Phosphorous-31 NMR Studies of MnROAD Test Track Cells

William C. Schuster, Janet M. Wolf, and Francis P. Miknis

Western Research Institute
365 N. Ninth Street
Laramie, WY 82072-3380
U.S.A.
* fmiknis@uwyo.edu
** wcs21@uwyo.edu

Abstract

Extensive work has been performed on the relationship between polyphosphoric acid (PPA) and hydrated lime in bitumen pavement mixes. Yet the final fate of the PPA in the paved road has not been determined. Perhaps as important, the mechanism of stiffening by PPA is not yet understood. Laboratory studies have shown that PPA and hydrated lime react in bitumen to form calcium phosphate salts; however, studies have not been performed on samples from an actual road mix. In this study, samples from Cells 33, 34, and 79 of the MnROAD Low Volume Pavement Test Track have been used as model pavements to determine the impact of hydrated lime when used as an antistrip additive in conjunction with PPA modified bit*umen*. The cells contain PPA, hydrated lime, a phosphate ester antistrip agent, and polymer. Samples of loose mix from the cells were carefully extracted and separated into a binder, fines, and bulk aggregates. Solid and liquid state ^{31}P NMR measurements were then made on the separated fractions. Phosphorous NMR signals were found to be present in all solid fractions of the extraction. Most of the signal was detected in the centrifuge fines as calcium phosphate, and little or no liquid state signal was detected in the extracted binder. These findings indicate that in the MnROAD cells, PPA reacted with hydrated lime to form mainly calcium phosphates. Also, a solid-state NMR signal that had a small chemical shift anisotropy was observed in the extracted binder. We attribute this signal to be from a reaction product between the Innoval W and lime.

KEYWORDS. NMR, FTIR, orthophosphoric acid, polyphosphoric acid, hydrated lime, antistrip , MnROAD.

1. Introduction

Modification of bitumen using polyphosphoric acid (PPA) has been receiving increased attention over the past several years. Indeed, the Phosphate Forum of the Americas recently issued two reports on the use of polyphosphoric acid in bitumen (PPA subcommittee 2009a, 2009b). The annual meeting of the AAPT in March 2010 held a symposium on polyphosphoric acid modification, and a workshop discussing current issues with PPA, its effect on binder properties, industry's perspective and binder testing results were discussed at a recent workshop in Minneapolis, MN in April 2007. The talks and discussion can be found at: https://engineering.purdue.edu/NCSC/PPA%20Workshop/2009/index.html. A circular of papers from the workshop will also be published by the Transportation Research Board (TRB). During that workshop there was significant discussion about the effects of lime on PPA modified binders. While laboratory studies [Ho et al. 2001, Miknis and Schuster, 2009; Arnold 2009; Huang et al., submitted] have shown that lime reacts with the PPA in bitumen binders, concerns were raised about whether this would happen in mixes taken from the field. Reviews of PPA modified binders have also been written (Asphalt Institute 2005, Chin and Oliver 2007).

The use of PPA and /or lime in bitumens has been shown to have a number of beneficial properties. For example, one of the main benefits of PPA addition is that it increases the high temperature performance of bitumen cement without adversely affecting the low temperature properties. In addition, PPA can act as a partial substitute and reduce the amount of polymer required to achieve a given PG grade (Orange et al. 2004a, 2004b).

Lime, on the other hand, has been shown to reduce stripping and moisture sensitivity, to increase stiffness and reduce rutting and oxidation and aging (Petersen et al. 1987). Little and Petersen (2005) have discussed the chemical and physical effects involved when using hydrated lime as a filler.

However, when PPA and lime are both added to a bitumen there are concerns about possible reactions between the acid and base (lime) which might negate the intended improvements expected from the additives (Chin and Oliver 2007). Laboratory studies in which PPA and lime have been added to a bitumen have shown that solid calcium phosphates were formed as a result of a reaction between PPA and lime (Miknis and Schuster 2009). The question of whether such reactions might happen in a real roadway was not addressed.

In this paper ^{31}P NMR has been applied to samples from the MnROAD test track in which both PPA and lime, in addition to a phosphate ester and polymer, were present. ^{31}P NMR measurements have been

made on tank bitumens and loose mix samples from cells 33, 34 and 79 of the MnROAD Low Volume Pavement Test Track. The purpose of the MnROAD Study is to investigate the field performance of polyphosphoric acid modified binders [Clyne et al. 2009]. Another project goal is to evaluate the impact of lime used as an anti-strip additive in conjunction with PPA in modified bitumen [Fee et al. 2008]. WRI is one of the partners in the MnROAD study to perform chemical analyses of the bitumen binders and mixtures. A description of the test track and construction of the cells has been given (Clyne et al. 2008).

2.   Experimental

In October 2007 four test cells were constructed at the MnROAD test track facility near Albertville, MN Clyne et al (2008). The test cells were constructed using the same base PG 52-34 bitumen, but the bitumen in each cell was modified to a PG 58-34 using different additives. The additives used and their amounts are listed in Table 1. Lime and Innovalt W are included in the table, although they were not considered as a stiffener in the bitumen, but as antistrip agents. Bitumens were modified to meet PG grade using polymer, PPA, or a combination of the two. The liquid antistrip agent, Innovalt W, was added to the trucks as they left the bitumen supplier. Lime was blown to the whole mix at the mix plant prior to paving of the cells. Sample of the loose mix were taken for each cell as they were delivered to the road site.

Table 1 Additives used in MnROAD cell formulations.

	Cell 33	Cell 34	Cell 35	Cell 79
PPA (115%) , wt %	0.75%	0.3%		0.3%
Polymer, wt %		1 % SBS	2% SBS	0.5 % Elvaloy
Antistrip, wt %	0.5 % Innovalt W	0.5 % Innovalt W		0.5 % Innovalt W
Hydrated Lime, wt %	1.0%	1.0%	1.0%	1.0%

2.1 *MnRoad Test Cell Loose Mix Separations*

Loose mix samples were analyzed in much the same way that the tank bitumens and the laboratory produced samples were previously analyzed [Miknis and Schuster, 2009]. The binders were extracted from the loose mix samples from cells 33, 34, and 79, and the solids that were removed were also preserved for NMR analysis. Formulations for the MnROAD cells are given in table 1 Three of the four test cells had PPA in their formulation and were studied using ^{31}P NMR. The loose mix binder extractions were performed as follows: a few grams sample of loose mix were placed in a flask and a

toluene/ethanol 85/15 mixture was used to dissolve the organic material. The liquid was decanted and centrifugation was used to remove the fine particles. The supernate was carefully decanted from the centrifuge tube. Solids collected in the centrifuge as well as the aggregate material left behind during the decant process were saved and dried in an oven. Rotary evaporation was used to remove the solvent from the supernate, yielding the extracted binder. The solids separated during the first decant were a bit more difficult to analyze. They were sieved to four different mesh sizes; +40, 60-40, 100-60, and -100. Aggregates above 40 mesh were too large to fit into the NMR sample rotors and were not studied further. A strong magnet was used to remove most of the magnetic particles from the other three sieved fractions. To do this, the samples were placed in capped vials and agitated while exposed to the magnetic field. Particles attracted to the magnet would collect in the end of the vial and the remaining sample would be poured out into another vial.

2.2 NMR Measurements

NMR spectra were collected on all of the above mentioned fractions. ^{31}P NMR spectra were acquired at a nominal frequency of 40 MHz. using a Chemagnetics CMX NMR spectrometer. Chemical shifts were referenced to orthophosphoric acid at 0 ppm. Typically, ^{31}P NMR spectra were acquired over a three hour period using a pulse repetition rate of 1 s. For the liquid state NMR, the samples were dissolved in deuterochloroform (CDCl$_3$).

Solid-state ^{31}P NMR measurements were made using single pulse excitation with high power decoupling and magic-angle spinning (SP/MAS). Spinning rates of 1.5 and 4.5 kHz were used. A 1 s pulse delay was used, and spectra were typically acquired over a 3 hour period. For the case of the sieved fractions, the 100 mesh samples were demagnetized before acquiring a NMR spectrum. The results were a great improvement over the results prior to the demagnetization process.

3. Results and Discussion

3.1 ^{31}P NMR of Tank Bitumens

Liquid state ^{31}P NMR spectra were acquired on the tank bitumens for cells 33, 34 and 79 (Figure 1). The salient feature in Figure 1 is that, although the acid strength of the PPA was 115% when added to the binder at the refinery, by the time it was added at the hot mix plant it had hydrolyzed to a concentration of ~100 %. This is noted by the large increase in the orthophosphoric acid resonance near ~0 ppm in the tank bitumens compared to the small orthophosphoric acid resonance in the neat 115% PPA, and the loss

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of phosphorous signal at -26 and ~-13 ppm due to middle or terminal groups of phosphate oligomers. Repeat NMR measurements on the tank bitumens taken over a year apart and from different batches of sample gave the same results.
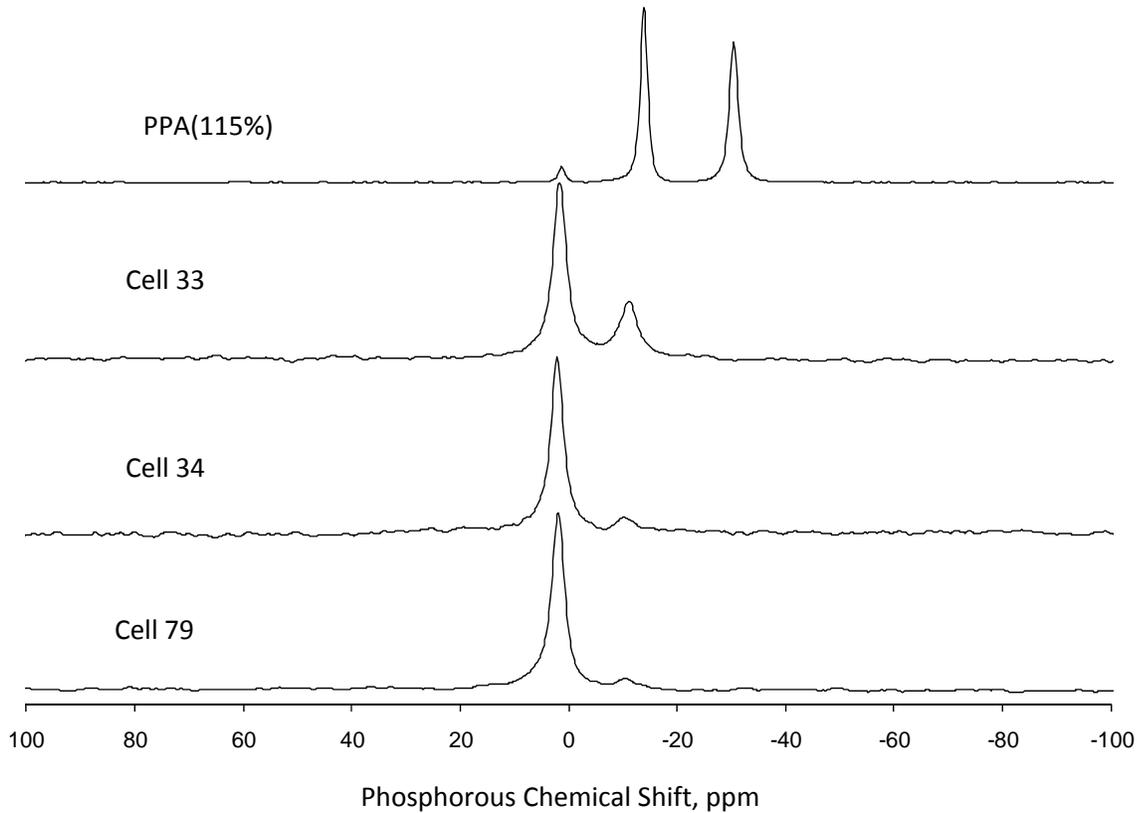

Figure 1. ^{31}P NMR spectra of polyphosphoric acid (115%) and tank bitumens from MnROAD cells 33, 34, and 79.

3.2 ^{31}P NMR of the Extracted Binder

Liquid state NMR measurements were made on the extracted binder from the MnROAD cells. The NMR result for cell 33 extracted binder is shown in Figure 2 Results for cells 34 and 79 were similar and are not shown. Comparison of the spectra in Figure 2 shows that, whereas a liquid-state phosphorous signal was observed in the binder before paving, only a weak liquid-state phosphorous signal was observed in the binder after extraction from the loose mix. These results are in agreement with those obtained in a previous study in which it was shown that lime reacted with the PPA in acid modified binders to form insoluble calcium phosphates [Miknis and Schuster, 2009].
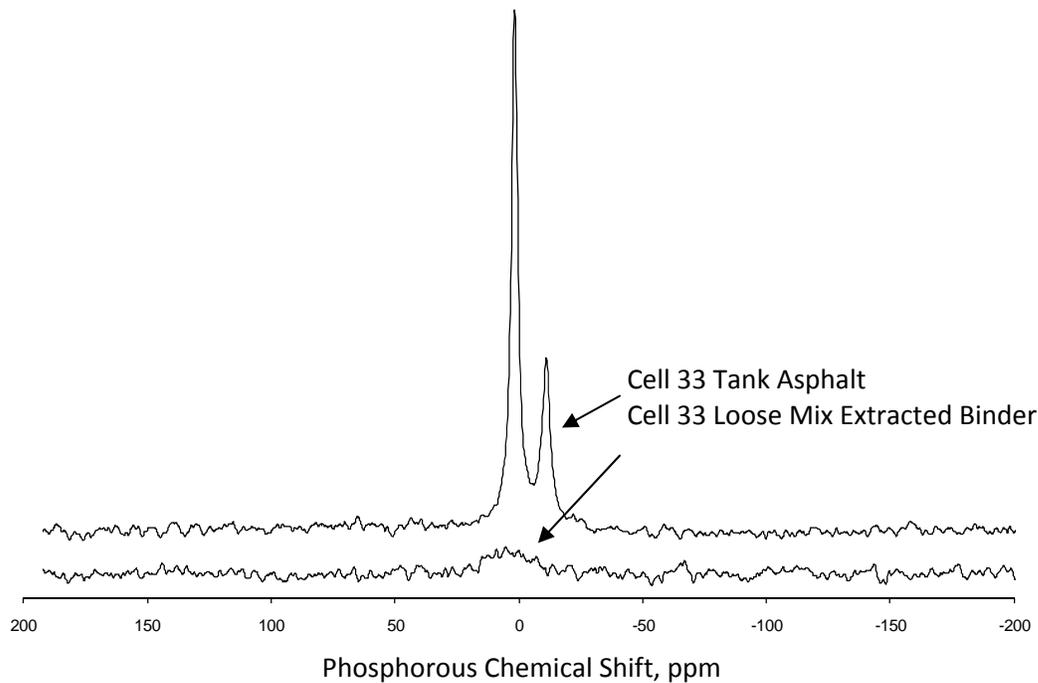
Figure 2. Liquid-state[31]P NMR spectra of MNRoad cell 33 tank bitumen and loose mix extracted binder illustrating the loss of soluble phosphorous NMR signal in the extracted binder .

3.3 ^{31}P NMR of fines and sieved fractions

As described earlier, a number of steps were taken in the binder extraction that were not taken in the previous MnROAD study. In particular, the fines were removed from the extracted binder by centrifugation and recovered for NMR analysis. In addition, the aggregate solids were sieved into 4 fractions (+40, 60-40, 100-60, and -100 mesh) and solid-state NMR measurements were made on the fractions passing -40 mesh screen size.

A spectral montage for cell 33 is given in Figure 3.   The 100 mesh fines were screened with a magnet to remove magnetic particles which would otherwise give distorted and noisier NMR signals. The effect of demagnetization on the spectral signal-to-noise ratio can be seen by comparing the -100 Mesh spectra before and after demagnetization.

A number of observations can be made about the results in Figure 3. First, the fact that a phosphorous signal was observed in all the fines fractions shows that phosphorous was distributed throughout the aggregate phase. However, comparing the signal-to-noise (S/N) ratios it appears that most of the

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phosphorous ended up in the fines and -100 mesh fractions   Spinning sidebands are noticeable in these spectra at ~100 and -100 ppm. Sidebands are not so noticeable in the 60-100 and 40-60 mesh spectra.
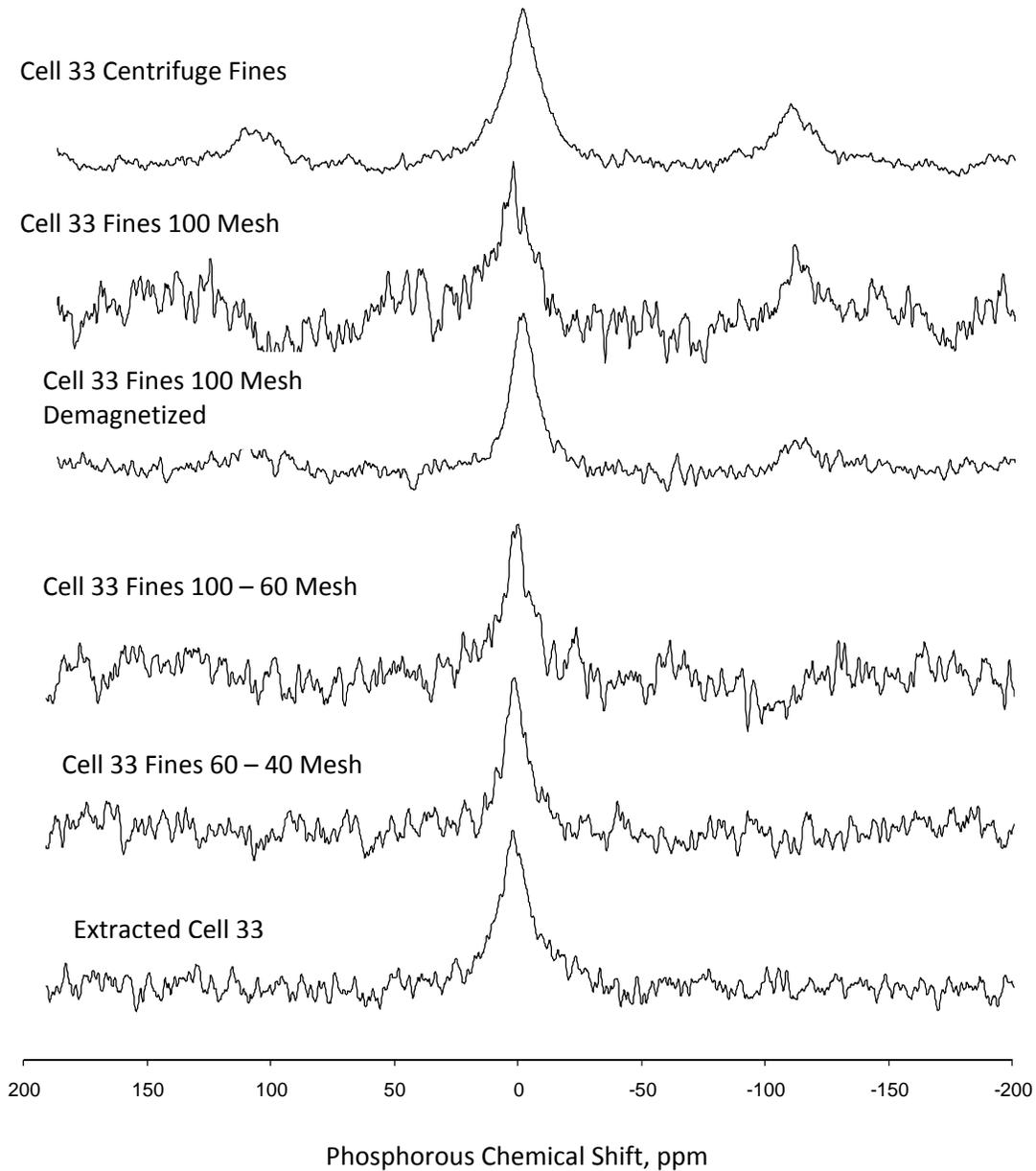
Cell 33 Centrifuge Fines

Cell 33 Fines 100 Mesh

Cell 33 Fines 100 Mesh
Demagnetized

Cell 33 Fines 100 – 60 Mesh

Cell 33 Fines 60 – 40 Mesh

Extracted Cell 33

| 200 | 150 | 100 | 50 | 0 | -50 | -100 | -150 | -200 |

Phosphorous Chemical Shift, ppm

Figure 3 Solid-state[31]P NMR spectra of fines from loose mix extracted binder in MnROAD cell 33.

An unexpected result was that a solid-state NMR spectrum of phosphorous was obtained for the extracted binder (see bottom spectrum, Figure 3). However, this spectrum did not have the characteristics of a solid state spectrum in that no spinning sidebands were observed, even for spinning at low speeds. Solid-state NMR spectra of the fines and extract of cells 33 and 79 at two different spinning speeds are shown in Figure.4 As mentioned, the spectra of the phosphorous in the extracted binders do not show any sidebands, except possibly a very weak one for cell 79 at ~100 ppm in the 4.5 kHz spectrum. Strong sidebands are observed at the slow spinning (1.5 kHz) spectra of the fines. The important features of these spectra are that the spectra show that phosphorous is in at least two different chemical environments. In the fines spectra it is expected that the phosphorous is in one or more solid calcium phosphate structures. The spectra of the extracted binders indicate that the phosphorous is in a solid environment with very small chemical shift anisotropy. The possible origin of this phosphorous signal is discussed later in this paper.

Cell 33 Fines
 @ 4.5 kHz spinning

Cell 33 Fines @
1.5 kHz spinning

Extracted Cell 33 @
4.5 kHz spinning

Extracted Cell 33 @
1.5 kHz spinning

Cell 79 Fines @
4.5 kHz spinning

Cell 79 Fines @
1.5 kHz spinning

Extracted Cell 79 @
4.5 kHz spinning

Extracted Cell 79 @
1.5 kHz spinning

Phosphorous Chemical Shift, ppm
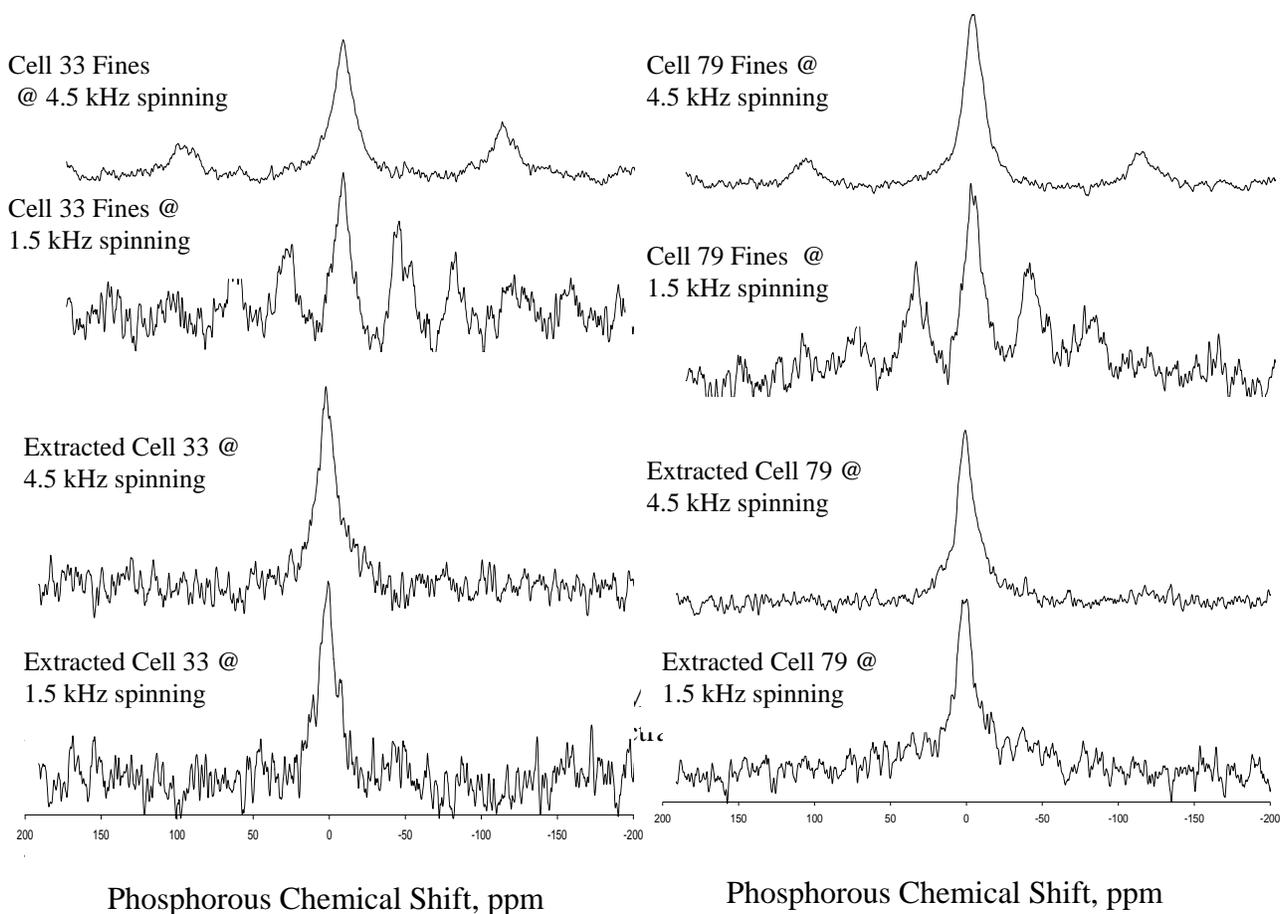
Phosphorous Chemical Shift, ppm

Figure 4 Solid-state Phosphorous NMR spectra of MN Road Cells 33 and 79 spinning at 1.5 and 4.5 kHz illustrating differences in the spinning sideband spectra between the fines and extracted binder.

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FTIR Analysis of the Centrifuge Fines

The amount of hydrated lime added to the MnROAD cells was in excess of the amount of hydrated lime that would be needed to precipitate out the phosphorous in the PPA as calcium phosphates. As such, the MnROAD cells should still contain hydrated lime. The centrifuge fines for cells 33, 34, and 79 were further analyzed by using the ATR attachment on a Perkin Elmer FTIR. A small amount of the fines were placed on the ATR diamond and light pressure was applied. Sixteen scans were acquired and averaged (Figure 5. Lime (calcium hydroxide) content was determined by the presence of the band at 3643 cm^{-1}, due to the hydroxyl group [Arnold et al. 2006]. The results were compared to a spectrum of pure lime. In all cases the spectra of the centrifuge fines contained a strong absorbance band at 3643 cm^{-1}, indicating the presence of lime in the centrifuged fines. Because there was an excess of lime relative to the PPA in the MnROAD cells, the phosphorous NMR signals from the centrifuged fines are most likely due to calcium phosphates, formed from the reaction of lime and PPA [Miknis and Schuster, 2009].
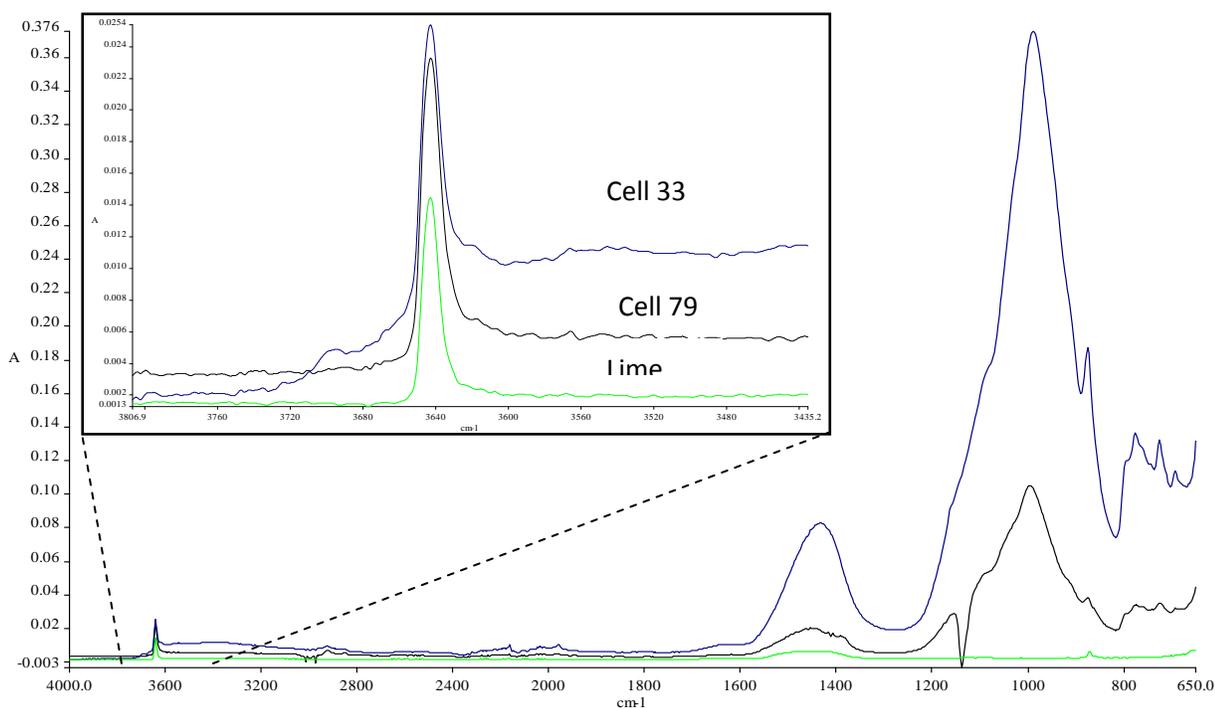

Figure 5. Infrared spectra of centrifuge fines extracted from cell 33 (blue) and cell 79 (black) and pure calcium hydroxide (green) showing the presence of lime in the centrifuge fiines.

3.5 ^{31}P NMR of Innovalt and Lime

Innovalt W is a phosphate ester antistrip agent that was also included in the mix design for the MnROAD cells studied here. The mechanism of action for Innovalt W is the hydrophilic phosphate head that binds to polar groups found on aggregate surfaces and an aliphatic tail that interacts strongly with the non-polar bitumen functionalities, hence forming a better bond between bitumen and aggregate. Innovalt W was included in the mix designs for the MnROAD cells that contained PPA to improve the rutting resistance and moisture sensitivity based on previous hamburg wheel testing in the laboratory. Although the non-polar group on the Innovalt W gives it a different solubility than PPA, the head group still has the potential to act like an acid and donate a hydrogen, the same way the PPA does. If this is the case, it may have some reactivity with lime as well.

The percentage of total phosphorous in the MnRoOAD cells due to the Innovalt W was substantial (21 % for cell 33, and 40 % for cells 34 and 79). As such, the likelihood that some of the phosphorous NMR signals could originate from the phosphorous in Innovalt W and not from the PPA cannot be ruled out. Consequently, a laboratory study was conducted in which 1 wt % of Innovalt W was added to SHRP bitumen AAB-1 in the same manner as done previously (Miknis and Schuster 2009). The bitumen was mixed in a shear blender at 2,000 rpm for 30 min. at 150°C after each addition of modifying agent.   PPA and Innovalt-W were added at the level of 1 wt%,

The Innovalt-W modified bitumen was then treated with hydrated lime (5 wt %) to see if there was any reaction between the Innovalt and lime. The results are shown in Figure 6. The low intensity of the liquid –state spectrum shows that when lime was added there was little soluble phosphorous remaining in the sample. However, the solid-state NMR spectrum shows a much stronger signal indicating that after lime addition, the phosphorous was in a solid form. The structure of the solid was not determined. Phosphate ester antistrips such as Innovalt-W are not considered to react with PPA (Asphalt Institute 2005), but to our knowledge detailed studies have not been made to determine whether Innovalt-W reacts with lime. The ^{31}P NMR results in Figure 6 indicate that Innovalt-W might react with lime, but not necessarily to form the same type of calcium phosphates as when PPA reacts with lime. This observation is based on the lack of any intense spinning sidebands in the solid-state spectrum. when spinning at 4.5 kHz. Previous ^{31}P NMR work (Miknis and Schuster 2009) had shown that PPA in bitumen reacts with lime to form calcium phosphates which have fairly intense spinning sidebands when spinning at 4.5 kHz.   The lack of sidebands in the spectra indicate that while the Innovalt-W apparently reacted with lime to form

an insoluble solid, the solid has a small chemical shift anisotropy. This would tend to rule out most calcium phosphates which have prominent sidebands at 4.5 kHZ spinning, (Miknis and Schuster, 2009). As noted, similar results were obtained for the MnROAD samples suggesting that, in that case, the phosphorous in the solid-state ^{31}P NMR spectra of the extracted bitumen samples might be due to an Innovalt-W/lime reaction.
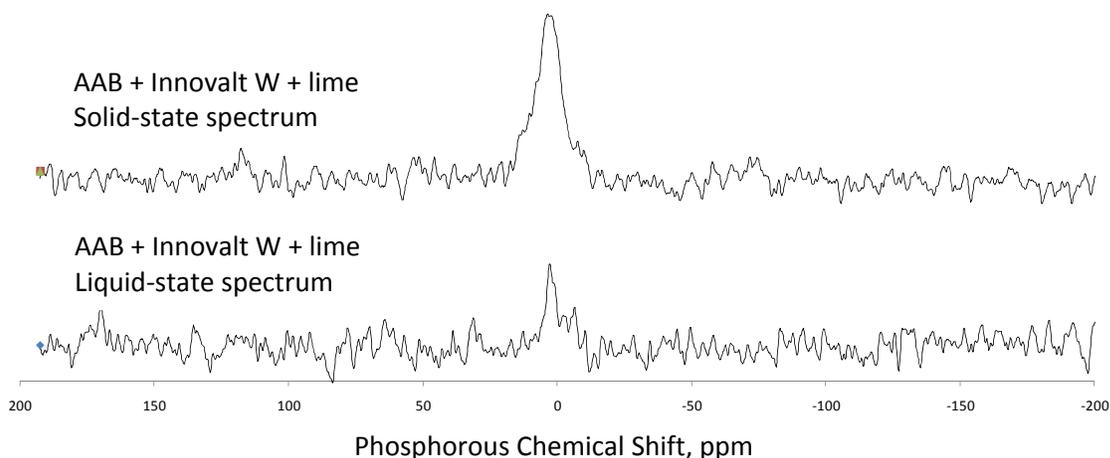

Figure 6. ^{31}P NMR spectra of bitumen AAB-1, modified with 1% Innovalt-W and 5 % lime.

4. Summary

Phosphorous NMR measurements made on Cells from the MNRoad Test Track have shown that there was reaction between the PPA and the lime in the MnROAD cells. This was noted by the strong solid-state phosphorous signals observed in the centrifuge fines and -100 mesh screened samples, both of which had prominent spinning sidebands indicating that the phosphorous was in a solid form.

Further evidence of the lime /PPA reaction was the lack of NMR signal in the liquid-state indicating that there no phosphorous in soluble form in the extracted binder. Although a liquid phosphorous signal was not observed in the extracted binders, a solid state spectrum was obtained from the extracted binder. However, there were no spinning sidebands in the spectra of these samples even when spinning at low speeds (1.5 kHz), suggesting the presence of a solid with very small chemical shift anisotropy. We attribute this signal as arising from a reaction between the Innovalt w and the hydrated lime.

The fate of the PPA in the MnROAD cells appeared to be that some PPA reacted with lime to form calcium phosphates, some portions may have adsorbed onto the fines in the aggregate as solid-state spectra were observed in all the sieved fractions, and some remained in the extracted binder as a solid phosphate with small chemical shift anisotropy. Laboratory experiments with Innovalt W and bitumen

suggest that the phosphate ester antistrip and lime also react, and the solid-state spectrum observed in the extracted binder may be due to this reaction product.

5. Acknowledgements

6. Disclaimer

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