

Phosphorus Nuclear Magnetic Resonance Testing of Asphalt Binders

TECHNICAL REPORT

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Abstract: In service aged asphalt samples, modified with 115% polyphosphoric acid (PPA), were analyzed by liquid and solids state phosphorous nuclear magnetic resonance spectroscopy (^{31}P NMR). MnDOT Cells 33, 34, and 79 were constructed with both PPA and the phosphate ester Innovalt-W, whereas Cell 35 did not contain PPA or Innovalt-W—and all the Cells were modified with 1.0% hydrated lime. Liquid state ^{31}P NMR showed significant phosphorous resonances for Cells 33, 34, 79 and no phosphorous resonances for cell 35. The observed resonances do appear near the region for broadened orthophosphoric acid described by others and they also fall within the region of phosphate esters. The major phosphorous resonance observed in the liquid state NMR is tentatively attributed to the phosphate ester Innovalt-W in the case of Cells 34 and 79, and the spectra for Cell 33 is more complex suggesting that PPA derivatives may be present in addition to Innovalt-W. Solid state ^{31}P NMR for asphalt from Cell 33 was nearly identical to that reported for fines isolated from Cell 33 indicating a significant amount of calcium phosphate. A set of asphalts constructed with hydrated lime which contain PPA and no Innovalt-W would help clarify the results.

Introduction.

Pholyphosphoric acid (PPA) is commonly added to stiffen asphalt improving its high temperature qualities without sacrificing low temperature performance. It has also been reported to impart favorable pavement characteristics with respect to cracking, moisture, adhesion, improved workability, and synergies when used in conjunction with polymers (Jaroszek, 2011; Transportation Research Circular E-C160, 2012). PPA is a dehydrated form of orthophosphoric acid (orthophosphoric acid = H_3PO_4 ; dehydration gives various forms but the complete dehydration product is P_2O_5) which is graded according to the $\text{P}_2\text{O}_5/\text{H}_3\text{PO}_4$ weight ratio. A brief review of PPA and its basic chemistry can be found in Masson (2008). The particular PPA used for the construction of the MnDOT cells 33, 34, and 79 was 115% which has a high $\text{P}_2\text{O}_5/\text{H}_3\text{PO}_4$ ratio meaning that it consists of more longer chains of repeat PO_3H units and very little free H_3PO_4 (Figure 1).

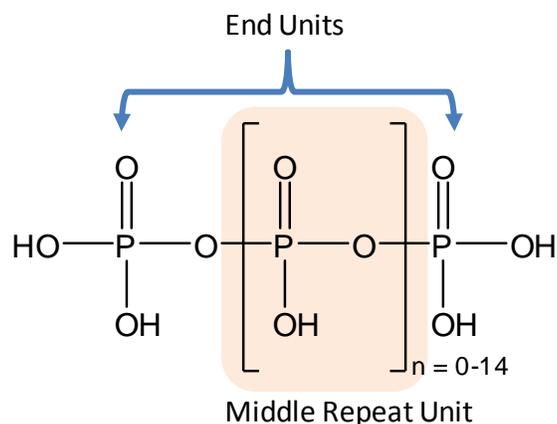
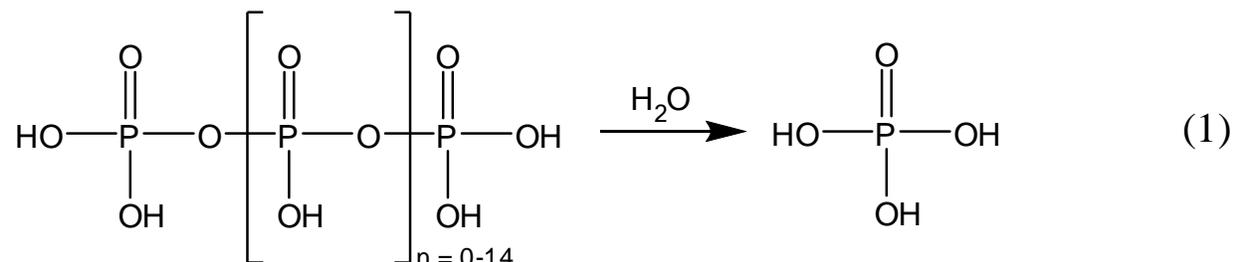
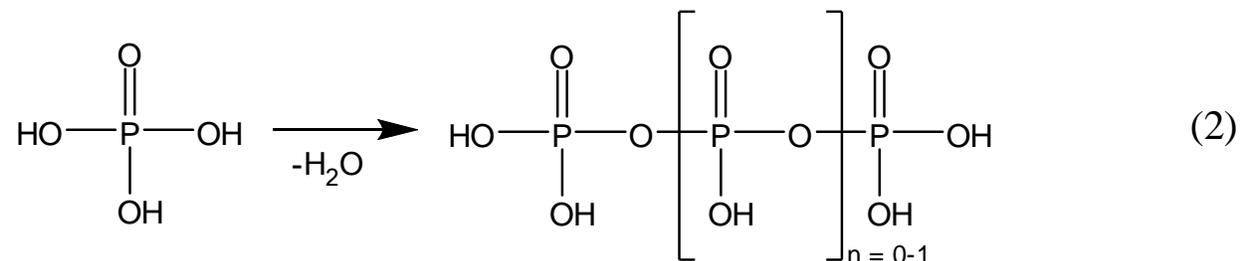


Figure 1. Representation of 115% PPA showing central PO₃H repeat units capped by end units (based upon data from 114% PPA reported by Masson (2008)).

In the presence of water PPA readily hydrolyzes to give H₃PO₄ (Equation 1), this process also occurs more slowly with residual water in asphalt or from moisture in the air and has been observed in laboratory when blending asphalt at elevated temperatures with PPA (Miknis and Thomas, 2008) and for tank asphalts that were blended with PPA (Schuster *et. al.* 2011).

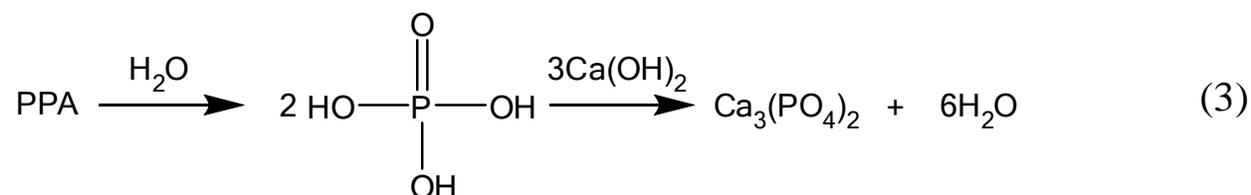


However, it should be kept in mind that PPA hydration in asphalt has also been shown to be reversible. In a study by Miknis and Thomas (2008) H₃PO₄ was added to asphalt and the mixture was heated which caused partial dehydration of the acid to give small amounts of PPA products, as detected by ³¹P NMR (Equation 2).

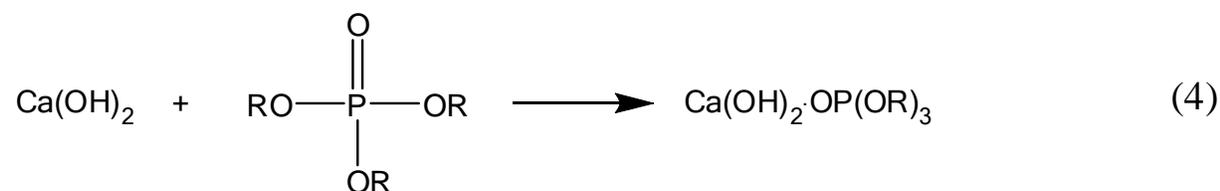


This may have implications for the long term reactivity of H₃PO₄/PPA species in asphalt especially since they are surrounded by a variety of reactive asphaltenic functional groups. To

date no systematic study has shown how PPA or H_3PO_4 does, or does not, react specifically with many of the functional groups found within asphalt. Some researchers point out that there are numerous types of chemical reactions and catalytic transformations that PPA can undergo with molecules having similar functional groups to those found in asphalt (Masson, 2008; Jaroszek 2011 and references therein). While others maintain that PPA merely undergoes hydrolysis to give H_3PO_4 and that PPA is not transformed into something new or it may serve to catalyze other reactions and/or merely hydrogen bond to asphaltene functional groups (Miknis and Schuster, 2009; Miknis and Thomas, 2008). What is agreed upon however is that in the presence of bases— or more specifically in the presence of hydrated lime (Equation 3)—PPA undergoes acid-base reactions to give insoluble calcium phosphate species (Miknis and Thomas, 2008; Miknis and Schuster, 2009; Huang et. al, 2011; Schuster *et. al.* 2011).



The main premise for this conclusion is that upon blending asphalt and PPA in the presence of excess hydrated lime a visible reaction occurs and no soluble phosphorous species are detected by liquid state ^{31}P NMR, and calcium phosphates are detected by solids state ^{31}P NMR— especially in fines recovered from binders. It is also important to be aware that the phosphate ester Innovalt-W has also been shown to interact with an excess of hydrated lime to give material that is sparingly soluble in asphalt which has not been further characterized but it is believed that the products are not the same as calcium phosphates (Equation 4, Schuster *et. al.*, 2011).



Generic Representation of Innovalt-W, R may be alkyl or H

The intention of this study is to address the long term fate of PPA in asphalt which was aged under real world conditions by liquid ^{31}P NMR and solid state ^{31}P NMR.

Experimental.

Samples from four test cells, which were constructed on October 2007, were cored and extracted by the Minnesota Department of Transportation in late 2013 (MnDOT) and provided to Western Research Institute (WRI). The samples were from test track Cell 33, Cell 34, Cell 35,

and Cell 79. All of the cells contained 1.0% hydrated lime and the balance of their composition is as follows: Cell 33 has 0.75% of 115% PPA and 0.5% Innovalt-W; Cell 34 has 0.3% of 115% PPA, 1% SBS polymer, and 0.5% Innovalt-W; Cell 35 has 2% SBS polymer; Cell 79 has 0.3% of 115% PPA, 0.5% Elvaloy polymer, and 0.5% Innovalt-W (values also reported in Schuster *et. al.*, 2011; TRB Circular E-C160 on page 115). The samples were extracted from cores at various depths and the samples used for this study were Cells 33b (BC13-07), 34b (BC13-10), 35b (BC13-13), and 79b (BC13-16), hereafter referred to simply as Cells 33, 34, 35, and 79.

Liquid state ^{31}P NMR were conducted at the University of Wyoming NMR Facility using a Bruker Avance III 400 MHz instrument. The ^{31}P NMR were acquired at 161.97 MHz using a standard proton decoupled pulse programs with a 2.0 second delay. Approximately 15,000-16,000 scans were acquired over about 10 hrs to give satisfactory spectra. All spectra were externally referenced to H_3PO_4 which was set to 0.00 Hz. The solutions were prepared by dissolving 0.25 g of asphalt in 0.75 mL of CDCl_3 (Cambridge Isotope Laboratories). These solutions were loaded into 10 mm medium walled glass NMR tubes fitted with a Teflon screw cap (New Era). Some samples were treated with the relaxant $\text{Cr}(\text{acac})_3$ (Aldrich) to determine if there was interference in the spectra due to paramagnetic impurities. 115% PPA and crystalline H_3PO_4 and H_3PO_4 (85% weight in H_2O) were purchased from Aldrich and used as received.

An approximate mixture of asphalt from Cell 35 with 0.3% of 115% PPA was prepared by adding 0.0007 g of 115% PPA to a vial that was previously dried in an oven overnight and cooled in a desiccator. To this vial was added 0.2500 g of Cell 35 using a spatula and then 0.75 mL of CDCl_3 was added and the mixture which was allowed to sit for several hours to dissolve the asphalt (a small amount of insoluble material was observed and is believed to be SBS). A similar procedure was followed to make the 0.3% crystalline H_3PO_4 and H_3PO_4 (85%) mixtures in asphalt from Cell 35 which was dissolved in CDCl_3 . For the crystalline H_3PO_4 mixture 0.0018 g of crystalline H_3PO_4 , 0.6240 g of asphalt from Cell 35, and 1.86 mL of CDCl_3 were used, and for the H_3PO_4 (85%) mixture 0.0013 g of H_3PO_4 , 0.3694 g of asphalt from Cell 35, and 1.104 mL of CDCl_3 were used.

Solid state ^{31}P NMR was conducted at Lawrence Livermore National Laboratories by M. Lee Davisson under the direction of Dr. Julie Herberg (Bowen) using a 400 MHz Avance Bruker spectrometer. The spectra were acquired using single pulse excitation with high power decoupling and magic-angle spinning (SP/MAS). 3 mm rotors and a spinning rate of 5 kHz were used. Difficulties were encountered with packing the rotors with asphalt which led the failure of several rotors and repeated cleaning of the probe. Spectra were obtained for H_3PO_4 (85%), 115% PPA, and asphalt from Cells 33 and 34. Work was carried out in an attempt to acquire spectra for Cell 79 but further work was not carried out.

Results and Discussion.

Previous ^{31}P NMR of asphalts from Cells 33, 34, 35, and 79 were conducted by Schuster *et. al.* (2011) on both the tank asphalts and on the extracted binder. For the tank asphalts it was observed that most of the PPA had converted to H_3PO_4 due to hydrolysis and the observed PPA/ H_3PO_4 ratio remained unchanged after 1 year when the sample was sealed in a can. From this study it appeared that most of the phosphorous species in the tank asphalt remained soluble. However, for binder extracted from aggregate—which was also mixed with hydrated lime—very little liquid ^{31}P NMR signal was observed. Previous work by the authors had shown that when 10% by weight of hydrated lime was mixed with 1.5% by weight of 105% PPA (very high content of H_3PO_4) a reaction occurred which gave no phosphorous signal in the liquid state ^{31}P NMR but a significant resonance in the solid state ^{31}P NMR was observed. It was shown that the large excess of hydrated lime efficiently reacted with the PPA to give calcium phosphates. Similarly, in the previous study of MnDOT asphalts it was assumed that for extracted binder from Cells 33, 34, and 79—which contained PPA and hydrated lime—a similar reaction had occurred to give insoluble calcium phosphates and that this was the reason for the very weak liquid state ^{31}P NMR resonances observed (Schuster *et. al.*, 2011).

In contrast, during this study it was found that ^{31}P NMR resonances were observed in the liquid state NMR for the extracted MnDOT binders. Spectra for Cells 33, 34, and 79 all showed a similar broad resonance centered at about 3-4 ppm (Figure 2). The spectra for Cells 33, 34, and 79 are very similar to each other and are close to other reported liquid state ^{31}P NMR of H_3PO_4 in asphalt (Miknis and Thomas, 2008). Spectra from Cells 34 and 79 had similar signal-to-noise ratios while the spectra of binder extracted from Cell 33 has significantly higher signal-to-noise suggesting there are considerably more soluble phosphorous species in asphalt from Cell 33. The ^{31}P NMR spectrum from Cell 33 also appears to have a secondary feature extending as a shoulder towards lower ppm till about -10 ppm. This may be present in the other samples and is only visible for Cell 33 due to its relatively higher concentration of phosphorus in the sample; Cell 33 was constructed with 2.5 times more PPA than Cells 34 and 79.

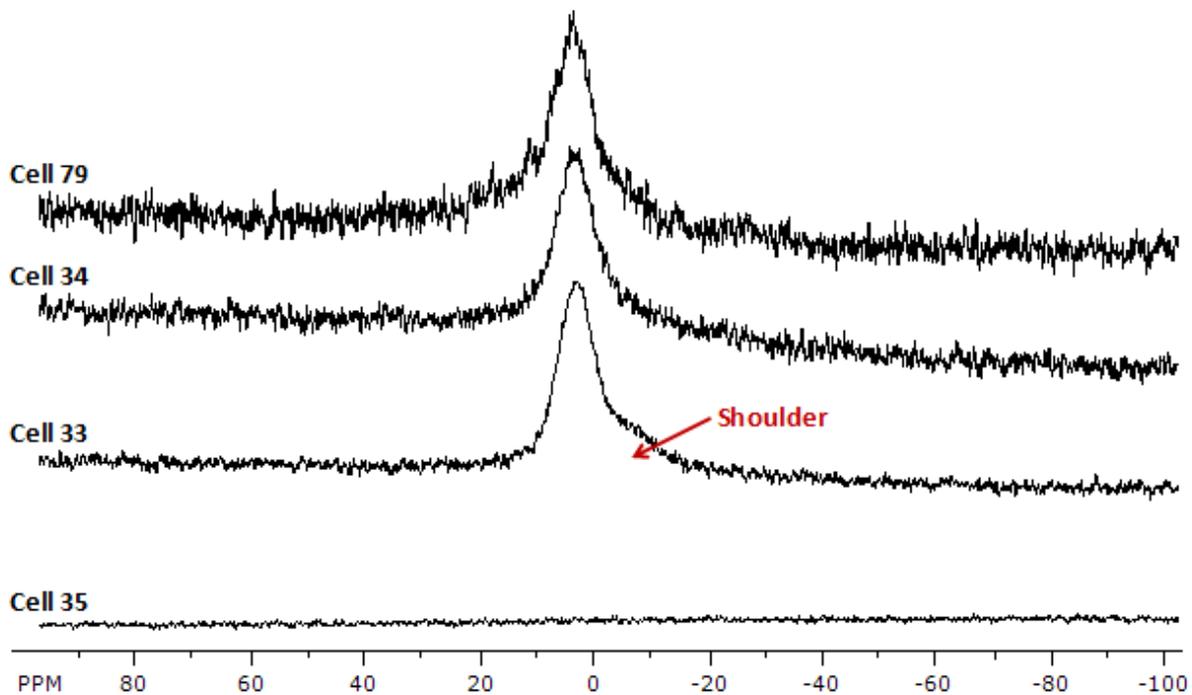


Figure 2. Liquid state ^{31}P NMR spectra of Cells 33, 34, and 79 in CDCl_3 .

Since Cells 34 and 79 were constructed with an excess of hydrated lime (1.0% lime and 0.3% PPA) and no other PPA resonances were observed, it is not expected that the main ^{31}P NMR resonance for Cells 34 and 79 be from H_3PO_4 —due to the hydrolysis of PPA. The other possibility is that the main phosphorus resonance could be due to Innovalt-W. Innovalt-W is a phosphate ester added to improve adhesion of asphalt to aggregate (Shuster *et. al.*, 2011). From the study by Schuster *et. al.* it was found that when Innovalt-W was blended with a large excess of 5% hydrated lime most of Innovalt-W became bound up with the hydrated lime. This resulted in very little signal being observed in the liquid state ^{31}P NMR but a significant signal in the solids state ^{31}P NMR. It is therefore likely that the main phosphorous resonance observed by liquid state ^{31}P NMR for Cells 34 and 79 are due to Innovalt-W since H_3PO_4 is more reactive with hydrated lime than Innovalt-W. The ^{31}P NMR spectra from Cell 33 is significantly different from Cells 34 and 70 which may be due to the fact that it was constructed with just enough PPA to consume most of the hydrated lime which would leave most of the phosphate ester Innovalt-W to be detected and possibly some PPA which was not neutralized by the hydrated lime.

To confirm if the phosphorous resonance observed in Cells 33, 34, and 79 were due to Innovalt-W more control samples should be analyzed. Such samples could be an asphalt containing no Innovalt-W but PPA, and a sample containing Innovalt-W but no PPA with and

without hydrated lime. In the absence of such samples a ^{31}P NMR spectra of 0.5% Innovalt-W mixed with the non-phosphorus containing asphalt of Cell 35 would be beneficial. In any case, the ^{31}P NMR spectra of Cell 33 was very similar to Cells 34 and 79 except that it clearly contained more phosphorus and a shoulder at lower ppm. It is possible that the shoulder observed in Cell 33 could be due to PPA since this asphalt was constructed with almost no excess of hydrated lime (1.0% hydrated lime and 0.75% PPA) or it could be another component of Innovalt-W. With this set of samples it is not possible to rule out the possibility that the observed resonances are due to other phosphate esters from the reaction of alcohols in the asphalt with PPA or PPA derivatives.

Since it has been observed that PPA undergoes hydrolysis to H_3PO_4 when mixed with asphalt, and since H_3PO_4 undergoes hydrogen bonding to asphaltic components, a comparison was made between the ^{31}P NMR spectra of Cell 33, H_3PO_4 (85%), crystalline H_3PO_4 , and a mixture of crystalline H_3PO_4 in asphalt from Cell 35. It can be seen from the spectra in Figure 3 that H_3PO_4 (85%) is hydrogen bonded to water and gives a sharp singlet, crystalline H_3PO_4 has hydrogen bonds to adjacent molecules of H_3PO_4 and that is why its resonance is broadened compared to H_3PO_4 (85%), and adding crystalline H_3PO_4 to asphalt from Cell 35 gives a slightly more broadened resonance shifted to slightly higher ppm.

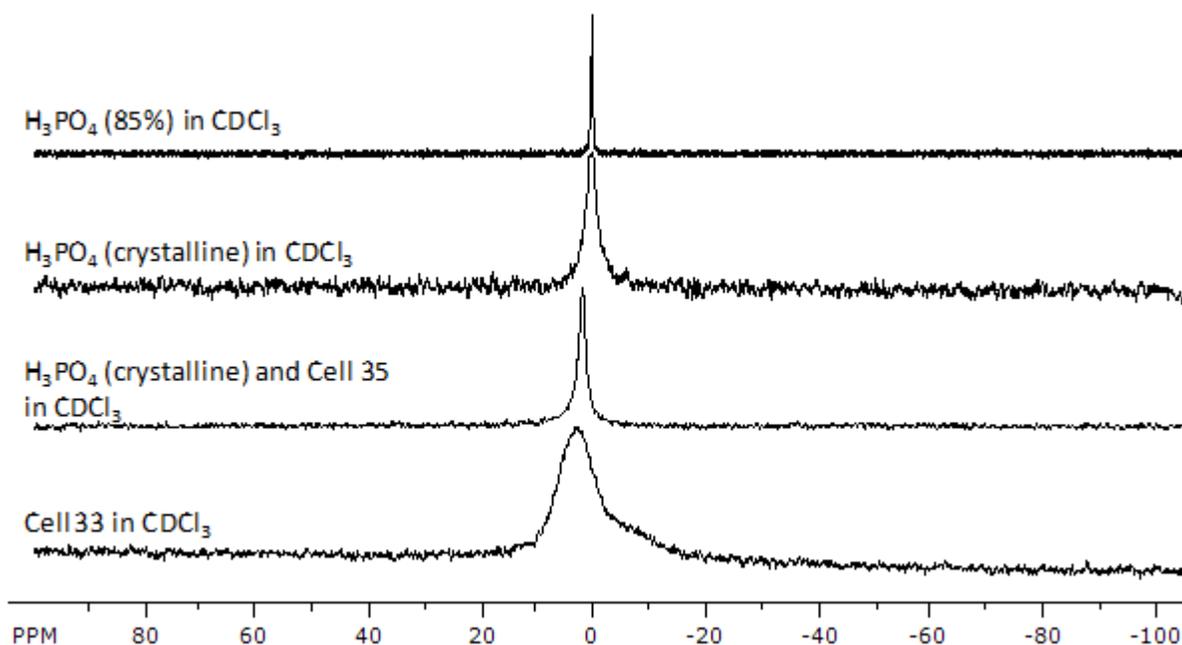


Figure 3. Liquid state ^{31}P NMR comparing Cell 33 to H_3PO_4 (85%), crystalline H_3PO_4 , and crystalline H_3PO_4 with asphalt from Cell 35 (30 mg of H_3PO_4 to 250 mg of Cell 35 asphalt in 0.75 mL of CDCl_3).

A liquid state ^{31}P NMR of 115% PPA was obtained in CDCl_3 and is displayed in Figure 5. It was initially found that 115% PPA was not readily soluble in ambient temperature CDCl_3 so the sample was heated to $80\text{ }^\circ\text{C}$ for 15 minutes to dissolve most of the material. The key features of any ^{31}P NMR spectra of PPA is the amount free H_3PO_4 and the ratio of the internally repeating linking phosphorous groups to the terminal phosphorus groups (Figure 4). In this case, very little H_3PO_4 is present indicating very little hydrolysis has taken place and the integration of the internal phosphorus units at -13.4 ppm to the capping phosphorous units at -30.0 ppm is 1:1 which shows that under these conditions the average structure of the soluble species has two central phosphorus units.

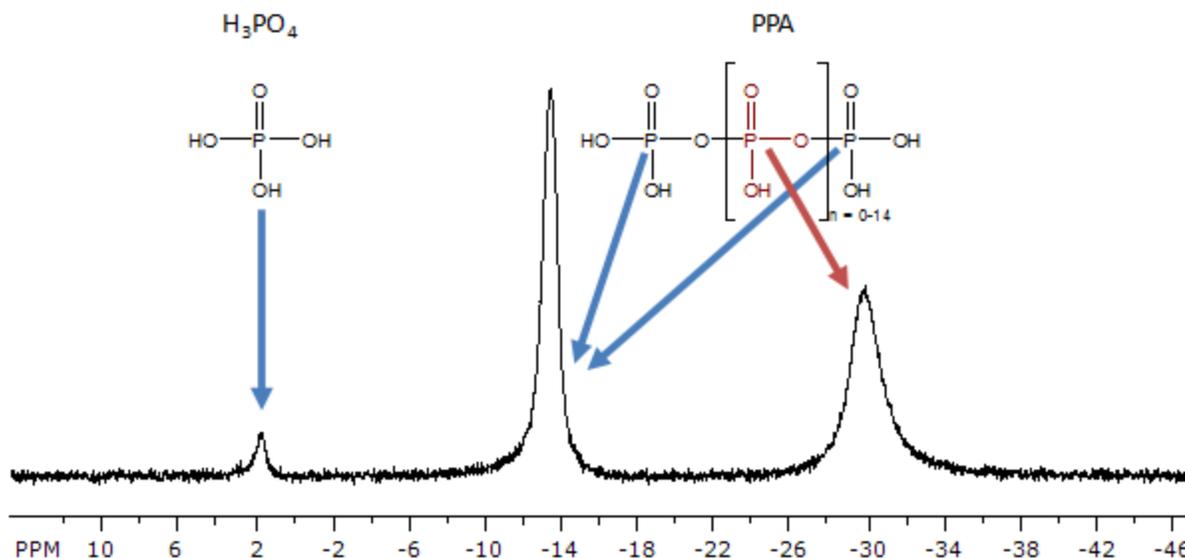


Figure 4. Liquid state ^{31}P NMR of 115% PPA in CDCl_3 , dissolved by heating to $80\text{ }^\circ\text{C}$ in a sealed NMR tube. Integration of the central phosphorus units to the end units is 1:1 suggesting that the average structure of the soluble species under these conditions has an $n = 2$.

To better determine if the main ^{31}P NMR signals observed in Cells 33, 34, and 79 are due to presumed Innovalt-W or possibly from H_3PO_4 or PPA a series of samples were prepared using the non-phosphorus containing asphalt from Cell 35 combined with 0.3% of one of the reference phosphorus compounds. The CDCl_3 solutions were prepared to have about the same concentration of phosphorous species (0.3 % PPA) in Cells 34 and 79. Therefore, 0.3% of crystalline H_3PO_4 , H_3PO_4 (85%), or 115% PPA were combined with non-phosphorous containing asphalt from Cell 35 and dissolved in CDCl_3 which were then analyzed by ^{31}P NMR. The ^{31}P NMR spectra of the sample containing 0.3% crystalline H_3PO_4 showed a very broad resonance centered around 2 ppm (not shown), the spectra of H_3PO_4 (85%) showed a single peak centered around 2

ppm, and the spectra for the sample containing 0.3% of 115% PPA gave three peaks. These three peaks are tentatively assigned as follows: 1.8 ppm as H_3PO_4 , a major peak at -8.5 ppm as the end phosphorus groups of PPA, a minor peak at -21.3 as central bridging phosphorus units. A comparison of the ^{31}P NMR spectra for the 0.3% of H_3PO_4 (85%) and 115% PPA with asphalt from Cell 35 are shown in Figure 5. The figure also shows the spectra from the asphalt of Cell 33 for reference. It can be seen that the resonance from the 0.3% H_3PO_4 is very close to the main resonance of Cell 33 but they are not exactly the same. Interestingly, the shoulder from Cell 33 is similar to the end units of PPA. Another experiment which would be helpful to determine if the phosphorous signals in 33, 34, and 79 are due to PPA derived species or Innovalt-W would be to add a base, such as pyridine, to neutralize PPA and H_3PO_4 to give insoluble phosphorous acid solids which would then not be detected by liquid state ^{31}P NMR. A base, such as pyridine, should not react with Innovalt-W and so Innovalt-W should remain soluble. It could then be assumed that if the signal in Cell 33 remained unchanged upon addition of excess base then the phosphorus resonances are likely due to Innovalt-W and not H_3PO_4 . Similarly, if the shoulder in the spectra of Cell 33 remains unaltered this would be strong evidence that the species is not due to PPA derivatives or H_3PO_4 .

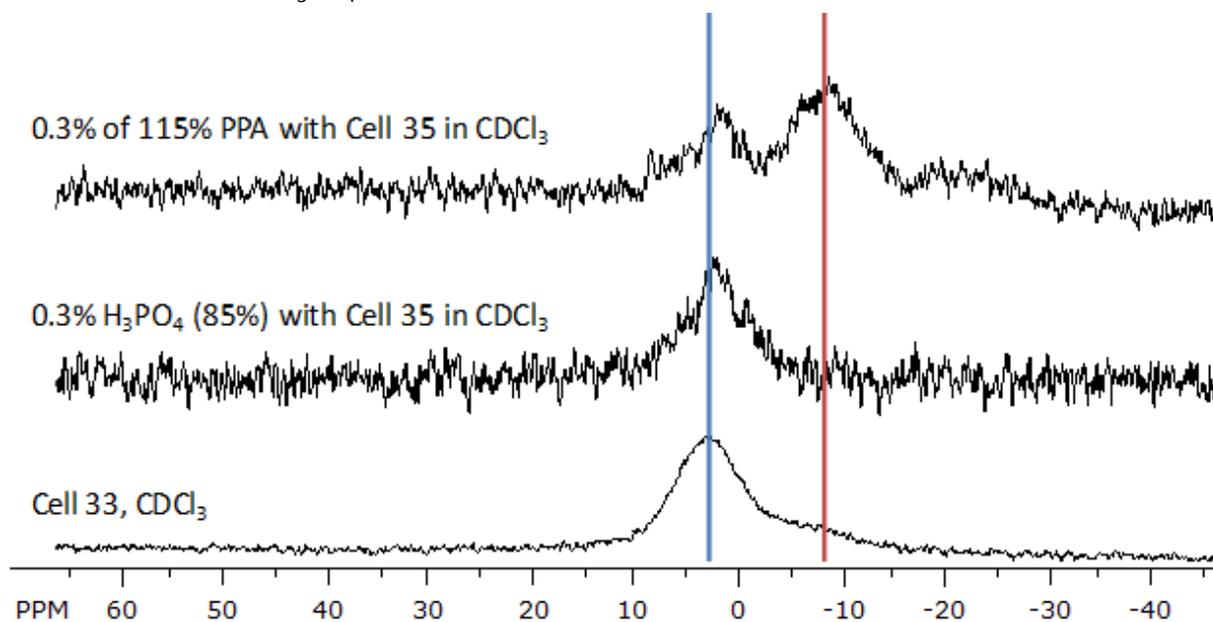


Figure 5. Liquid state ^{31}P NMR using CDCl_3 of Cell 33, asphalt from Cell 35 modified with 0.3% by weight of 115% PPA, and asphalt from Cell 35 modified with 0.3% by weight of crystalline H_3PO_4 .

Solid state ^{31}P NMR of asphalts was challenging for the staff at Lawrence Livermore National Laboratories (LLNL). Problems were encountered with filling the rotors with asphalt and spinning the samples. Solids state ^{31}P NMR spectra were obtained for H_3PO_4 (85%), 115% PPA,

and asphalt from Cells 33 and 34. ^{31}P NMR spectra for H_3PO_4 and 115% PPA were similar to spectra obtained from solution ^{31}P NMR (Figure 6).

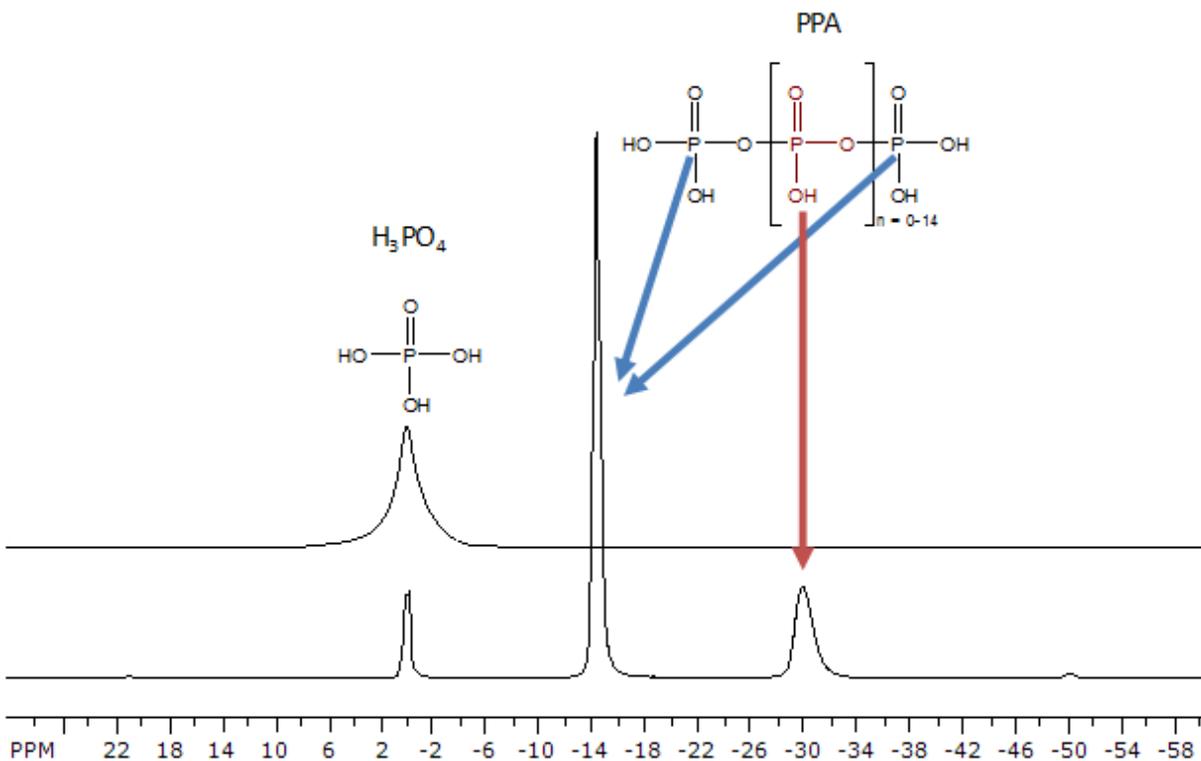


Figure 6. Solids state ^{31}P NMR of H_3PO_4 (85%) and 115% PPA.

The solid state ^{31}P NMR spectra for asphalt from Cell 33 was similar to reported spectra for fines gathered from asphalt from Cell 33 in a previous study (Schuster *et. al.*, 2011). The spectra shows spinning sidebands while spinning at 5 kHz showing that the phosphorous appears to exist in a solid environment similar to calcium phosphates already reported (Schuster *et. al.*, 2011). Figure 7 shows the solid state ^{31}P NMR spectra of asphalt from Cells 33 and 34 spinning at 5 kHz. The spectra from Cell 34 appears to be quite different from Cell 33 but this may be due to technical difficulties experienced at LLNL while filling rotors and spinning samples.

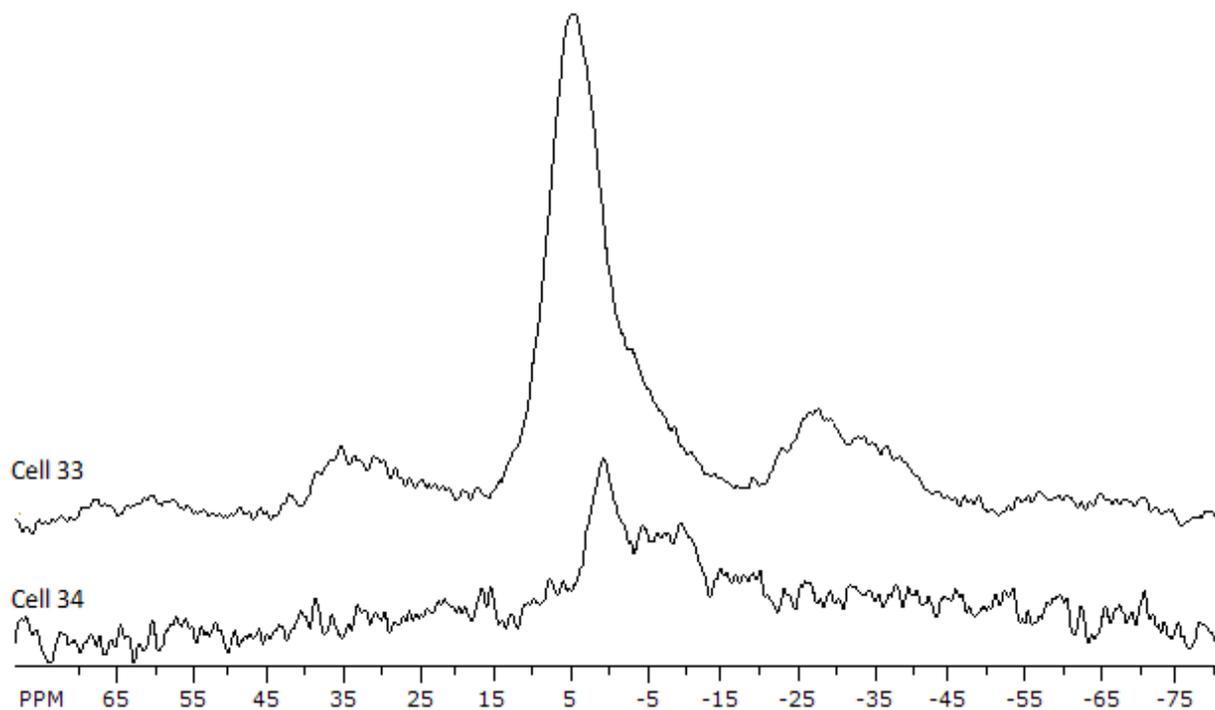


Figure 7. Solids state ^{31}P NMR of Cells 33 and 34.

Suggestions for Further Study.

To more accurately determine the fate of PPA in asphalt over time, it would be beneficial to have control samples which contained PPA and no Innovalt-W and samples which contained Innovalt-W and no PPA. It may also be advantageous to use pyridine or N-Methyl-2-pyrrolidone to extract the strongly adsorbed asphalt binder from the aggregate after the initial toluene/ethanol extraction to remove strongly adsorbed species. In this way a comparison can be made to see if some phosphorus species strongly adsorb to the aggregate interface that are not detected in the extracted binders. This may also help to explain the interaction between Innovalt-W and aggregate, and Innovalt-W and hydrated lime. It would be beneficial to have a liquid ^{31}P NMR spectra of Innovalt-W to compare to the spectra from Cells 33, 34, and 79. Mixing Innovalt-W at 0.5% with Cell 35 and comparing that spectra with the ones obtained for Cells 33, 34, and 79 would also help clarify if the observed liquid state ^{31}P NMR spectra are due to PPA or H_3PO_4 . A simple experiment could be carried out using a base to precipitate phosphorous acid species such as H_3PO_4 , PPA, or PPA derivatives from Cell 33. Control experiments would also need to be conducted to ensure that the base does not interact with Innovalt-W. This would help to determine if the phosphorus resonances in Cells 33, 34, and 79 are acidic phosphorous species or non-acidic phosphate esters assuming that these phosphate esters and Innovalt-W do not have acidic P-OH groups.

Conclusion.

Asphalts from Cells 33, 34, 35, and 79 that aged under real world conditions were analyzed by liquid and solid state ^{31}P NMR. An important finding of this study was that soluble phosphorous species in the asphalt can be analyzed by liquid state ^{31}P NMR. For asphalt from Cell 35 there were no detectible resonances in the liquid state ^{31}P NMR spectra. This is consistent with the fact that this asphalt was constructed with no PPA and no Innovalt-W—which is a phosphate ester. For Cells 34 and 79 the liquid state ^{31}P NMR spectra were nearly identical showing a small amount of soluble phosphorous species which are tentatively attributed to Innovalt-W. This assignment is based on the fact that these asphalts were constructed with an excess of hydrated lime which is known to readily react with PPA to produce insoluble calcium phosphates. Liquid state ^{31}P NMR for Cells 33, 34, and 79 shared the same major resonance centered around 3-4 ppm, however the spectrum for the asphalt from Cell 33 was considerably different from Cells 34 and 79. The spectra from Cell 33 had significantly more phosphorus signal and a shoulder extending to lower ppm. The spectra from Cell 33 indicated that there was significantly more soluble phosphorous species present than for Cells 34 and 79. This is likely since Cell 33 was constructed with significantly more PPA so that the amounts were nearly stoichiometric with respect to hydrated lime, whereas Cells 34 and 79 were constructed with the same excess of hydrated lime. It is known that Innovalt-W binds with hydrated lime to give poorly soluble Innovalt-W/hydrated lime species which are not calcium phosphates. Since all the Cells were constructed with the same amount of Innovalt-W, and the fact that Cell 33 contained significantly more PPA, it is reasonable to assume that if most of the hydrated lime was preferentially neutralized by PPA then more unbound Innovalt-W would be detected by liquid state ^{31}P NMR.

The assumption of this work was that as asphalt oxidizes it produces more carboxylic acids and alcohols which may react with PPA and PPA derivatives overtime in the asphalt to make phosphate esters. This set of samples already contained the phosphate ester Innovalt-W, therefore it is not possible to discern if PPA and its derivatives had converted into phosphate esters since a considerable amount of phosphate ester was already added. With a proper set of control experiments it would be possible to determine if the observed resonances in Cells 33, 34, and 79 are mainly due to Innovalt-W, PPA, PPA derivatives, other phosphate esters, or some combination. For comparison, experiments were conducted by preparing 0.3% mixtures of non-phosphorous containing asphalt from Cell 35 with crystalline H_3PO_4 , H_3PO_4 (85%), and 115% PPA. The main phosphorous resonance (H_3PO_4) in these spectra did not exactly match the chemical shift for the main peak for Cells 33, 34, or 79. This further supports the assumption that the liquid state resonances may be due to Innovalt-W and not due to PPA or PPA derivatives. Control samples of asphalts containing PPA and hydrated lime without Innovalt-W and samples containing Innovalt-W and hydrated lime without PPA, in addition to other experiments, would

help to confirm the composition of the soluble phosphorous species. Solid state ^{31}P NMR of Cell 33 was similar to spectra previously reported indicating the presence of calcium phosphate (Schuster *et. al.*, 2011).

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