate ions are formed during the combustion of fuels [53] and would accumulate in the lubricant of an engine. Sulfate ions result from the combustion of sulfur-containing molecules in diesel fuel and would also be present in the lubricant [54]. However, ions present in the asphalt are not likely to have been carried over into the water trap by the trichloroethane solvent used in the extraction because a) ionic compounds are not volatile b) ionic compounds are not soluble in trichloroethane. For the nitrate and sulfate ions to show up in the water trap during extraction, they would have to have been produced in the extraction process as gases like sulfur dioxide, sulfur trioxide, and various oxides of nitrogen. Once these gases dissolve in water, they form ions of sulfite, sulfate, nitrite and nitrate. The source of the gases could be the sulfur and nitrogen compounds present in the asphalt mixture which could be converted to the oxides in the presence of metals (e.g. wear metals in waste oil) during the extraction process. Hence, based on the ions collected in the water trap during the extraction of cores taken from the project F0212(56)187, one could surmise that the presence of sulfate and nitrate/nitrite ions as well as the inferred presence of metals which catalyzed the decomposition of trichloroethane in **both** samples (albeit much more energetically when iron in the form of rust was additionally present) could point to the possibility of the presence of waste lubricants (or just their residues) in the pavement core.

5.4 Inorganic Composition of Asphalt Cements from Cores

Table 8 provides a comparison of the inorganic composition of the asphalt cements obtained from

- four cores from a pavement built in 1958 [55] (bottom lifts, US212 MRM 206) ,
- one core from a pavement which contained salvage material (49%) from the same aged pavement, along with virgin aggregate and fresh AC-5 asphalt cement (US212 MRM 188) and
- one core from a pavement prepared with AC-5 and virgin aggregate only (US73 MRM 147).

A number of observations can be made regarding these results.

- Even though the same procedure was used to extract the asphalt from all cores, the amount of ash and silica in the asphalt cement from the recycled mix (US212 MRM 188) is extremely high when compared with the values obtained from cores of the other two pavements.
- When compared with the asphalt cement obtained from the core taken from US73 MRM 147, the asphalt cement from the three cores taken from US212 have much higher concentrations of aluminum, calcium, iron, magnesium, phosphorus, silicon and zinc. Diesel engine soot has been reported to contain calcium, iron and zinc [56]; lubricants for diesel fuel contain magnesium, phosphorus and zinc as additives [57] and wear debris in the lubricating oil of a diesel engine has been reported to contain aluminum, calcium, iron, magnesium, phosphorus, silicon and zinc [58].
- When compared with cores from US73 and from the recycled mix (US212 MRM 188), cores from the original pavement (US212 MRM 206, bottom lift) have higher concentrations of copper, lead and manganese. Copper and manganese are metals found as viscosity control additives in lubricants [59]. The detection of lead in the asphalt of the aged pavement would be a reflection of the use of alkyllead anti-knock additives of gasoline at that time. Lead would be present not only as a deposit on the surface of pavements but also as a component in the used oil of cars and trucks using leaded gasoline as a fuel. A gradual ban on leaded gasolines starting from 1975 would mean that used oil generated by all vehicles at the time of construction of the recycled mix at US212 MRM 188 (1989) would not likely have contained detectable amounts of lead.

5.4.1 Fines in the Asphalt Cement

Reviewing the results shown in Appendix A and taking into account the supplementary assessment in Appendix B, it appears that the fines in the asphalt cement (obtained from the core taken at US212 MRM 188) are a mixture of mineral aggregate and wear metals.

5.5 Inorganic Composition of Asphalt Cements in Sample Cans

Table 9 compares the inorganic content of asphalt cement (AC) samples collected in the field from tankers hauling the AC from the refinery to the construction site. Examination of these samples provides insight into the composition of the asphalt cement before its ownership passed to the contractor. These samples were taken from construction sites on US73 in 1989, US212 in 1989 and US212 in 1990. The contractor for the 1989 projects was Heavy Constructors Ltd [60]. For the 1990 project the contractor was Border States Paving Inc [61]. The supplier of AC-5 for all three projects was the Little America Refinery of Sinclair Oil Corporation [16a][62]. For all the samples, the concentrations of inorganic elements are less than 10 parts per million except for the elements calcium, iron, nickel, silicon, sodium and vanadium.

5.6 Mineral Aggregate from Extracted Cores

5.6.1 Fines Content

The aggregate obtained from the cores after extraction as shown in Table 10 reveals that the core from the recycled pavement (US212 MRM 188) had a significantly higher amount of fines (9.9%) than did the core from the original pavement (7.5% for the core from US212 MRM 206). Both cores had been extracted by Method A of ASTM D2172.

5.6.2 Inorganic Composition of the Aggregate

After asphalt had been extracted from the cores from US73 (MRM 147) and US212(MRM 188), the mineral aggregate remaining had been separated into two fractions:

- the fines, which passed through a 75 micron (200 mesh) sieve and

- the stones, which were picked from the material retained on the 4.76 mm (#4) sieve.

The inorganic composition of both the fines and the stones was determined by ICP emission spectroscopy. Table 11 compares the inorganic composition of the fines and stones from cores obtained from both US73 MRM 147 and US212 MRM 188.

Upon ignition, the fines from the two cores lost some weight due to the combustion at 500°C of organic materials. The fines from US73 MRM 147 lost 3.87% of its weight (leaving an ash content of 96.13% or 961,300 ppm), while the loss on ignition for the fines from US212 MRM 188 was 7.42%. The apparently high loss on ignition from US212 MRM 188 may be attributed to the organic content of shales that could have been included in either the aggregate of the original pavement built in 1958 and/or in the aggregate added to the recycled mix used in pavement construction in 1989. The loss on ignition test was not carried out on the stones - they were assumed to be entirely mineral in nature, without any organic materials.

The ratio of distribution of silica and the elements in fines versus stones was not equal to one, indicating that the fines were not simply the abrasion products of the stones in the same aggregate pit. In fact, the spread in ratios of inorganic compounds in the fines versus stones indicates that there is no relationship whatsoever between the fines and the stones in the two cores. Elevated levels of the following elements were found in the fines of US73 MRM 147: silica, boron, chromium, copper, iron, lanthanum, lithium, magnesium, manganese, nickel, silicon, titanium, vanadium and zinc. In US212 MRM 188, excessive amounts of the following elements were found in the fines (relative to the stones): silica, aluminum, barium, lanthanum, lithium, nickel, phosphorus, silicon and zinc.

5.6.3 Inorganic Composition of the Asphalt Cement versus the Fines

If the inorganic composition of the asphalt cement extracted from the cores were the result of fines in the core, then one would expect to find a constant ratio between the inorganic composition of the fines and the asphalt cement, except for those elements found in asphalts sampled at the job sites - calcium, iron, nickel, vanadium. Table 8 compares the inorganic content of the asphalts extracted from cores at US73 MRM 147 and from US212 MRM 188 with the inorganic content of the fines with which they were in contact.

The concentrations of elements in the asphalt cement extracted from the core at US73 MRM 147 were below 10 ppm except for barium, calcium, iron, nickel and vanadium (Tables 3 and 13). The appearance of elevated levels of barium could be attributed to its presence in fairly high levels in both the fines and the stones from the same core (Table 11). The presence of calcium, iron, nickel and vanadium can be attributed to their natural presence in the asphalt cements, as found in the asphalt cements collected prior to their use in pavement construction (Table 9).

The inorganic materials whose concentrations exceeded 10 ppm in the asphalt cement extracted from the core at US212 MRM 188 include silica, aluminum, barium, calcium, iron, magnesium, nickel, phosphorus, silicon and vanadium (Tables 8 and 13). While the concentrations of calcium, iron, nickel, silicon, sodium and vanadium of asphalt delivered to

Table 13 - Comparing Inorganic Composition of Asphalt Cement and Fines

Inorganic Materials	US73 MRM 147			US212 MRM 188		
	Concentration, mg/kg (ppm)		**Asphalt to Fines ratio***	**Concentration, mg/kg (ppm)**		**Asphalt to fines ratio***
	Fines (-200 sieve)	Extracted Asphalt Cement		Fines (-200 sieve)	Extracted Asphalt Cement	
Ash @ 550°C	961,300	396	1.00	925,800	9750	1.00
Silica	63.5	0.0000	0.00	54.3	4050	7103.81
Aluminum	12,400	4.38	1.00	13,100	234	1.70
Barium	933	34.5	92.50	697	33.5	4.58
Beryllium	<1	1.47	>3675.00	<1	1.56	>148.57
Boron	34.6	<0.5	<25.00	87.9	1.53	1.66
Cadmium	<2	<0.2	-	<2	<0.2	-
Calcium	60,900	29.9	122.75	55,900	490	0.84
Chromium	16.4	0.60	91.50	18.6	0.80	4.10
Cobalt	<10	1.64	>410.00	13.3	2.10	15.04
Copper	18.7	2.87	383.75	25.6	1.02	3.79
Iron	19,300	13.2	1.75	48,900	988	1.92
Lanthanum	23.5	<0.5	<50.00	17.5	<0.5	<2.86
Lead	<20	<0.6	-	27.9	<0.6	<1.90
Lithium	10.4	<0.3	<75.00	16.3	<0.3	<1.90
Magnesium	7,020	4.34	1.50	11,600	101	0.83
Manganese	1,020	1.18	3.00	4,700	1.12	0.02
Molybdenum	<20	<0.3	-	<20	<0.3	-
Nickel	16.6	38.1	5737.5	44.2	41.0	88.34
Phosphorus	630	2.18	8.75	1,200	26.0	2.07
Silicon	1,160	<1	<2.25	1,530	20.8	1.30
Strontium	144	0.2	3.50	140	3.06	1.99
Tellurium	<60	<3	-	<60	<3	-
Titanium	372	<0.4	<2.50	260	<0.4	<0.19
Vanadium	31.9	133	10422.5	46.8	149	303.24
Zinc	53.1	0.71	33.50	68.6	3.39	4.70

* Normalized on the basis of ash content

the construction site also exceed 10 ppm (Table 9), the concentrations of calcium and iron are more than ten times higher in the extracted asphalt cement. The presence of elevated barium levels in the asphalt cement extracted from the core at US212 MRM 188 may be attributed to the high levels of barium in the fines since the level of barium in asphalt cements extracted from both cores are very similar - 34.5 ppm for US73 MRM 147 and 33.5 ppm for US212 MRM 188 - roughly 25 to 30 times higher than the concentration of barium in the asphalts as received from the refinery (Table 9).

In Table 13, when one examines the ratio of elements in asphalt to fines there is no relationship between the inorganic composition of the asphalt cements and the fines from either core (US73 or US212), even when one excludes calcium, iron, nickel, silicon and vanadium. Excluding those 5 elements from consideration, the asphalt to fines ratios still range from zero (silica) to 0.15 (copper) for the core from US73 MRM 147 and from 0.0002 (manganese) to 74.59 (silica) for the core from US212 MRM 188. This indicates that the high inorganic content of the asphalt cement, except perhaps for presence of barium, cannot be attributed to the fines in the mix.

5.7 Organic Composition of the Extracted Asphalt Cements

The first 14 organic compounds in the list shown in Table 12 are identical for the asphalts extracted from cores at both US73 MRM 147 and US212 MRM 188. The remaining 25 compounds identified in the asphalt cement extracted from US73 MRM 147 - substituted naphthalenes, phenanthrenes and pyrenes, along with long-chained alkanes - are all types of molecules one would expect to find in an asphalt cement [63]. Another name for 2-methyl-3-phenyl indole, identified as another compound in the asphalt cement from US73 MRM 147, is 2-methyl-3-phenyl benzopyrrole. Pyrrolic compounds have also been identified as a normal constituent of asphalts [64].

Of the remaining 23 compounds identified in the asphalt cement obtained from the core at US212 MRM 188, all but three compounds have been identified as normal constituents of asphalt. Even thiophenes are normal constituents of asphalt [19]. The compound 4,9-

dimethylnaphthothiophene has, however, also been identified as a component of diesel-particle extracts [65]. The three unusual compounds include the acids and ketone in the list "Nonahexacontanoic acid, hexadecanedioic acid or cyclopentadecanone", the oxygenated hydrocarbon "1-ethenyloxy hexadecane" and the compound N-butyl benzenesulfonamide. While *high* molecular weight acids and ketone are normal components of an asphalt [20], the presence of these *low* molecular weight oxygenated compounds indicates that they may be products of incomplete combustion of diesel fuel (which would wind up in the used oil), additives normally present in diesel engine lubricants as anti-wear agents (fatty acids, esters and ketones [66]) or decomposition products of synthetic oils, which are organic esters [21]. The 1-ethenyloxy hexadecane could to be the product of incomplete combustion of an alkane or alkene.

The presence of N-butyl benzenesulfonamide in the asphalt cement extracted from the core at US212 MRM 188 is curious. It is not a compound that is normally found in asphalt. It is a frequent pollutant in ground water and in landfill leachates [67]. It has been used as a plasticizer, antistatic agent, lubricant, softener, dispersing agent, pigment carrier and binder with polyamides, as a viscosity depressant and vulcanizing agent for poly(vinyl chloride), a release agent for toy moulding compositions, heat stabilizer for neoprene latex, in photosensitive compositions, in acetate fibre filters and adhesives, for dust control in pigments and as a lubricant for clock parts [22]. Possible sources of this compound in the asphalt mix could be the aggregate (washed by ground waters contaminated with N-butyl benzenesulfonamide) or waste materials from manufacturers of polyamides, poly(vinyl chloride), plastic moulded toys, neoprene latex, acetate fibre filters or photosensitive compositions, from users of pigments (like printers or paint manufacturers), or from a clock manufacturing/servicing facility.

6. TEST METHODS FOR DETECTING CONTAMINANTS

The most damaging effects of contaminants in asphalt mixes are likely to be on the aging rate of the asphalt cement - specifically how the viscosity of the asphalt cement changes during mixing and construction and after placement on the road. Thus, an indirect approach to detect not only organic and inorganic contaminants, but also asphalts that are in themselves prone to rapid oxidation (due either to the presence of natural metal oxidation catalysts or unsaturated organic molecules susceptible to oxidation), is by an accelerated aging test such as SHRP's rolling thin film oven - pressure aging vessel (RTFO-PAV) test [68]. The RTFO test simulates aging during mixing while the PAV test simulates aging of the asphalt cement after it has been placed on the road. The cost of a rolling thin film oven, including a digital readout is $6525 (James Cox & Sons Inc, Colfax CA) while the cost of a self-contained pressure aging vessel (the PR9300 of Rainhart Co., Austin TX) is $11,950.

6.1 Organic Materials

The instrumental method often used in the detection and at least partial identification of organic compounds is infrared (IR) spectroscopy. Careful scrutiny of the infrared spectrum of a suspected asphalt and comparison with the IR spectrum of asphalt samples from the refinery would pick up the introduction of contaminants with functional groups other than those normally found in asphalt. Contaminants such as lignin from gasohol plants, chlorinated solvents, alkylamine distillation residues, coal tars from metallurgical plants, waste coal, pulping liquor waste, aromatic sulfonate wastes and possibly some plastics could be detected by simple examination of the infrared spectrum of the asphalt. However, when the contaminant contains materials whose chemistry (or functional groups) are similar to those found in asphalt, one would have to use differential infrared spectrometry [64] to detect the contaminant. South Dakota Department of Transportation currently has the equipment to detect such contaminants.

Another analytical technique with wide application in the detection and identification of organic compounds and contaminants combines gas chromatography with mass spectrometry (GC/MS) for lower molecular weight compounds. This technique would be most useful in detecting impurities like waste oil, waste oil distillation bottoms, petroleum-based solvents, chlorinated solvents, petroleum distillation residues, shale oil distillation residues and pyrolysis products of cellulosic wastes. Sample preparation may be expedited (eliminating tedious and time-consuming asphalt extraction and recovery steps) by the use of a supercritical fluid extractor. Volatile materials could be detected with a head-space unit attached to the GC/MS. Combining GC/MS with a means of pyrolyzing high molecular weight compounds (like polymers) would broaden the range of contaminating compounds that could identified. The approximate cost of a gas chromatograph/mass spectrometer with appropriate software to identify organic compounds is $60,000; a pyrolyzer add-on would cost between $13,000 and $14,000; the cost of a head-space apparatus is about $15,000 and the cost of a supercritical fluid extractor would be about $50,000. (Approximate prices obtained from Hewlett Packard Ltd.)

Many of the organic wastes that would be added to asphalts are not as likely to adversely affect the performance of the asphalt as some inorganic catalysts of oxidation do unless they are present in sufficient amount to adversely affect the rheology (i.e. penetration and/or viscosity) of the asphalt . Hence, from the perspective of a highway department, the most effective means of detecting organic impurities in asphalt would be to determine its penetration and viscosity after rolling thin film oven aging and/or after aging in a pressure aging vessel. In addition to the cost of the RTFO and PAV, equipment would be needed to measure the rheology of the asphalt before and after aging. This could include a Brookfield Rotary Viscometer (approximately $6000 with a temperature control unit, software and accessories), a penetrometer (traditional technology), a Bending Beam Rheometer (approximately $21,500 with a cooling unit) or a Dynamic Shear Rheometer (about $35,500).

6.2 Inorganic Materials

The presence of excessive amounts of inorganic materials is most readily detected by inductively coupled plasma (ICP) emission spectrometry, which provides analysis of over 20 elements in one step. The cost of a sequential ICP is between $90,000 and $100,000 (sample analysis time 15-20 minutes while that of a simultaneous ICP (analysis time of about 2 minutes per sample) ranges from $135,000 to $200,000. Alternatively, an analysis of asphalt for an indicator metal like iron by atomic absorption (AA) spectroscopy may suffice for control purposes. South Dakota DOT currently owns an atomic absorption spectrometer.

7. CONCLUSIONS

The original observation of corrosion of a copper condenser can be attributed to the presence of metals and metal oxides - present not only in the 1,1,1-trichloroethane used to extract the asphalt from the cores (the cores from US212 between LaPlante and the Missouri River were the last ones to be extracted) but also in the asphalt extracted from the cores . In the presence of moisture, these metals and metal oxides decomposed the solvent to form hydrogen chloride.

The presence of unusually high concentrations of metals known to catalyze the oxidation of asphalts may have accelerated the cracking of the pavement on US212 between LaPlante and the Missouri River. These metals were present in quite high concentrations in the original pavement built in 1958 (or in patching material that may have coincidentally been placed on top of the original pavement at the core site at MRM 206), and in even higher concentrations in the recycled pavement, 49% of which was the original pavement. While all the metals found in the asphalt cement could have originated in the Pierre shales from that area, comparison of the inorganic composition of the aggregate, the fines and the asphalt cement obtained from the same core strongly suggest that the mix was contaminated from another source. The most likely source, based on analysis of both the organic and inorganic components of the asphalt cement extracted from the cores, may be waste oil or, more likely, a waste oil sludge or distillation residue. The waste oil in the 1958 pavement appears to have come, at least in part, from vehicles using leaded gasolines (which would not only deposit lead on the road from the exhaust but would also contain lead in their waste lubricant); the waste oil composition in the recycled mix, containing products of incomplete diesel fuel combustion, appears to have originated from diesel engines.

8. RECOMMENDATIONS ON POLICIES AND PROCEDURES

1. Test the aging properties of the asphalt cement delivered

One of the sites of either intentional or inadvertent contamination of an asphalt cement would be at the refinery where waste materials (likely other refinery products) would be mixed into the asphalt. The new SHRP specifications for asphalt cements apparently allow significant leeway in the materials that can be added to the asphalt without putting it "out of spec". Testing of the aging properties of asphalt cements delivered would ensure that while SHRP specifications are being met, long term performance of the binder is not being jeopardized.

2. Prevent contamination at the construction site

Another source of contamination would be at the construction site where ashes or fines containing metals could be introduced into the mix, through the combustion of metal-containing fuels (like waste oils, their residues or sludges), or by the addition of metal-containing waste oils, their residues or sludges into the asphalt storage/mixing tanks. Contamination of the mix at the construction site would preferably be prevented by discussions with the contractor and occasional inspection of the contractor's equipment and tanks at the construction site.

3. Sample asphalt pavement cores soon after construction

If lack of manpower or cooperation make it impossible to prevent contamination by communications with the contractor and inspection of the construction site, checks on possible contamination could be made by examining asphalt extracted from the cores soon after construction.

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APPENDIX A

Scanning Electron Microscopy
and
X-ray Diffraction Analysis
of
Fines in Asphalt Cement
Extracted from a Core taken at US212 MRM 188

Summary of Results

This report summarizes the results of X-ray diffraction (XRD) analysis and scanning electron microscopy / X-ray energy spectrometry (SEM/XES) observations / analyses on centrifugation solids from a TRIAD Ltd. sample.

The sample was composed of a very small quantity of light brown dried powder. When the material was crushed, the mortar was stained as if a small amount of bitumen or asphalt remained.

The XRD trace did not show well defined minerals or metals, but some peaks were tentatively identified (Figure 1). With the XRD trace and the XES information, it appears there is Quartz, iron sulphide, Calcium carbonate, Chlorite, Illite and Iron or Iron Oxides present in the sample.

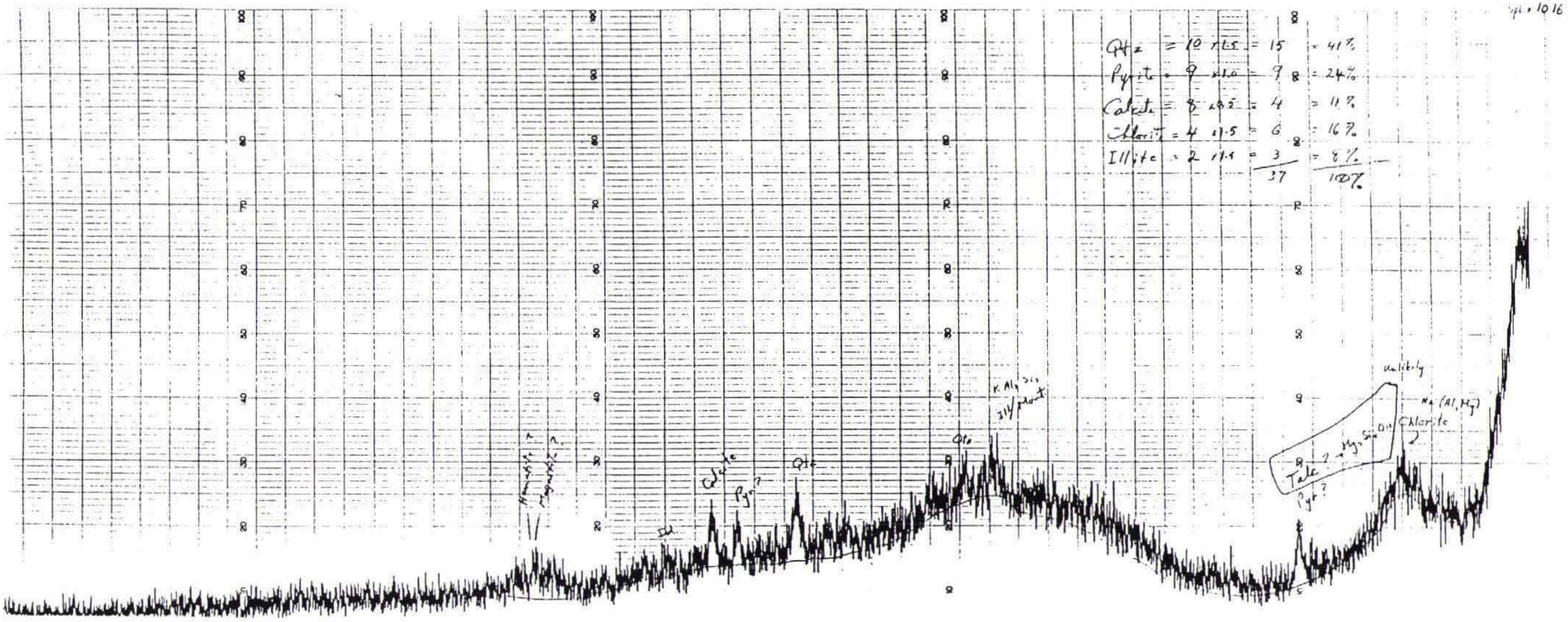
X-Ray diffraction analysis suggests the crystalline components consist of about 41% quartz and 24% iron sulphide. The remainder appears to consist of about 11% calcium carbonate and 24% illite and chlorite clay. Non-crystalline components that can not be detected by XRD analysis are indicated by the raised XRD background (see copy of diffractogram).

The SEM photographs (Plates 1A, 1C, 2A) showed two types of minerals; one flaky, the other more solid. The former could have been the Chlorite or Illite, whereas the latter could have been quartz, calcium carbonate or iron sulphide. Most of the material seemed to be normal rock forming minerals and some oxidation products, but some iron metal may be present. Copper was only found as a trace.

The analysis suggest the centrifuged solids consist mainly of natural crystalline materials. Quartz, calcium carbonate, illite clay and chlorite clay are indicated. Some oxidized iron and possible iron and copper wear metal are suggested by the XES analysis. The XRD suggests the iron sulphide is FeS_2 which usually occurs in its natural form as pyrite.

Figure 1 shows a copy reduction of the X-ray diffractogram.

Figure 1
Bulk X-Ray Diffractogram
Triad Solids



Qtz = 10 ×1.5 = 15 = 41%
Pyrite = 9 ×1.0 = 9 = 24%
Calcite = 8 ×0.5 = 4 = 11%
Chlorite = 4 ×1.5 = 6 = 16%
Illite = 2 ×1.5 = 3 = 8%
37 100%

SEM Photomicrographs
and
XES Spectra

Fig A1

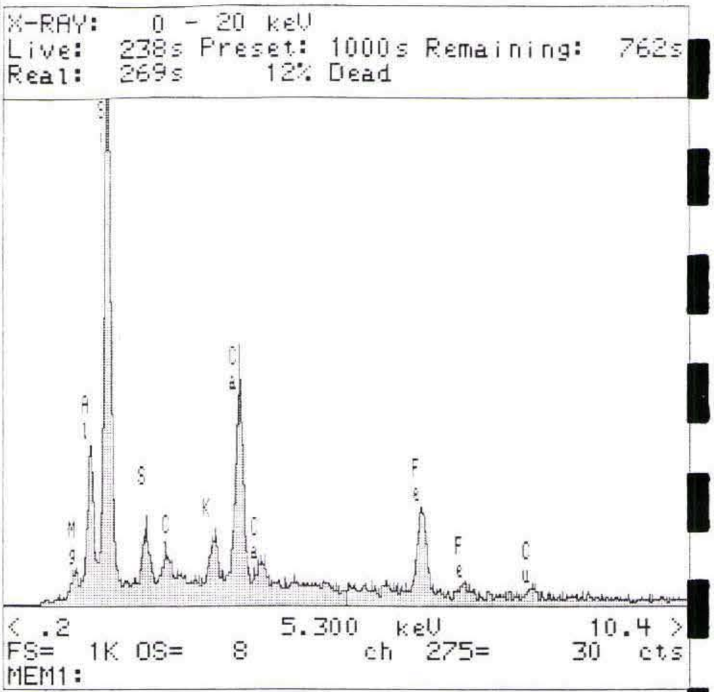
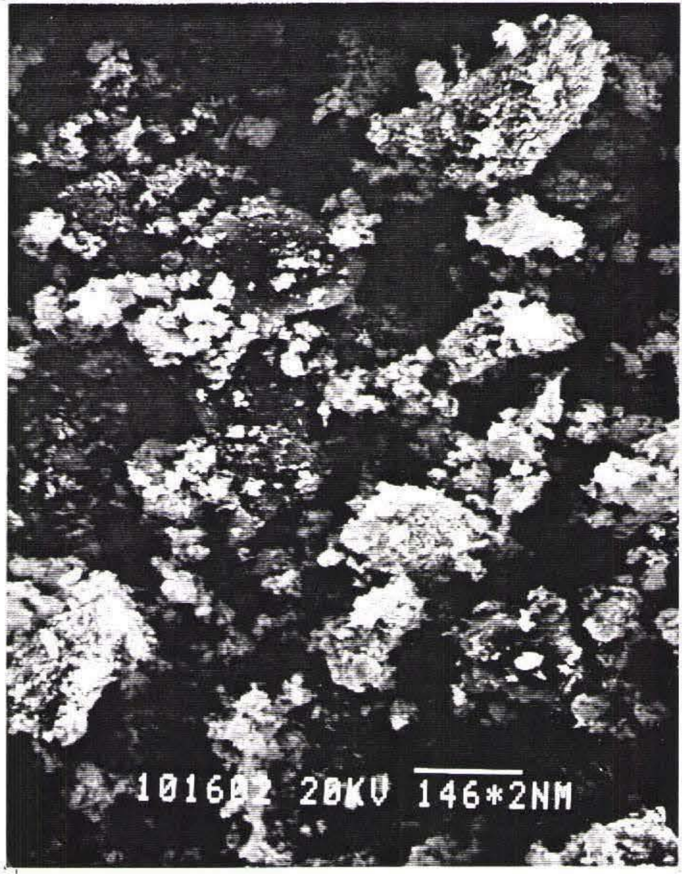
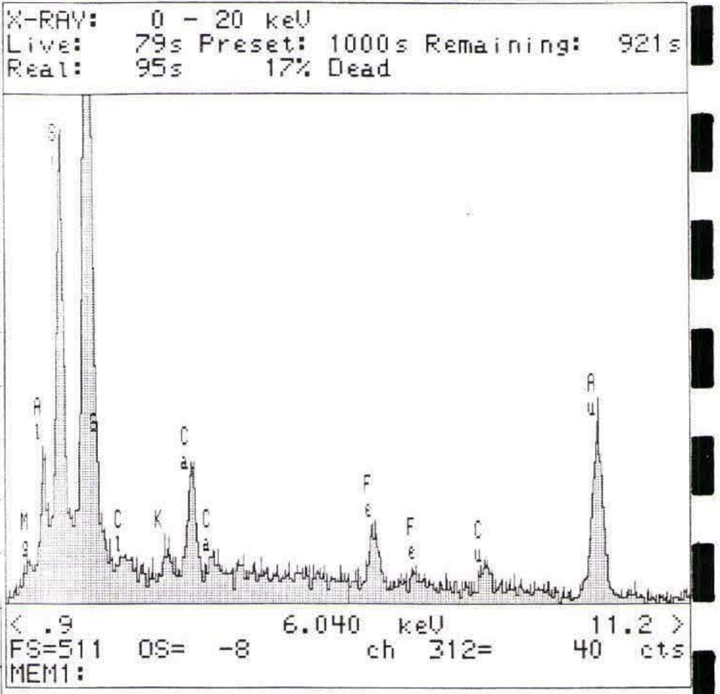


Fig B1





Plate

SEM/XES Plate 01
Centrifugation Solids
TRIAD Ltd.

Sample No. E94-0489-2

A-B Scanning electron photomicrograph (A) and corresponding X-ray energy spectograph (B) of centrifugation solids from a TRIAD Ltd. sample. The material consists of irregularly shaped fine particles with finer coatings and occasional fibres as seen at the I-9 position. Strong responses from silicon (Si), calcium (Ca), aluminium (Al) and iron (Fe) suggest the presence of pyrite, quartz, calcite and magnesium/aluminum silicate minerals. Weaker responses from copper (Cu), sulphur (S) and potasium (K) indicate metallic sulphides and likely other potasium rich silicates. This XES was done without a gold coating, whereas the SEM photograph was gold coated. **Photo A X350**

C-D Scanning electron photomicrograph (C) and corresponding X-ray energy spectograph (D) of centrifugation solids from a TRIAD Ltd. sample. The material consists of irregularly shaped fine particles with finer coatings. Two types of grains are apparent: a flaky type at the C-4 position and a more solid type at the F-8 position. Strong responses from silicon (Si), calcium (Ca), aluminium (Al) and iron (Fe) suggest the presence of pyrite, quartz, calcite and magnesium/aluminum silicate minerals. Weaker responses from copper (Cu), sulphur (S) and potasium (K) indicate metallic sulphides and likely other potasium rich silicates. This SEM and XES were done on a gold coated sample and the gold (Au) metal now responds. **Photo A X1000**

A	B
C	D

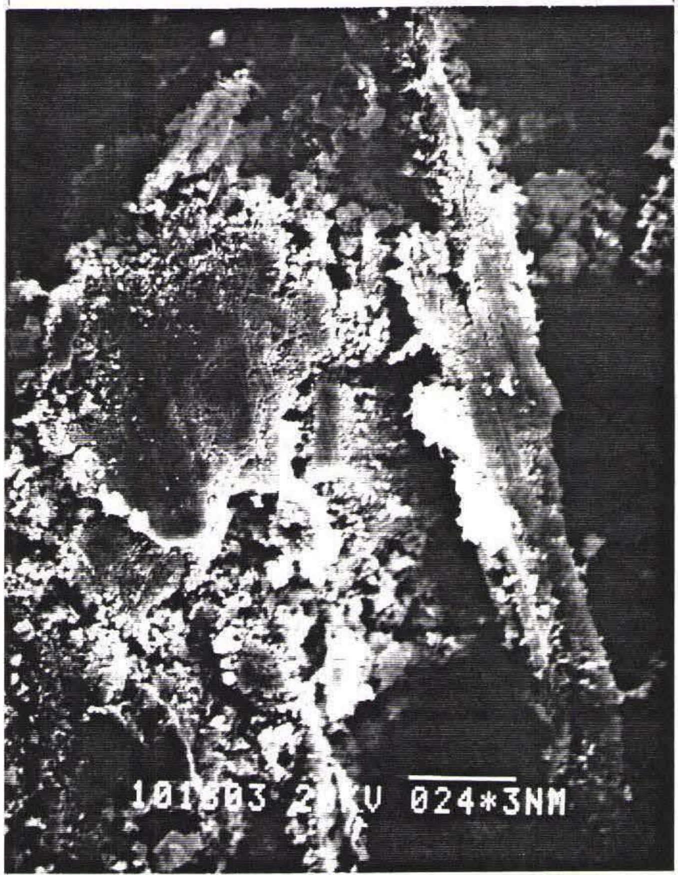


Fig A2

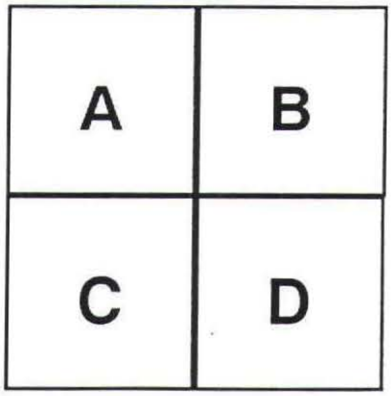
A | B
C | D

Plate

SEM/XES Plate 02
Centrifugation Solids
TRIAD Ltd.

Sample No. E94-0489-2

A-B Scanning electron photomicrograph (A) of centrifugation solids from a TRIAD Ltd. sample. The material consists of a larger irregularly shaped particle with finer coatings and corrosion characteristics. This material could be iron or iron oxide as determined from morphology This SEM was done with a gold coating. **Photo A X600**



APPENDIX B

Scanning Electron Microscopy
and
X-ray Diffraction Analysis
of
Fines in Asphalt Cement
Extracted from a Core taken at US212 MRM 188

A Metallurgist's Perspective

TEST LABS
INTERNATIONAL LTD.
METALLURGISTS, MECHANICAL ENGINEERS AND FIRE INVESTIGATORS
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- litigation
- fire investigation
- insurance investigations
- failure analysis
- corrosion
- chemical analysis
- hardness and tension testing
- metallography

Report No. 94-TL0434

December 14, 1994

SCANNING ELECTRON MICROSCOPY OF METAL PARTICLES FOUND IN AN ASPHALT SAMPLE

for

Triad Ltd.
Technical Research, Investigations and Development
787 Haney Street
Winnipeg, Manitoba
R3R 0Y7

ATTENTION: Dr. Elaine Thompson
Chemist and President

1.0 INTRODUCTION

Dr. Elaine Thompson submitted a number of scanning electron photomicrographs as well a energy dispersive x-ray (EDX) chemical analysis spectra of particles recovered from an asphalt sample taken from a highway in South Dakota. It was explained that a sample of asphalt had been dissolved in toluene and that the resulting solution had been centrifuged to separate the solids.

2.0 IDENTIFICATION OF PARTICLES

An examination of the scanning electron photomicrographs, labelled as Figs. A1 (at x350) and B2 (at x1000) would indicate that the all the particulate matter appears as "flaky, crusty" particles typical of oxide, corrosion compounds, or inorganic compounds.

The two "flattened" particles shown in Fig. A2 at a magnification (cf ×600) would be typical of metal or alloy which has been flattened or deformed. The particles exhibit parallel linear markings which would be typical of the surface of a bearing insert such as used for an automotive crankshaft or connecting rod bearing. These type of bearing inserts would be typically manufactured from lead-tin antimony babbitt alloys. Babbitt and bearing insert materials are typically "soft metals" whereas the steel used in crankshafts and connecting rods is much harder and hence much harder to deform. Aluminum alloys which are fairly soft and very deformable are also commonly used for engine compounds.

3.0 CONCLUSIONS

My best "educated" opinion would be that the "flattened" particle shown in Fig. A2 is a softer metal particle such as copper, aluminum brass or a babbitt bearing alloy. The flattened particle would be typical of a portion of a bearing insert.

Dr. Wayne Tennesey, P.Eng.
Metallurgist and Mechanical Engineer

PROVINCE OF MANITOBA
W. W. TENNESEY
Dec 14/94
REGISTERED PROFESSIONAL ENGINEER

94-TL0434/94-12-14/Triad.Rep/HDD34/pm