

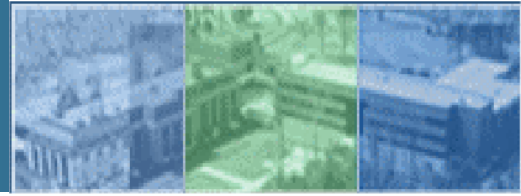
Update on THHRC Research into the Phosphoric Acid Modification of Asphalt

The Office of Research, Development, and Technology (RD&T)
Turner-Fairbank Highway Research Center (TFHRC)
McLean, VA

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NCAUPG January 2008

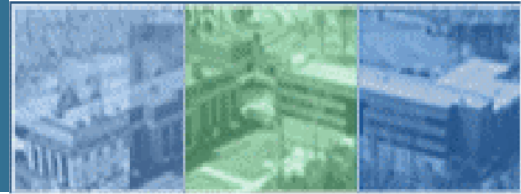




Some Old News + Latest Results

1. Effect of Acid Grade
2. Stiffening Effect is Asphalt Dependent
3. Simple Qualitative Test
4. Effect of Moisture
5. Effect on Antistrip Additives
6. Fatigue

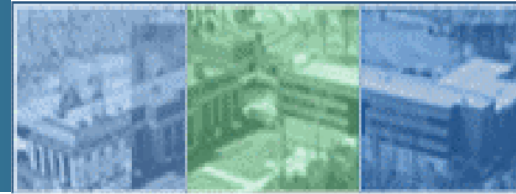




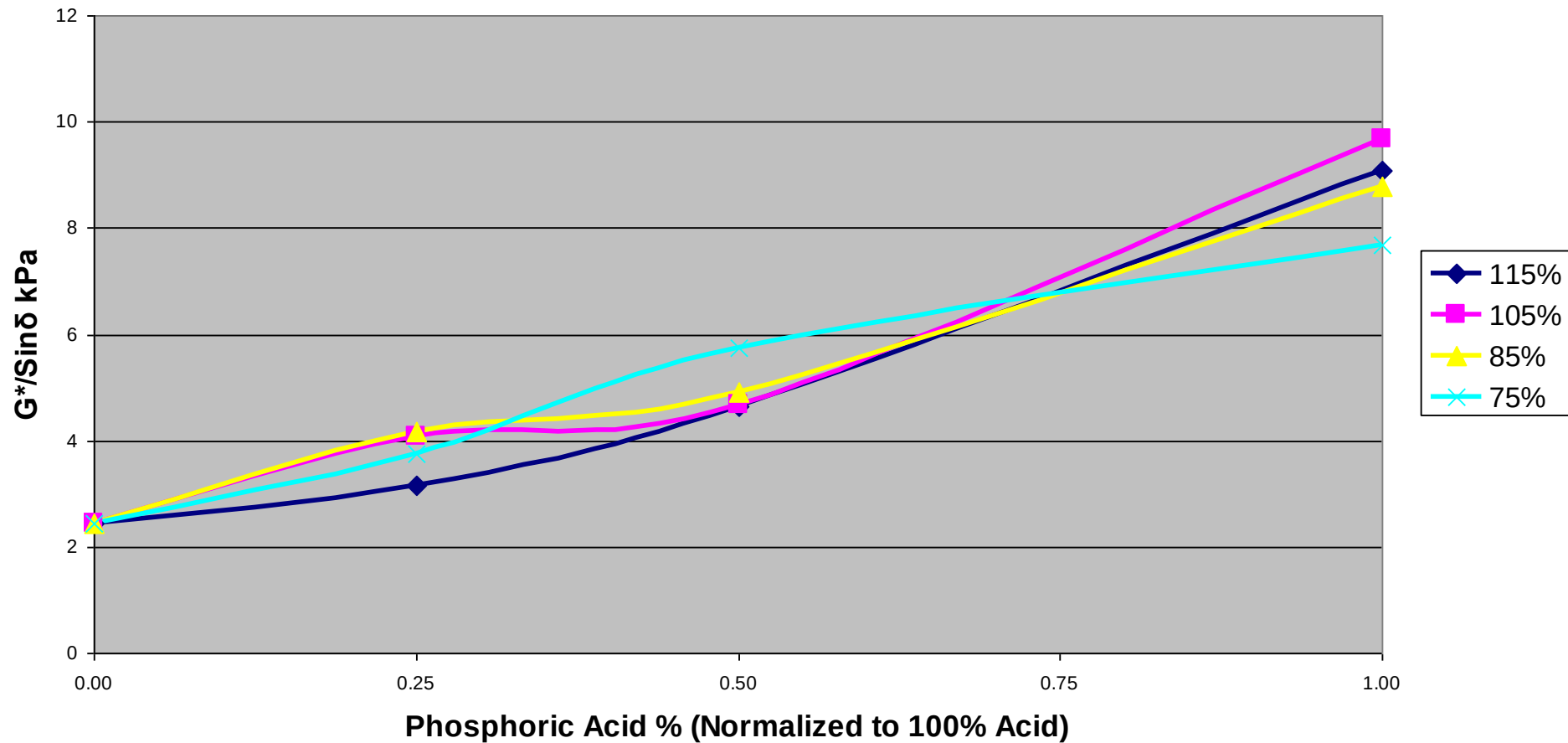
Effect of Acid Grade and Asphalt Source

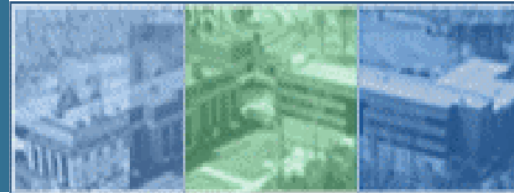
- All acid grades give similar stiffness increase
- Grades containing water may give foaming problems
- Stiffness change is asphalt dependent



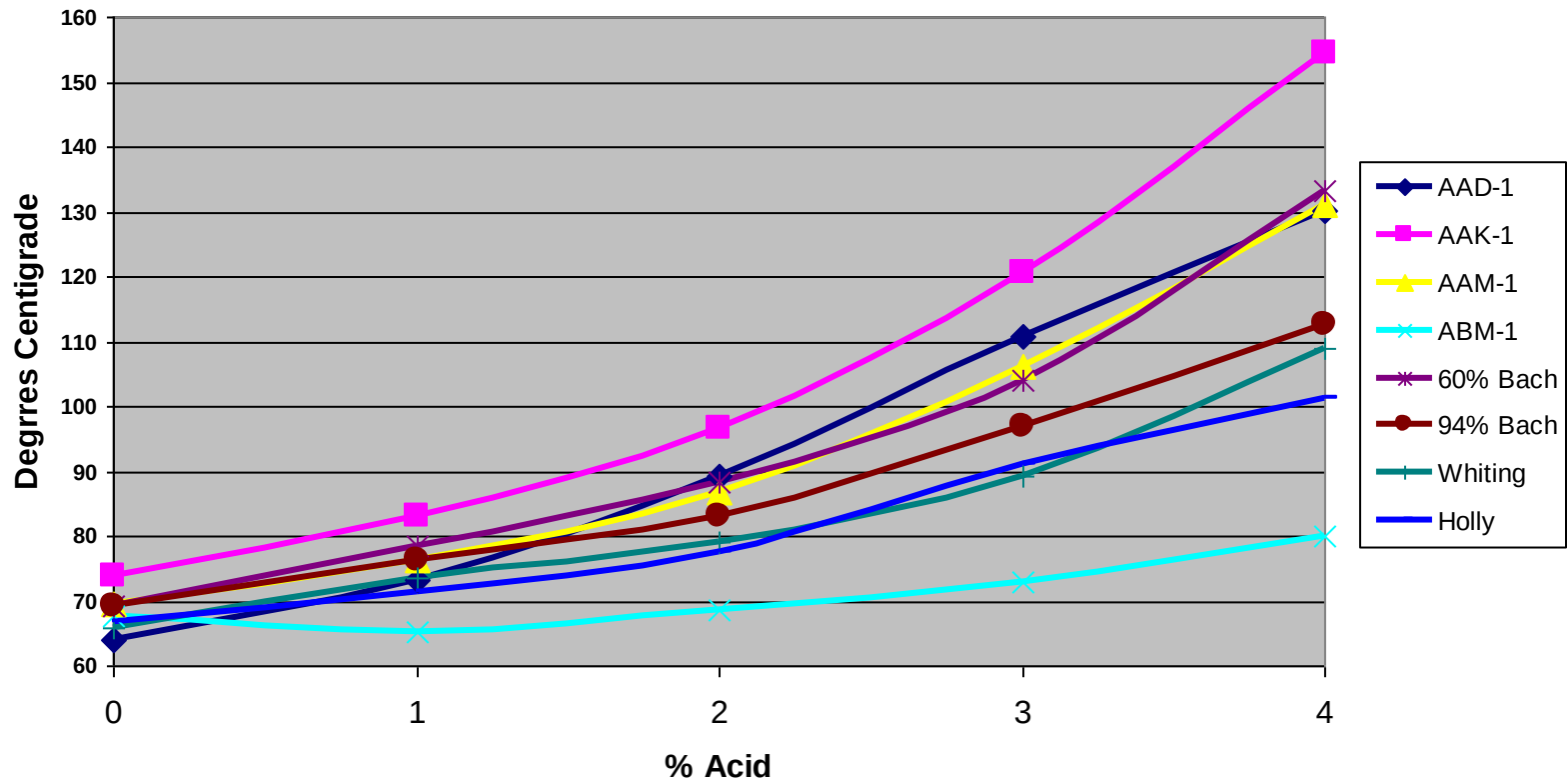


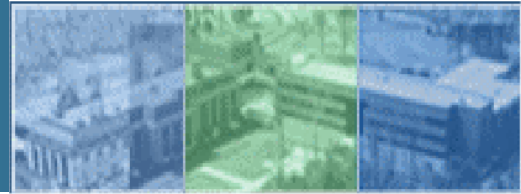
Stiffness of AAK-1 Modified with Phosphoric Acid 24 hrs 165°C





Effect of 115% PPA Acid Modification on Original PG Grade

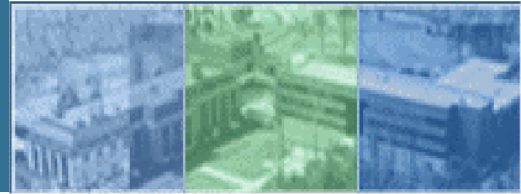




Susan P. Needham Test for Phosphate in HMA

- No special equipment or expertise needed
- Requires a few inexpensive chemicals
- Test is rapid and simple
- A blue color is developed after 5 minutes
- Test can detect 0.1% PPA in asphalt
- Details available on TFHRC Website

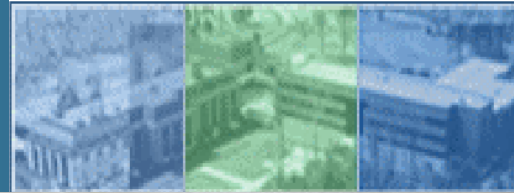




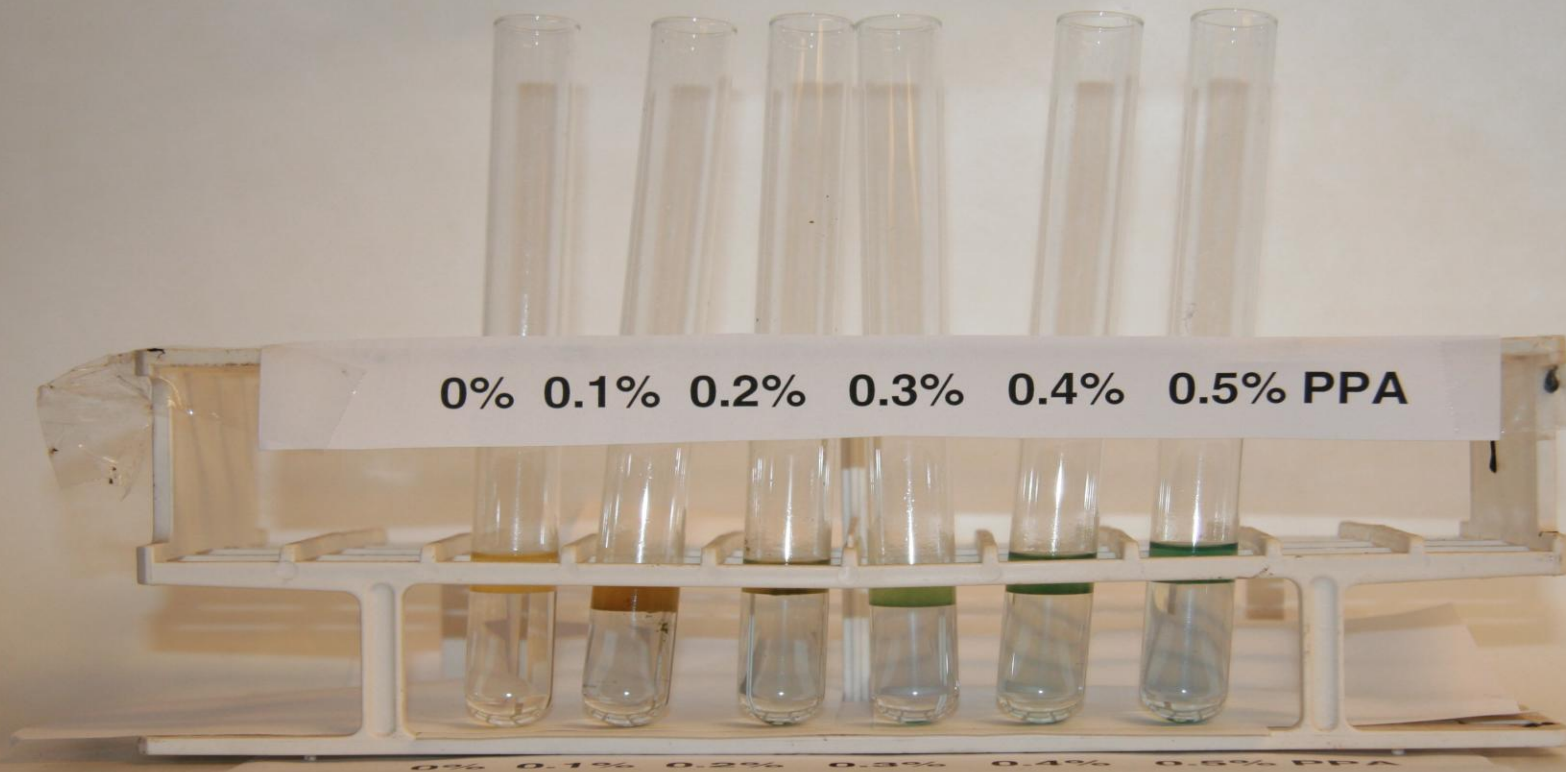
Susan P. Needham Test for Phosphate in HMA

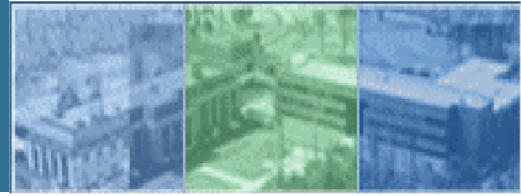
- Quantities are not critical
- Put 1 gram of hot asphalt into a 1oz can
- Add 1ml of n-butanol and swirl in the can
- Add 2mls water
- Add 1 ml of ascorbic acid/ammonium molybdate solution
- A blue color is developed in the water phase within a few minutes.





Susan P. Needham Test for Phosphate in HMA

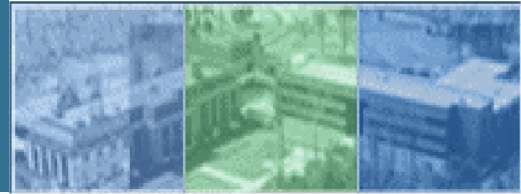




Moisture Sensitivity

- Does adding a hydrophilic material like phosphoric acid impart moisture sensitivity to the binder?



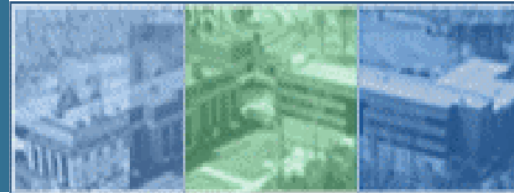


Moisture Sensitivity

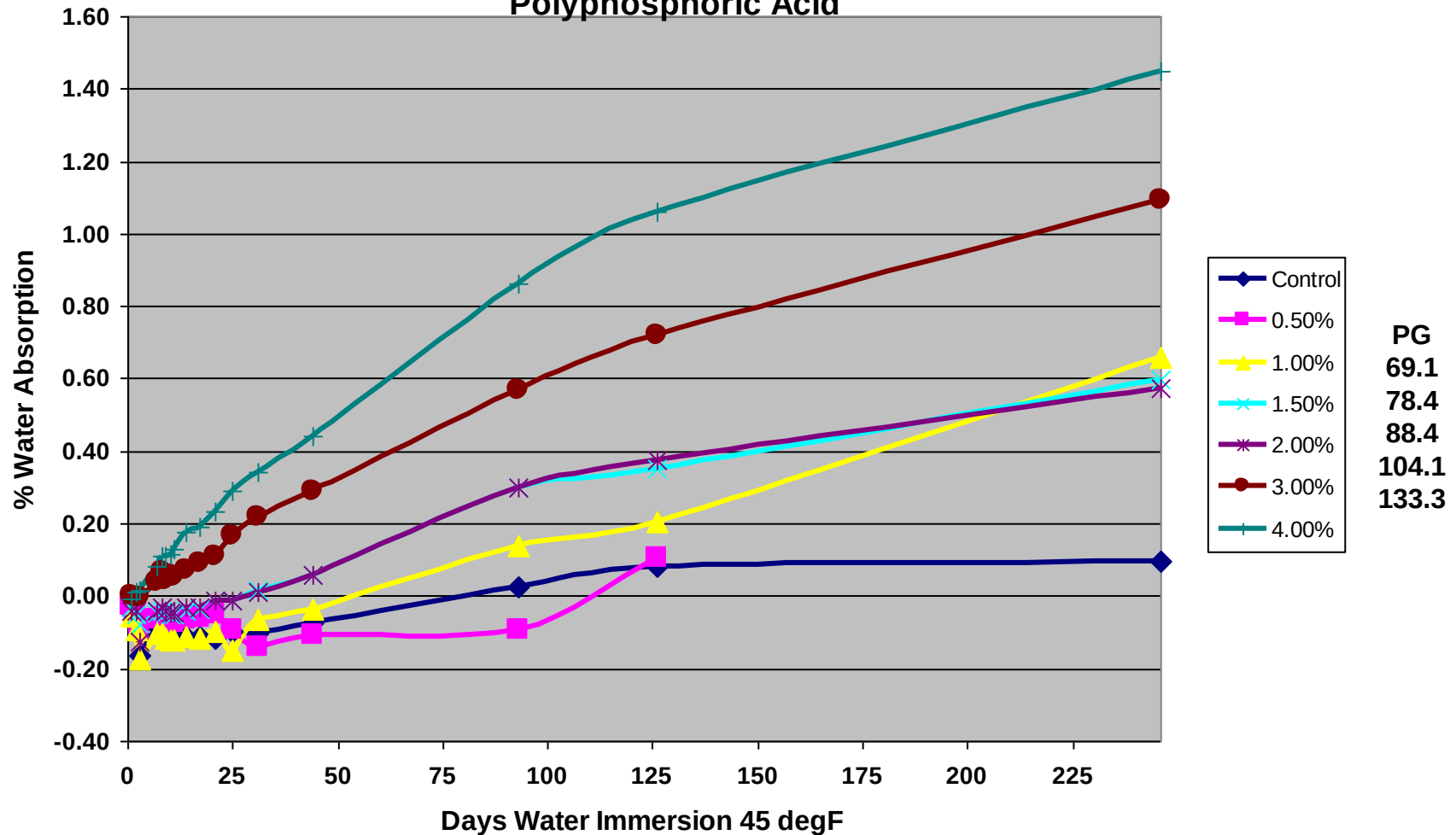
- BBR Beams and DT samples of neat binder and 50% mastics were soaked in a 45°F water bath
- Beams were dried with a paper towel and weighed
- For this Asphalt (Citgo) water absorption increases with increasing PPA particularly at levels greater than 1-1.5%



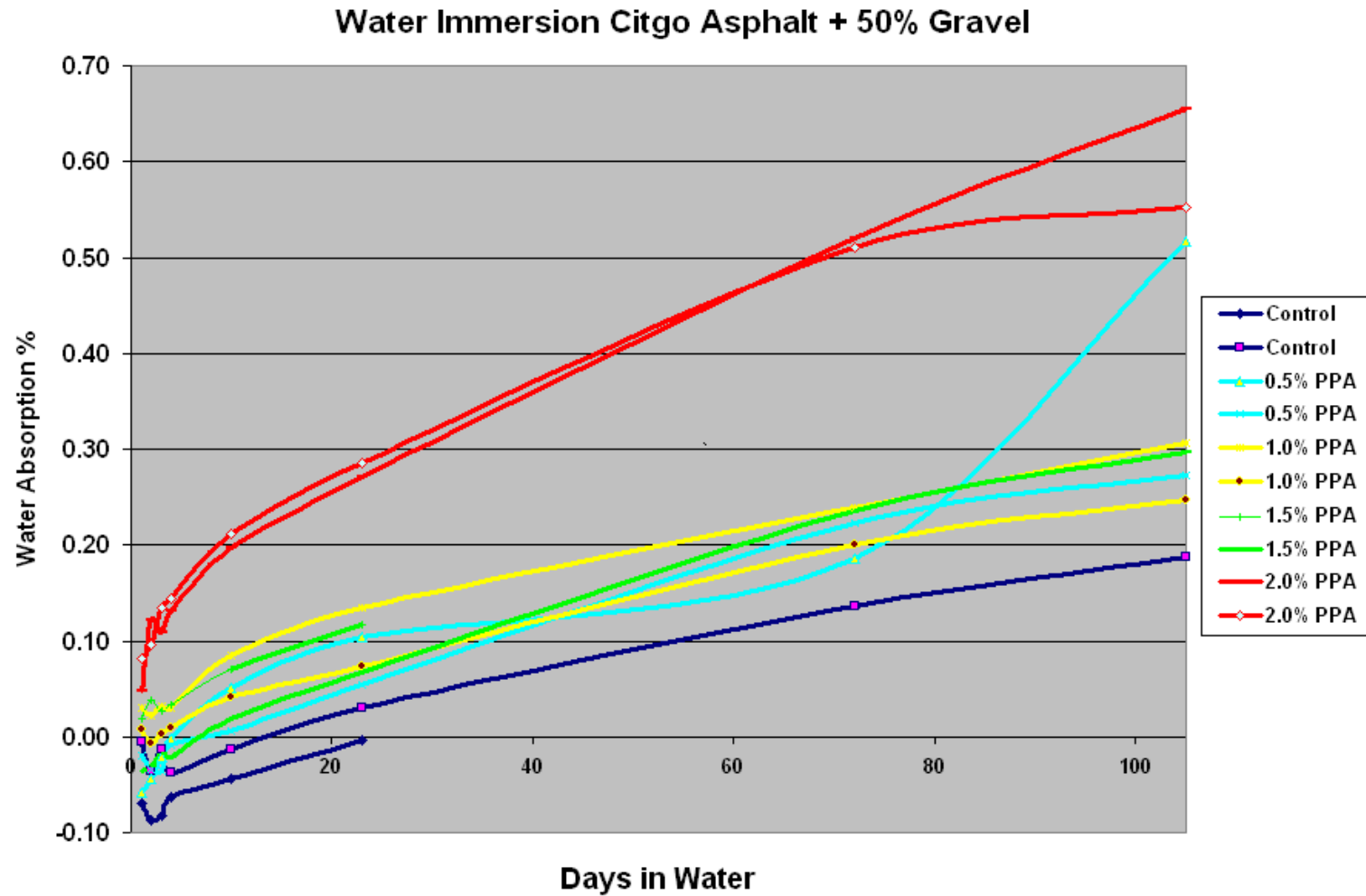
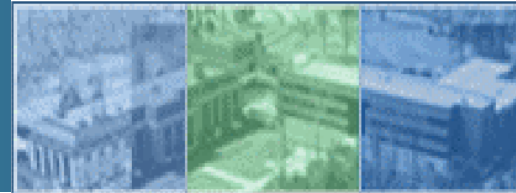
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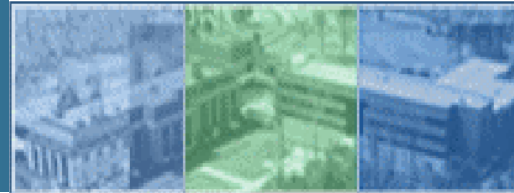
Water Absorption of Citgo Asphalt BBR Beams Modified with 115% Polyphosphoric Acid



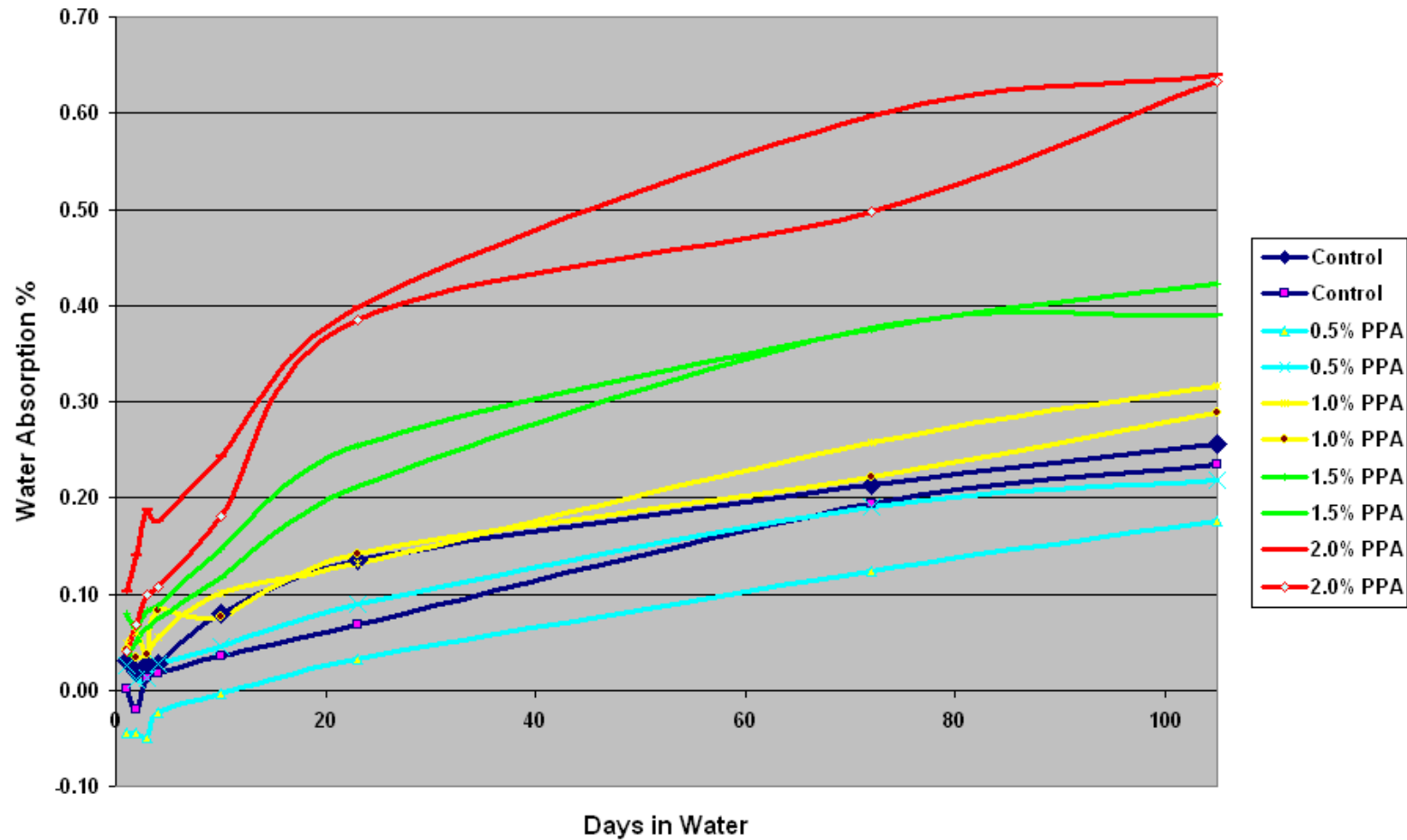
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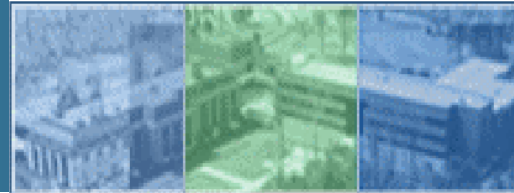


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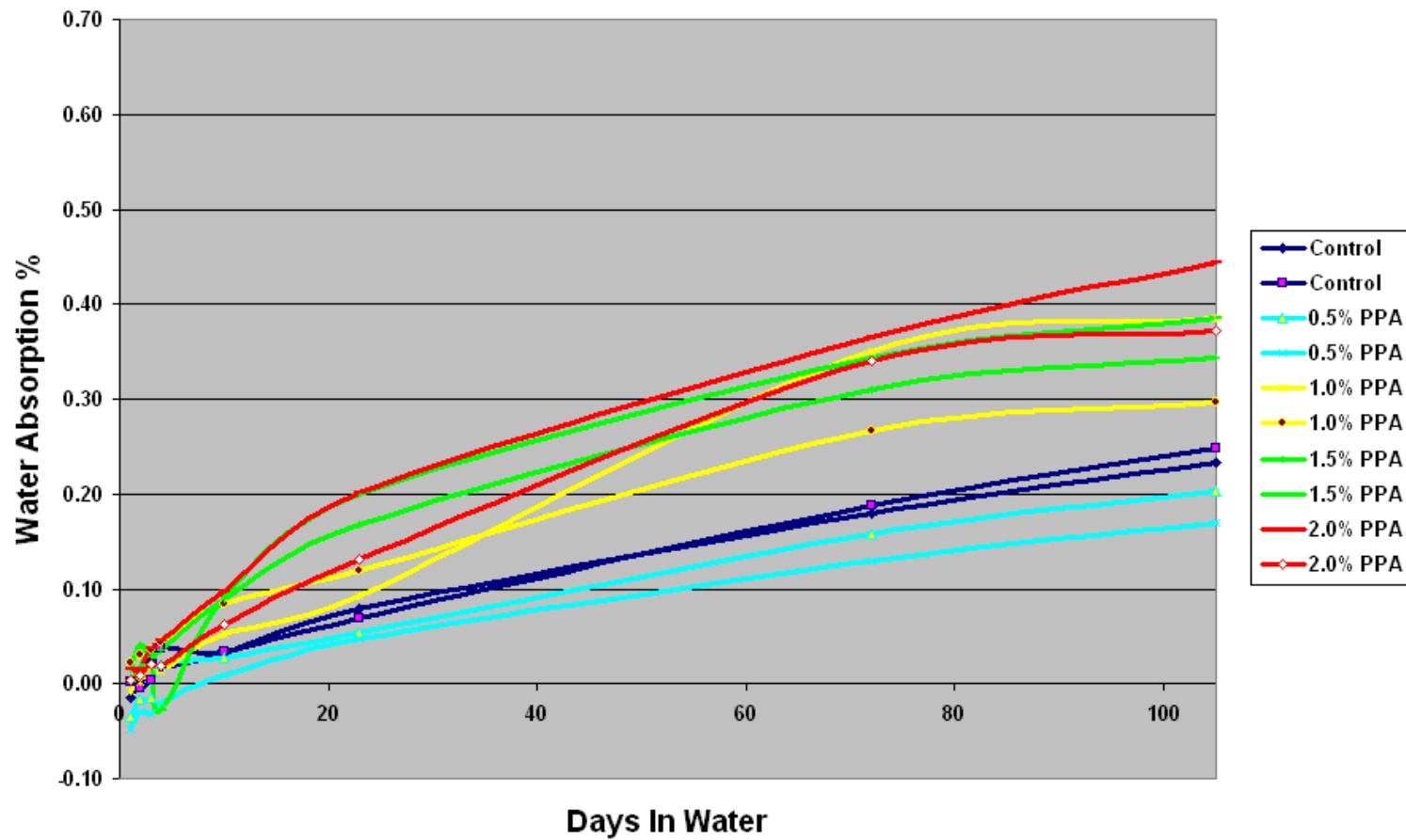


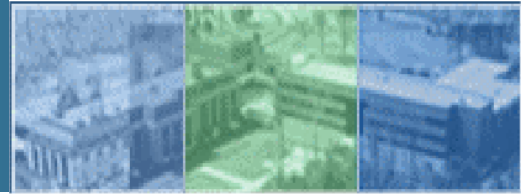
Water Immersion Citgo Asphalt + 50% Diabase





Water Immersion Citgo Asphalt + 50% Sand

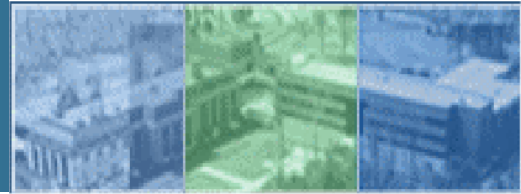




Hamburg Testing Rationale

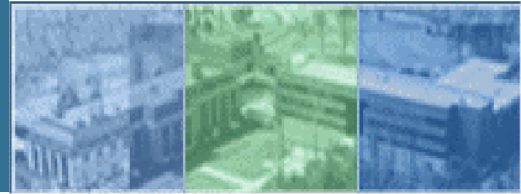
- There is no perfect test to measure stripping
- We chose Hamburg at 50°C
- The tests are not meant to be exhaustive
- Criterion is “Does PPA make it better or worse”
- Tests are done in duplicate
- Both results are shown on the charts





Hamburg 2000 Passes

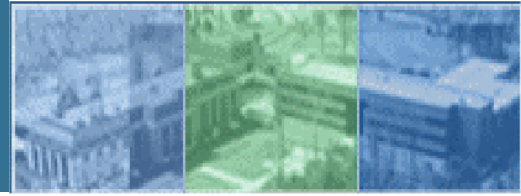




Effect on Antistrip Additives

- Expectation has generally been that lime and amines cannot be used with PPA modification since the alkalinity of the antistrips would be neutralized by the acidity of the PPA and vice versa
- From this acid/alkaline viewpoint a non amine antistrip, like a phosphate ester, we would not expect to be affected by PPA
- If only things were that simple.....

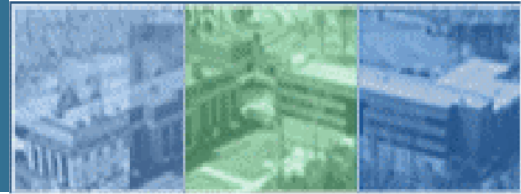




Materials Used

- Asphalt from Citgo
- Stripping Sandstone Aggregate from MD (Banned by MDDOT)
- Limestone Aggregate from MD
- Granite from GA
- Amine Antistrip from Arr-Mazz- LA-2, LOF65-00
- Non Amine from Innophos – Innovalt-W (a phosphate ester)
- Lime from Chemical Lime Company



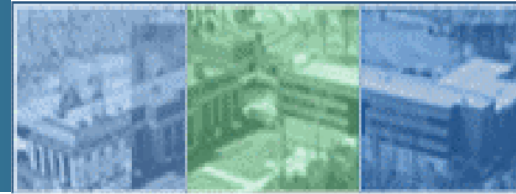


Effect of Phosphoric Acid Alone

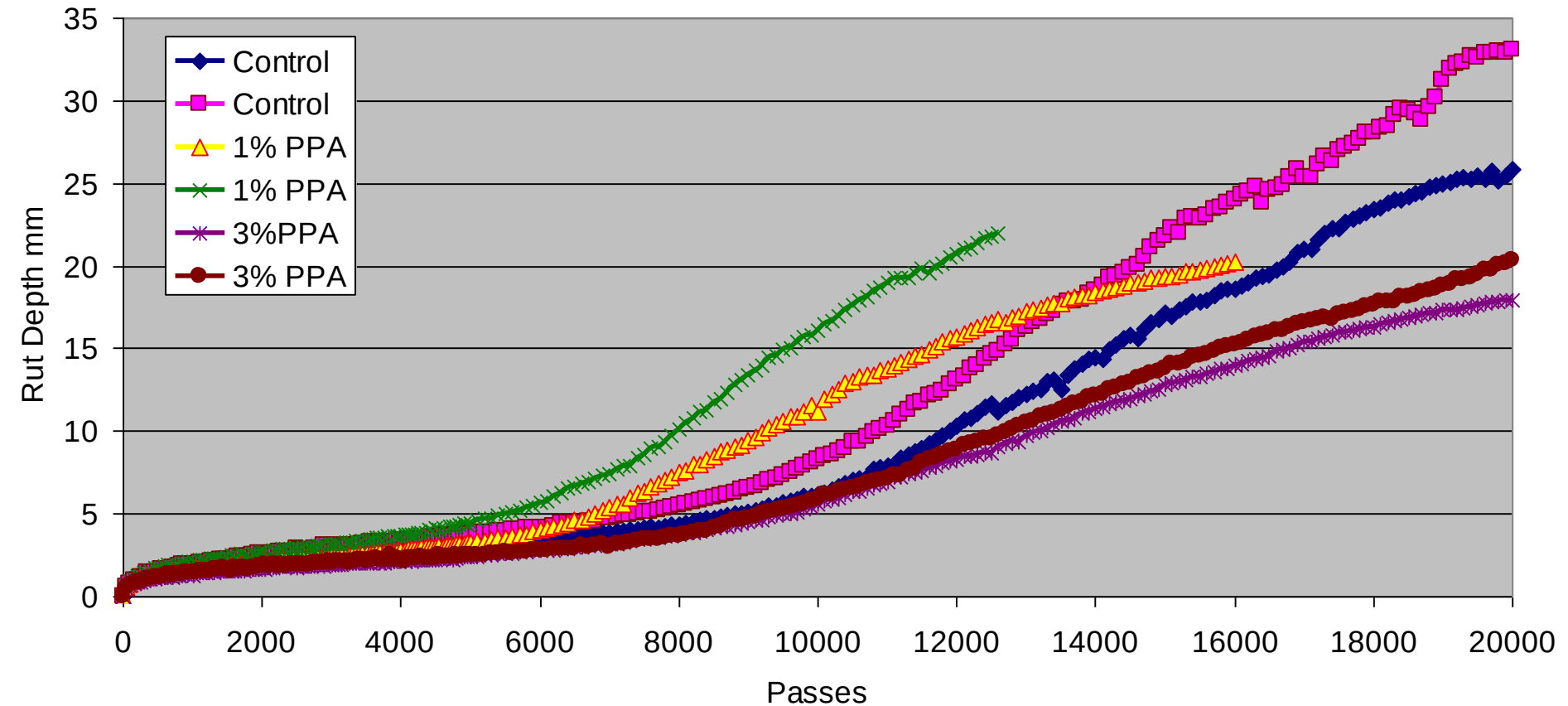
- Samples contain no antistrip
- Neat binder modified with phosphoric acid



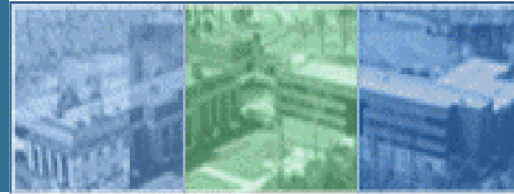
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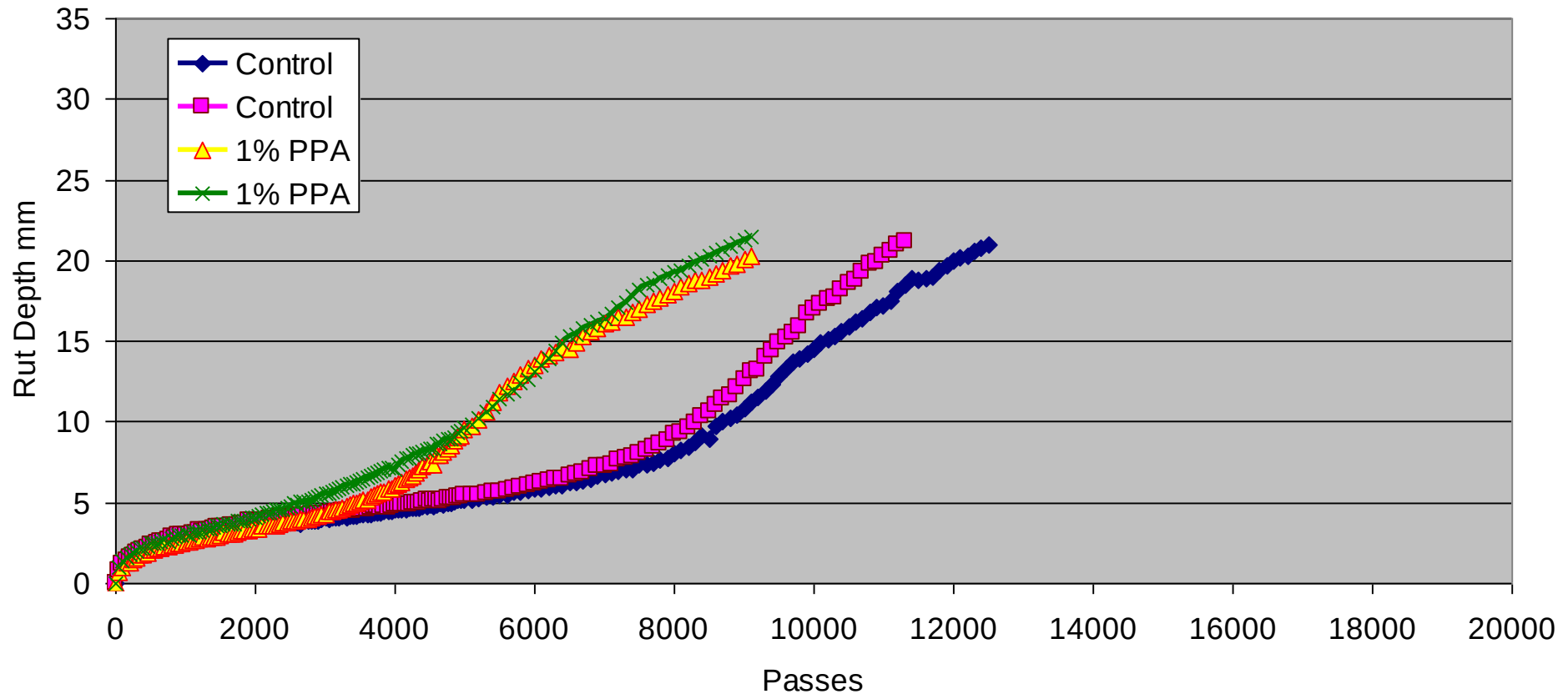
Hamburg 50degC Citgo Asphalt Sandstone Aggregate



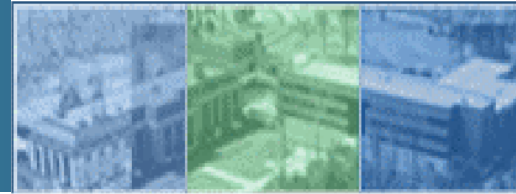
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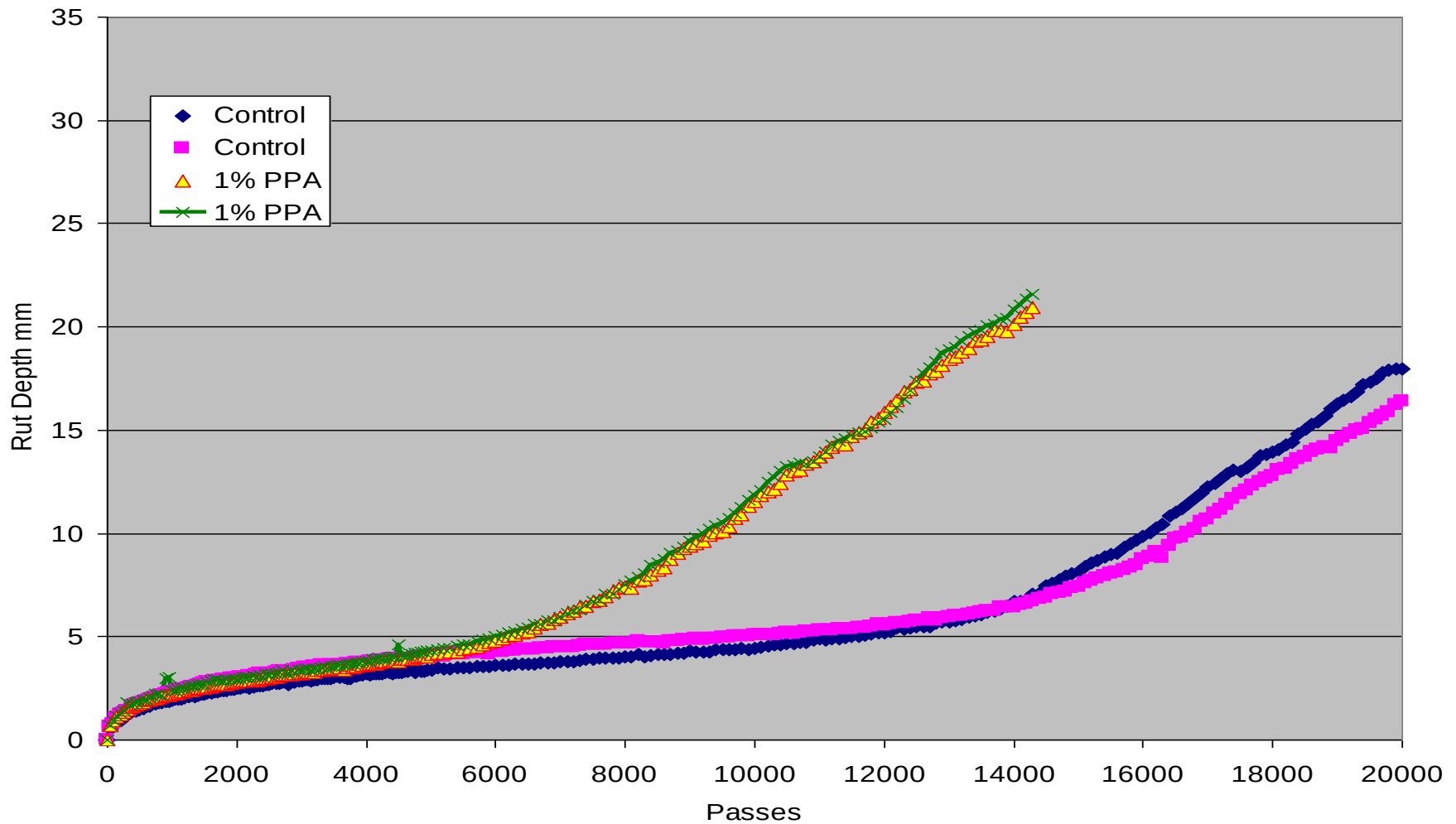
Hamburg 50degC Citgo Asphalt Limestone Aggregate

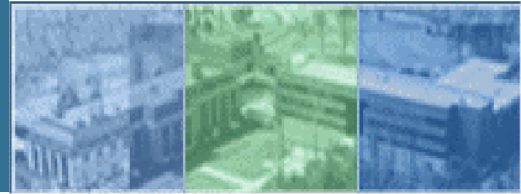


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Hamburg 50degC Citgo Asphalt GA Granite Aggregate

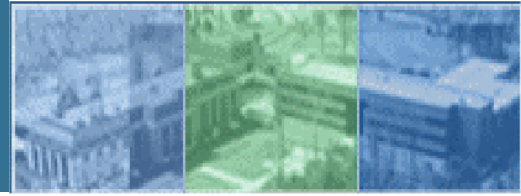




Phosphoric Acid Alone

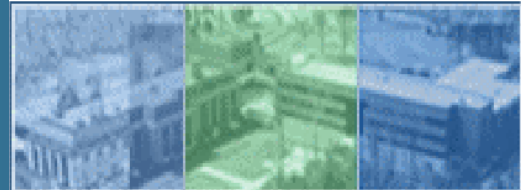
- With all three aggregates the addition of PPA to the binder made the stripping worse
- One exception was with 3% PPA and sandstone aggregate.
- The addition of 3% PPA makes this asphalt far too stiff to be used. We think it is a stiffening effect we are seeing rather than an increase in moisture resistance



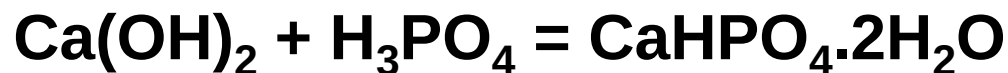


Is Lime Neutralized by the Phosphoric Acid?





First some chemistry



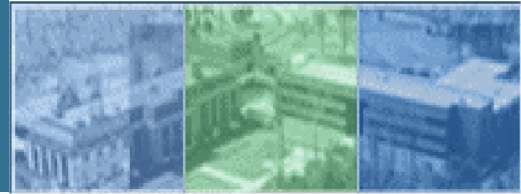
74 lbs

98 lbs

172 lbs

**If the mix contains 1% Lime and 1%
Phosphoric Acid There is a Large Excess of
Lime (25X)**



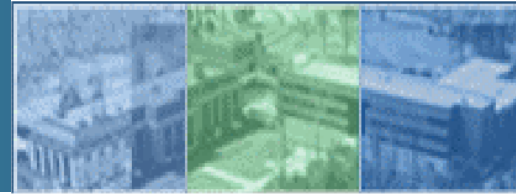


Lime Treated Aggregate

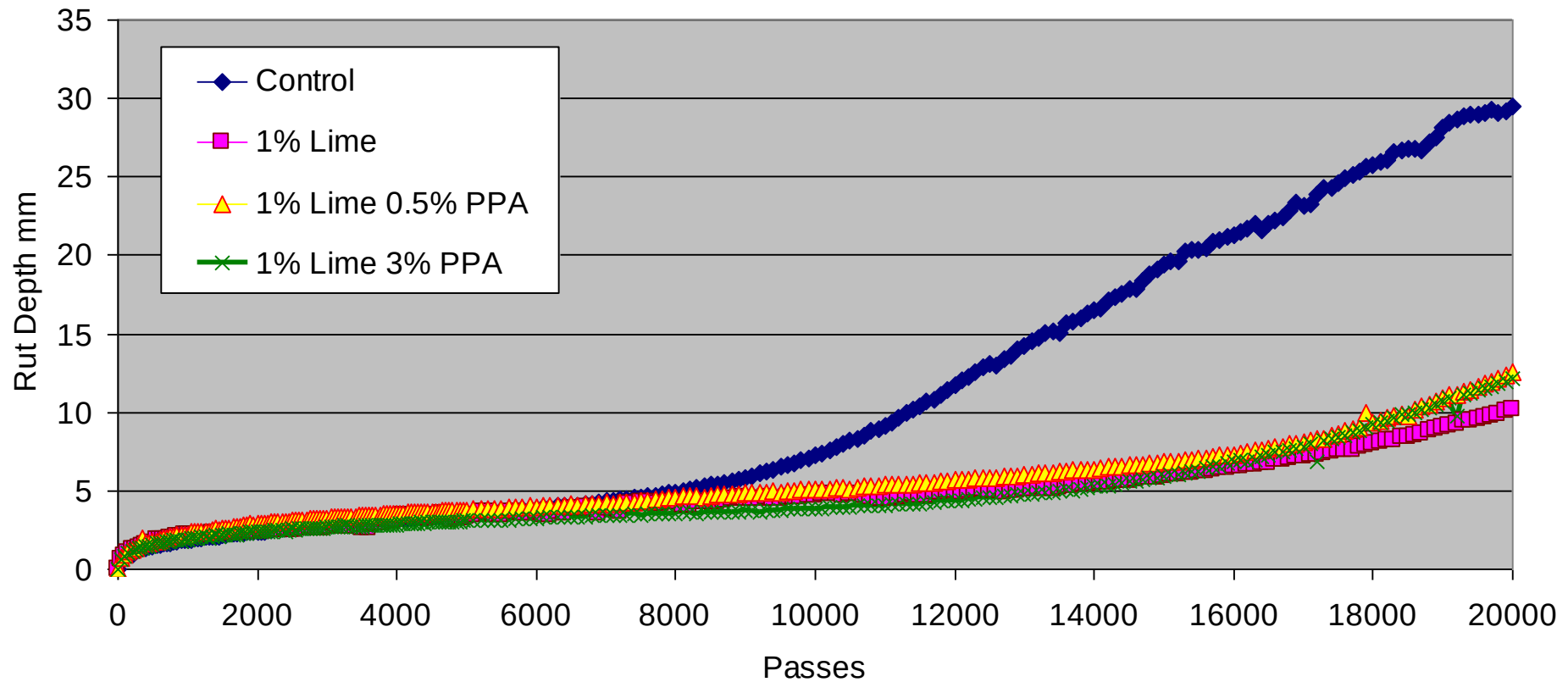
- **Aggregates were treated with 1% lime added as a wet slurry and dried.**
- **Chemistry shows the lime overwhelms the PPA by 25:1**



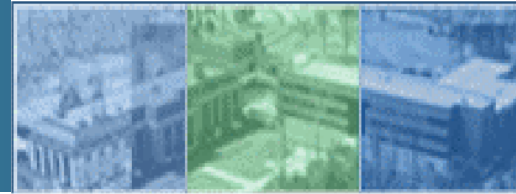
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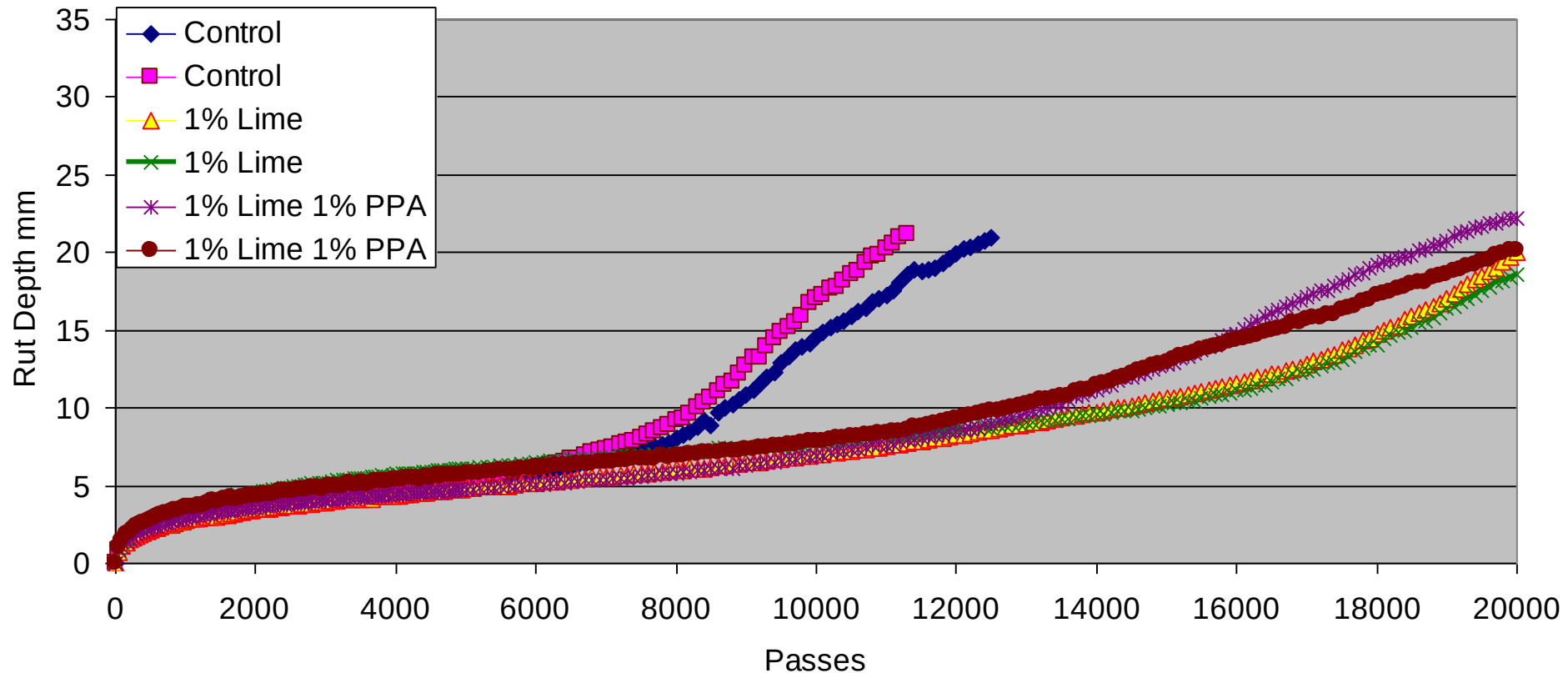
Hamburg 50degC Citgo Asphalt Lime Treated Sandstone Aggregate



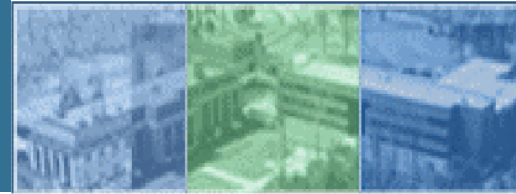
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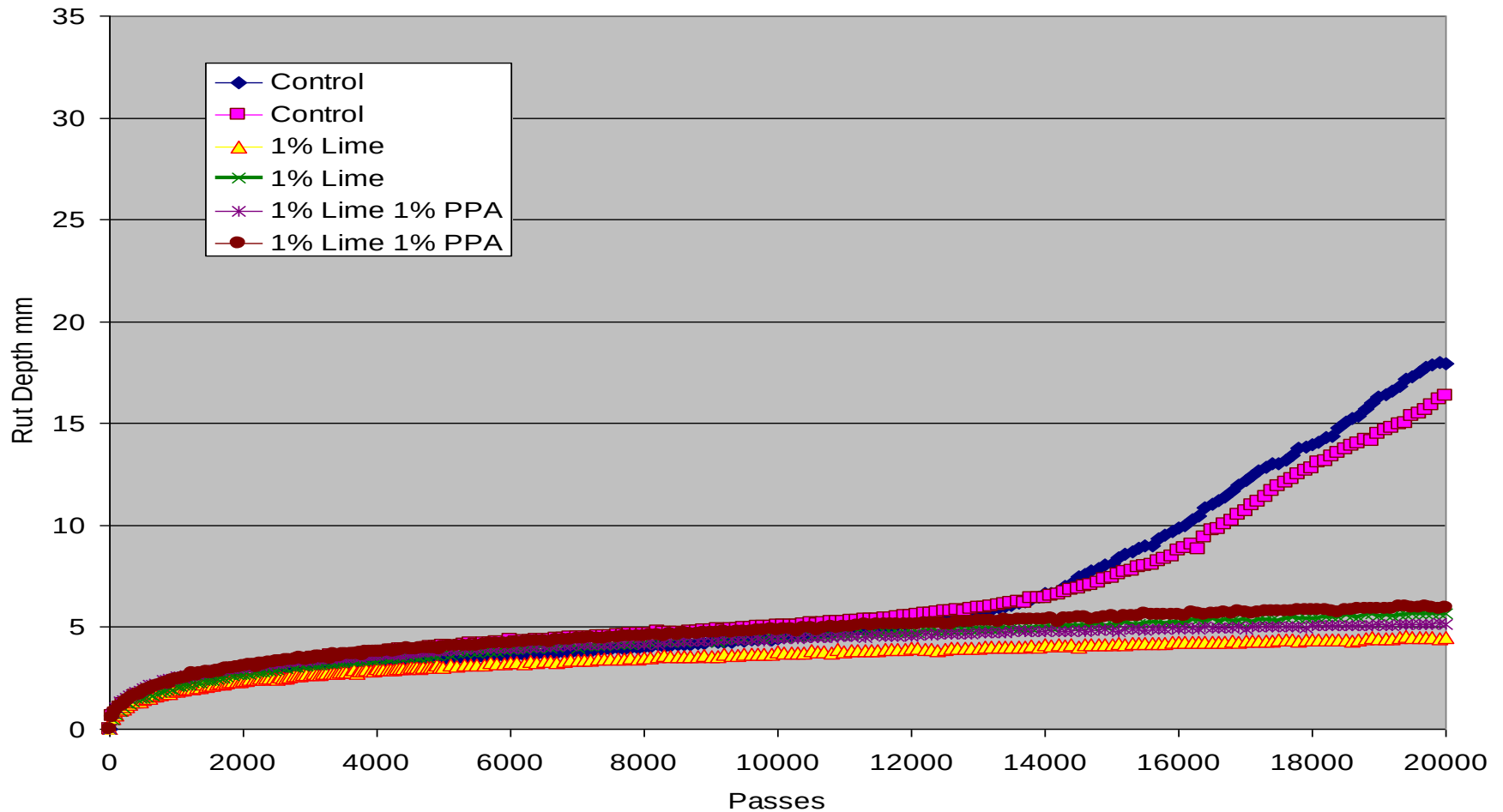
Hamburg 50degC Citgo Asphalt Lime Treated Limestone Aggregate

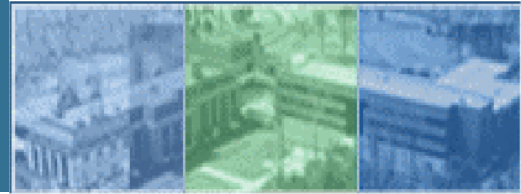


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Hamburg 50degC Citgo Asphalt GA Granite Aggregate

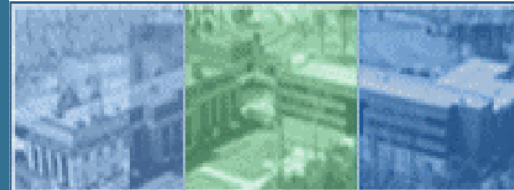




Lime Treated Aggregate

- **Lime showed up very well in the tests**
- **Stripping was unaffected by PPA modification**



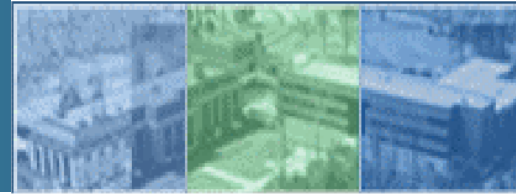


More Chemistry-Titration of Amine Antistrip with PPA

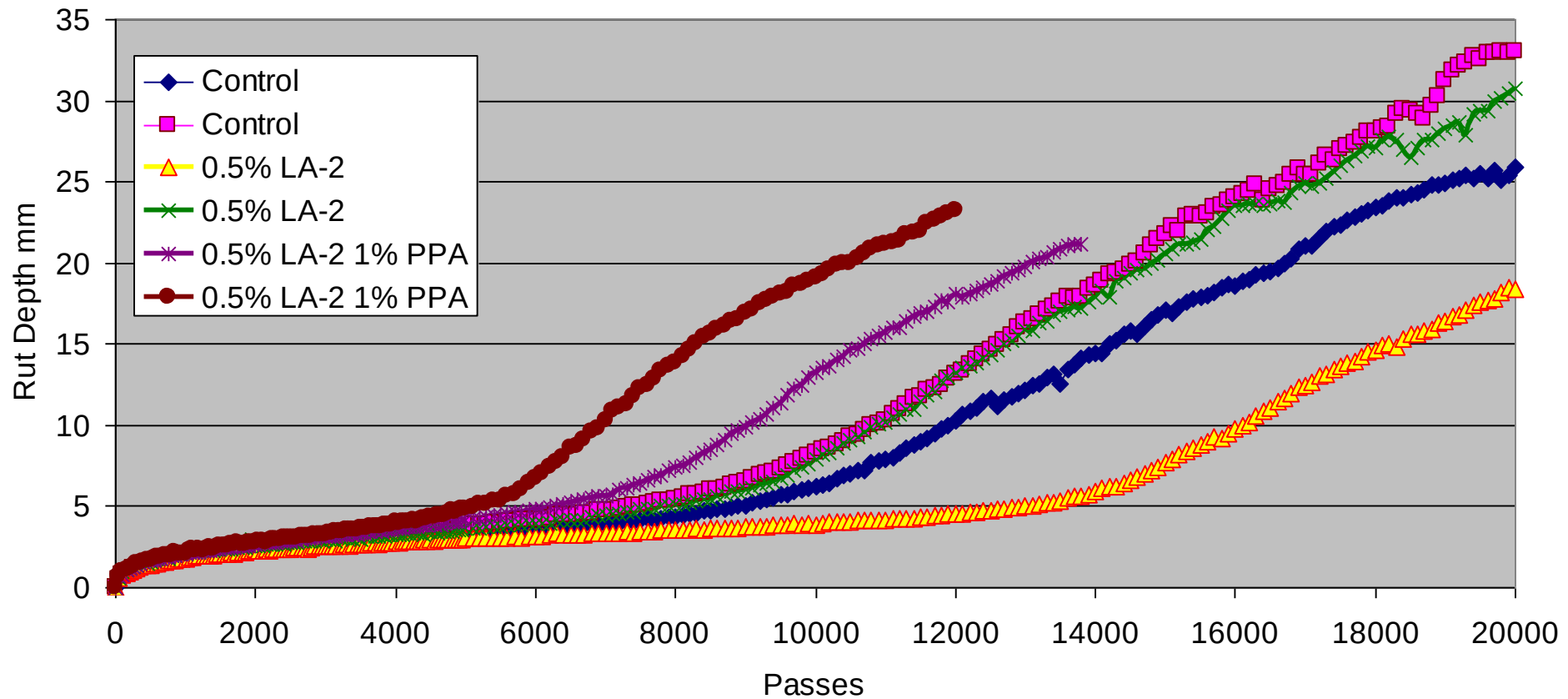
- Titrate an ethanol solution of antistrip with phosphoric acid
- 1gm Adhere LOF 65-00 equivalent to 0.49 gm PPA
- 1gm Adhere LA-2 equivalent to 0.57 gm PPA
- If the binder contains 0.5% of antistrip and 1% of PPA then the PPA is in excess, about 25% being neutralized by the amine



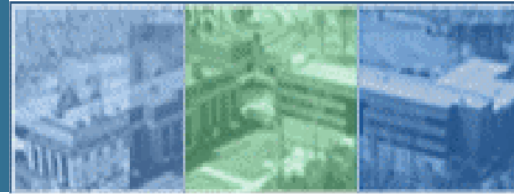
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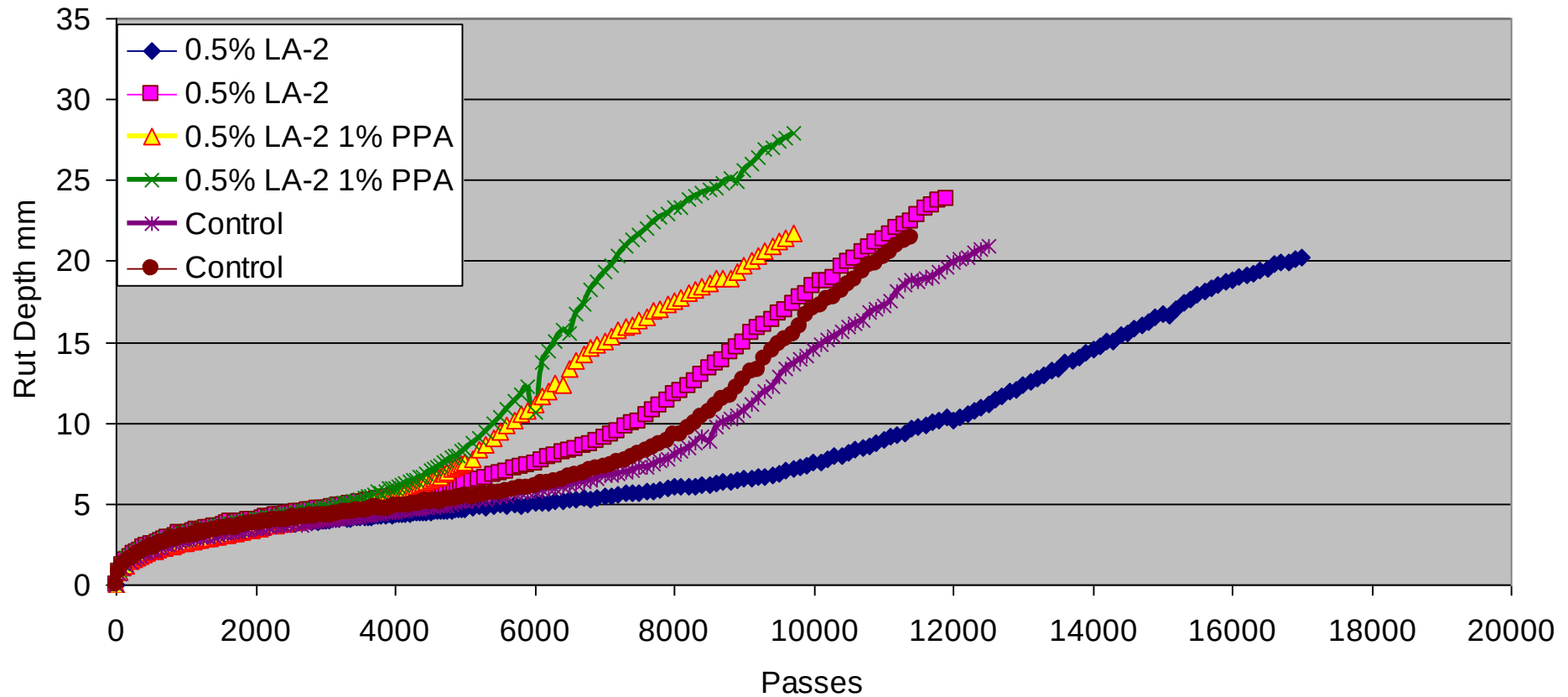
Hamburg 50degC Citgo Asphalt Sandstone Aggregate



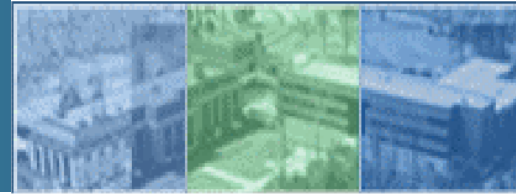
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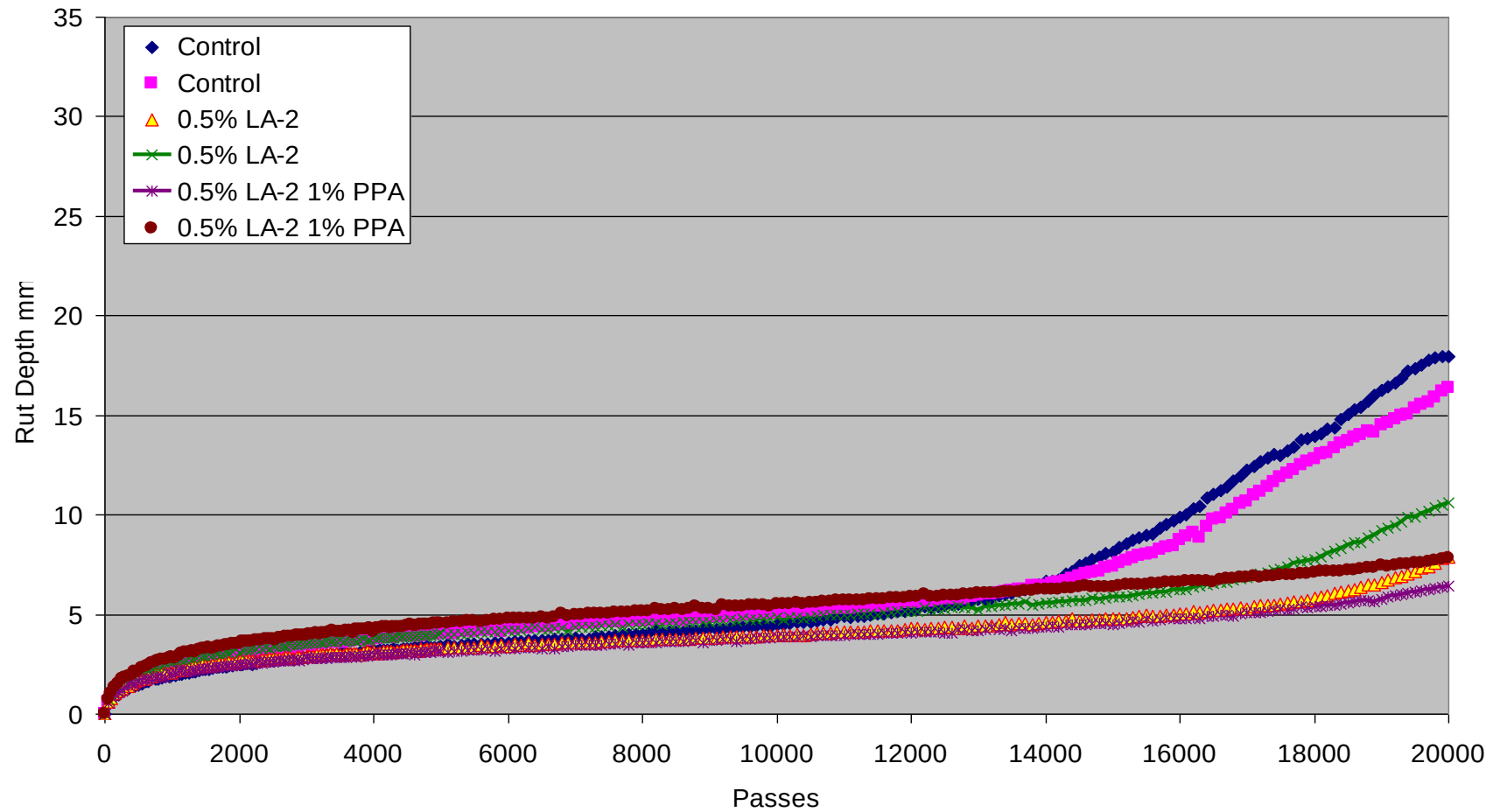
Hamburg 50degC Citgo Asphalt Limestone Aggregate

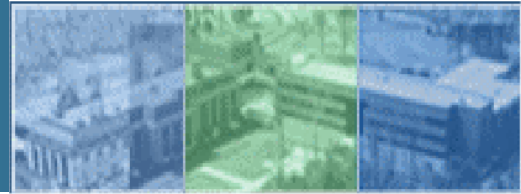


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Hamburg 50degC Citgo Asphalt GA Granite Aggregate



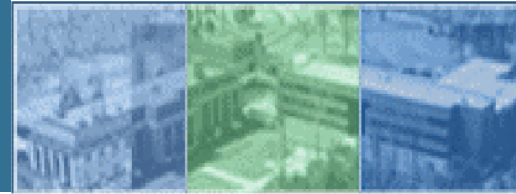


Arr-Mazz LA-2

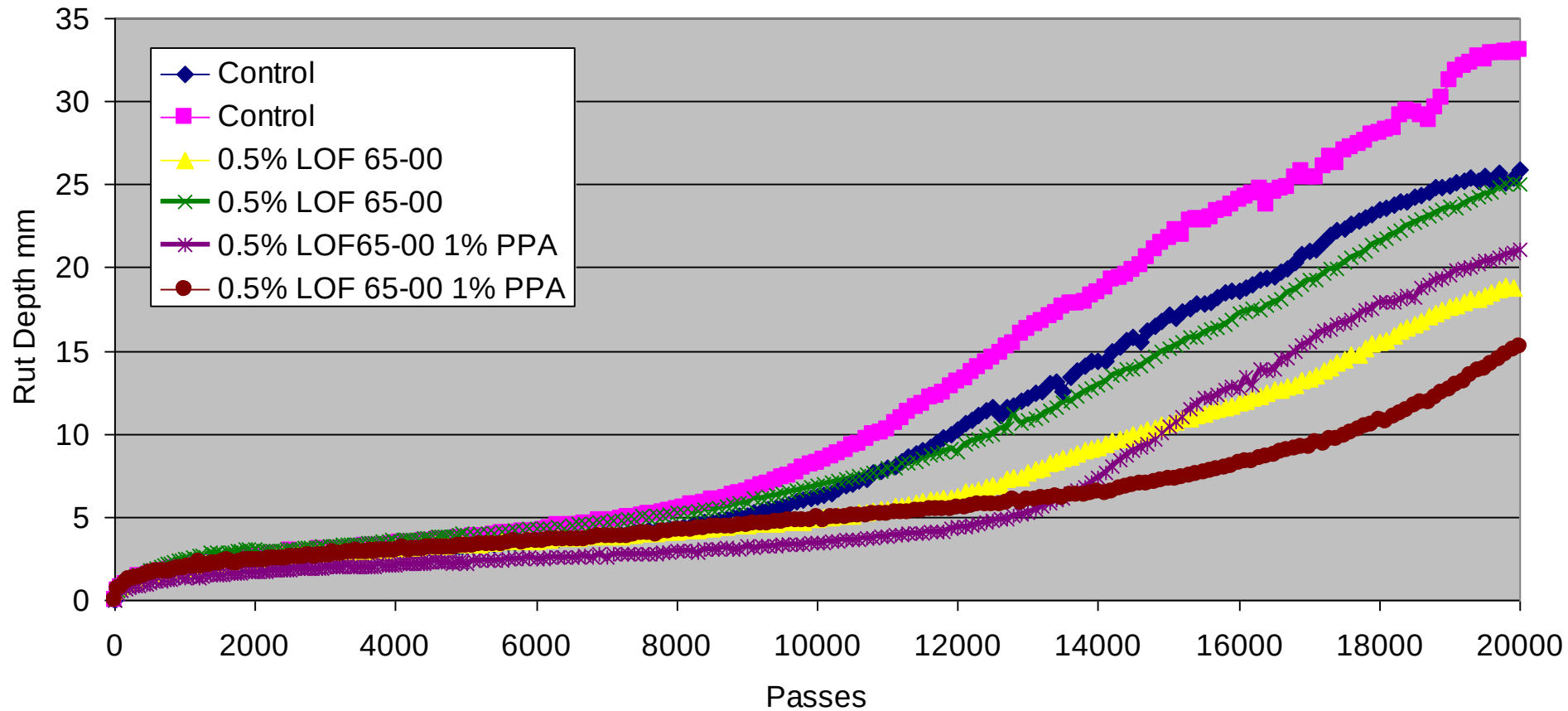
- Additive did not work well with Sandstone or Limestone
- PPA worse with both Sandstone & Limestone
- Additive worked well with GA Granite
- PPA modification showed no effect with Granite.



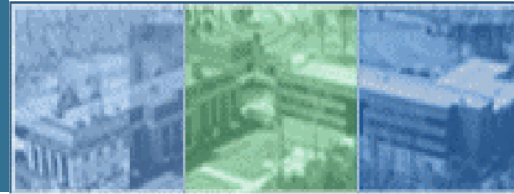
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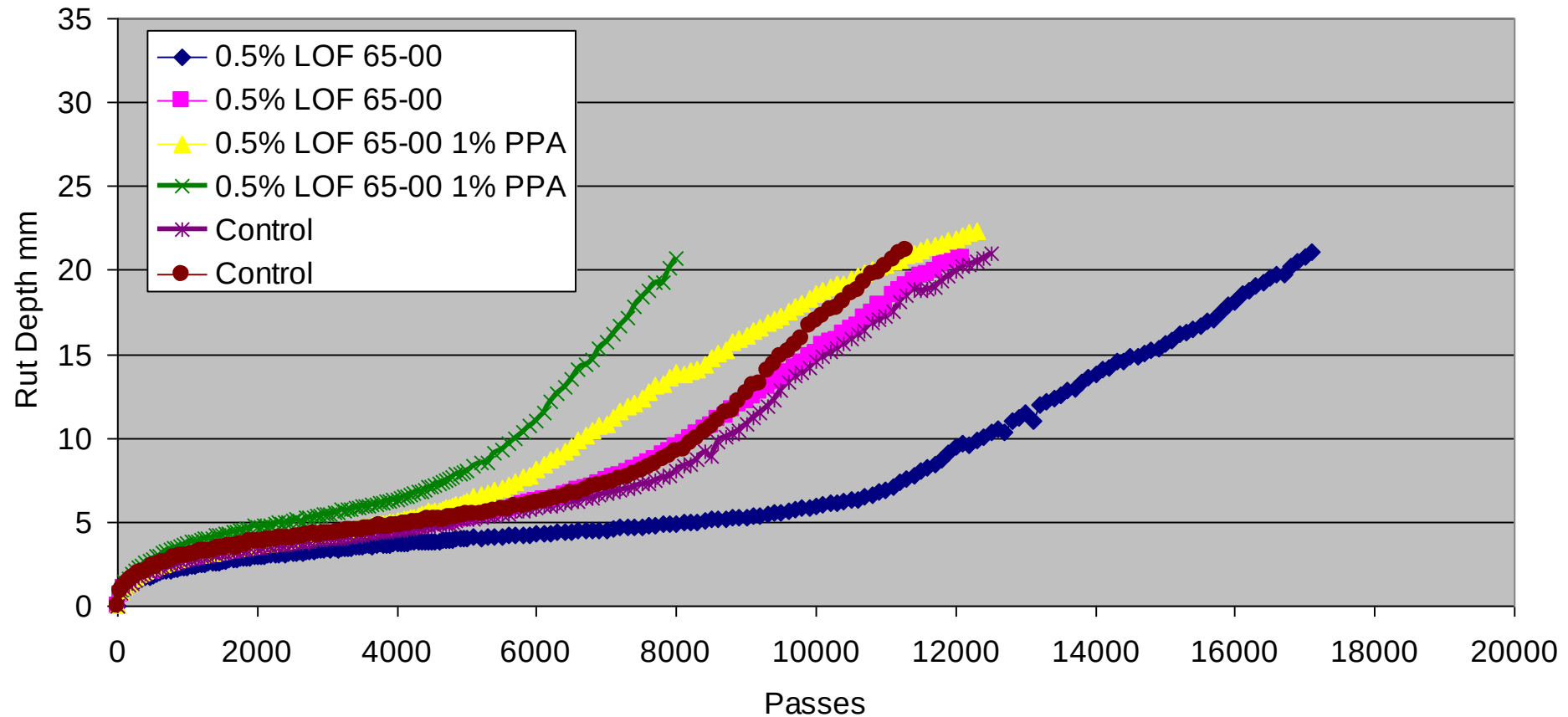
Hamburg 50degC Citgo Asphalt Sandstone Aggregate



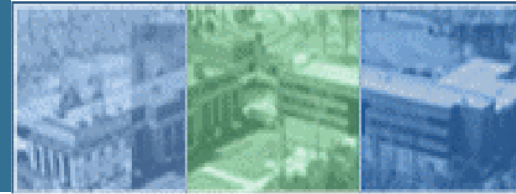
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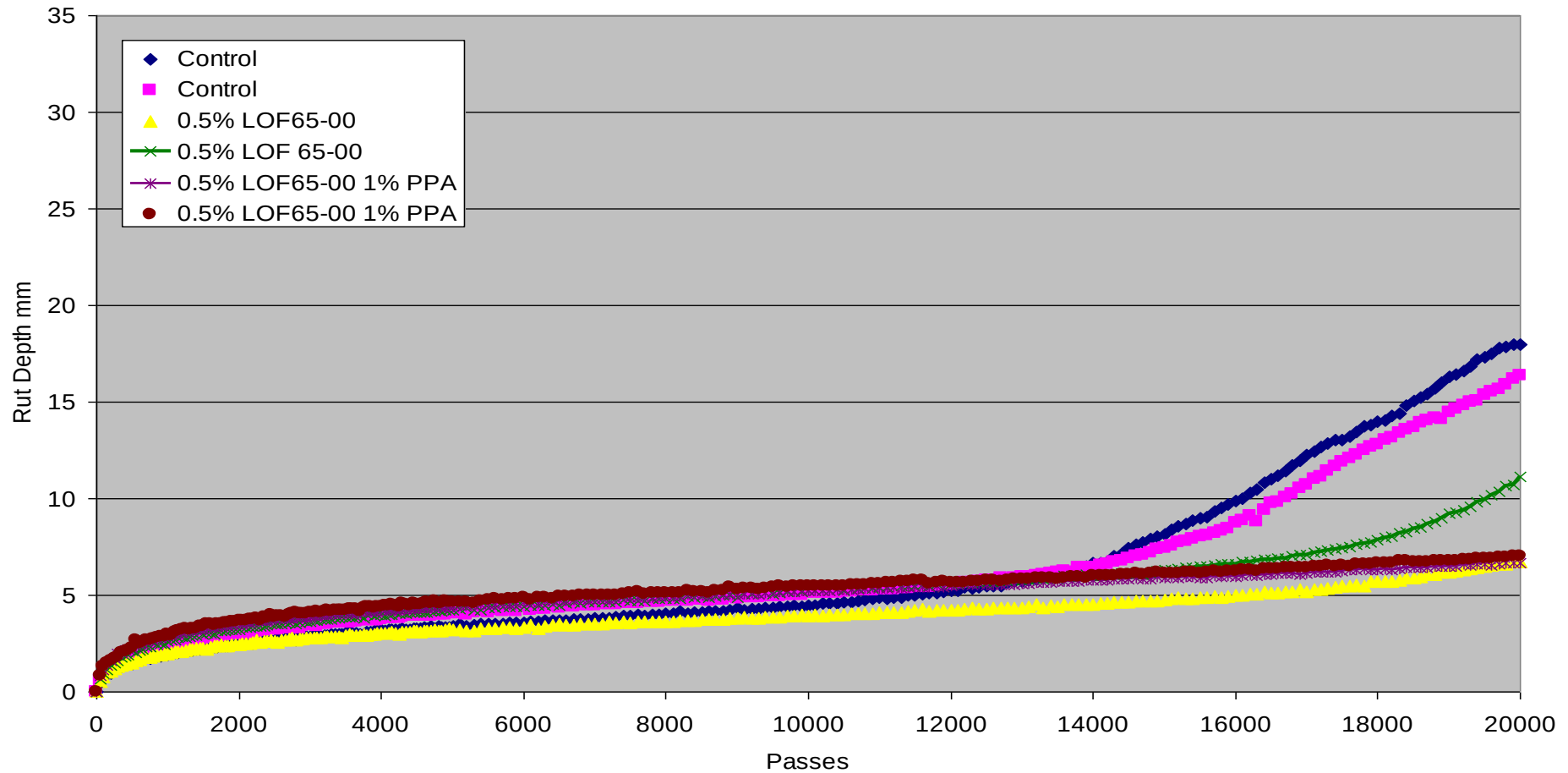
Hamburg 50degC Citgo Asphalt Limestone Aggregate

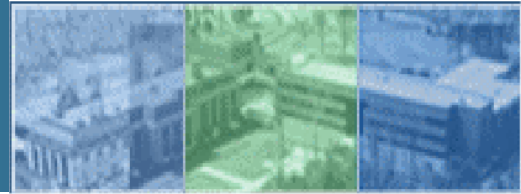


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Hamburg 50 degC Citgo Asphalt GA Granite Aggregate



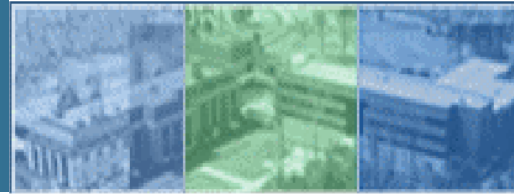


Arr-Mazz LOF 65-00

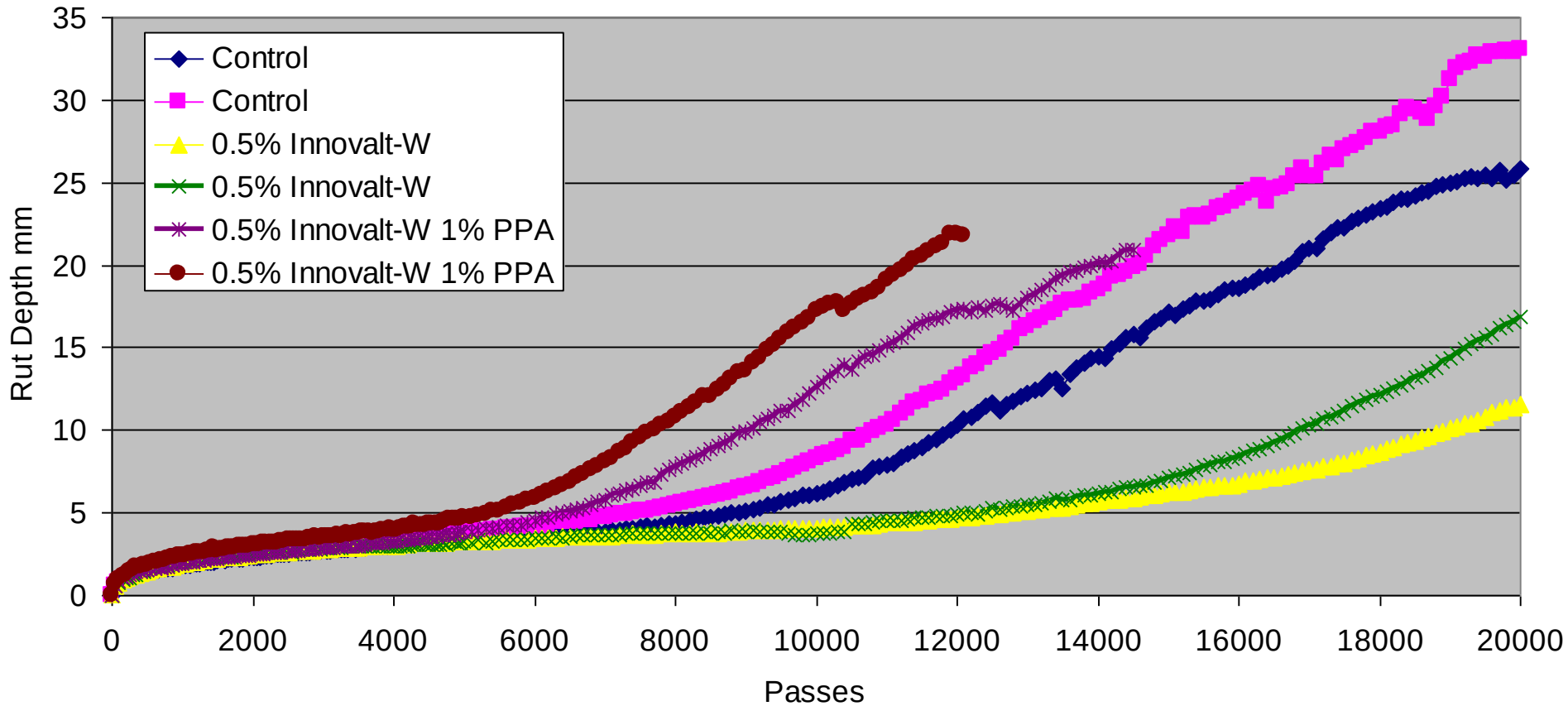
- Additive almost passed the test (20mm 20K passes) with Sandstone
- PPA Modification did not have much effect
- Additive did not work well with Limestone
- PPA modification made it worse
- Additive worked well with Granite
- PPA modification had no effect



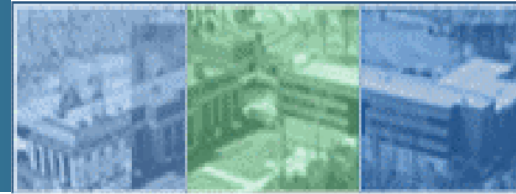
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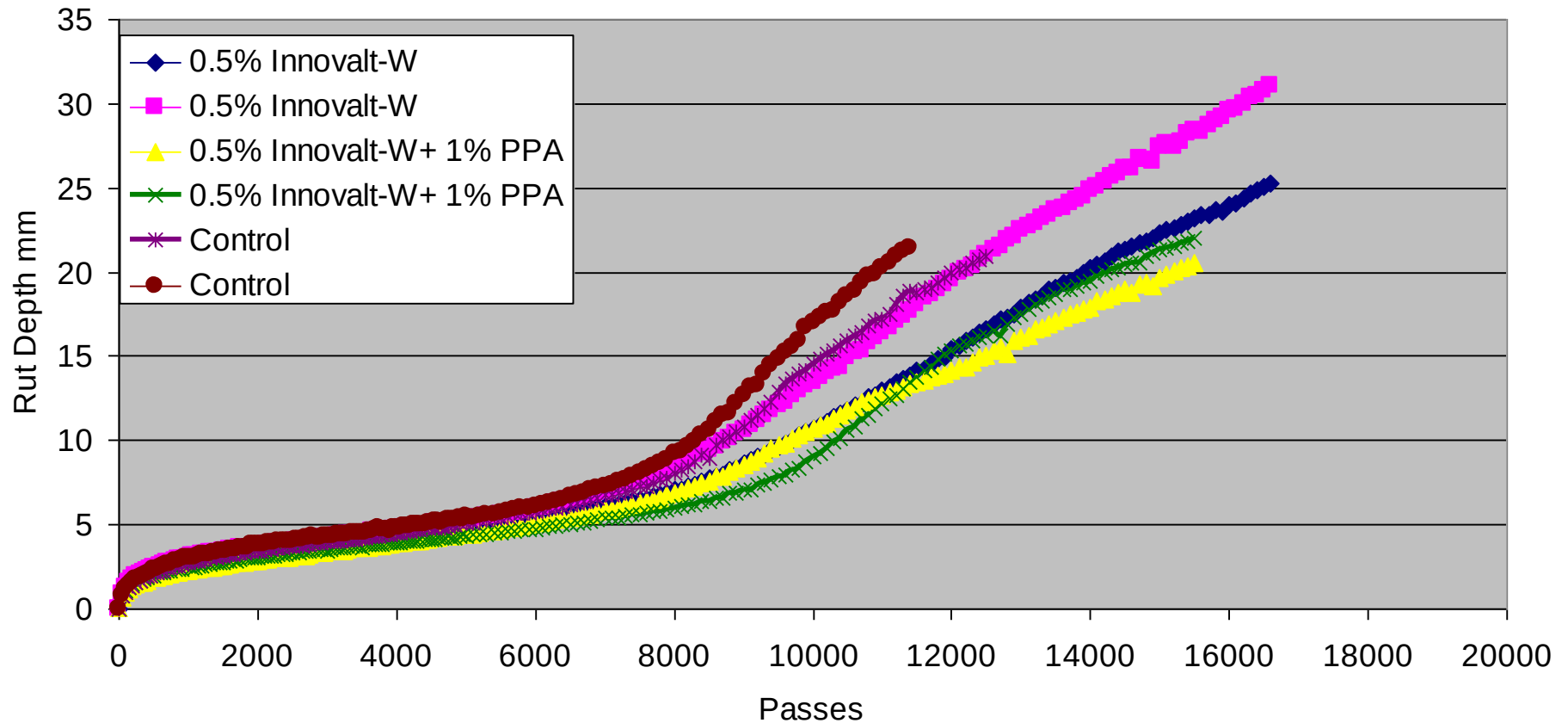
Hamburg 50degC Citgo Asphalt Sandstone Aggregate



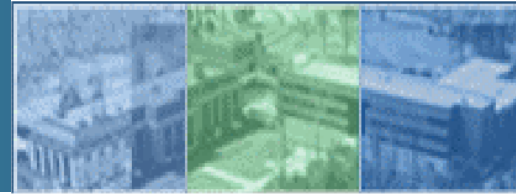
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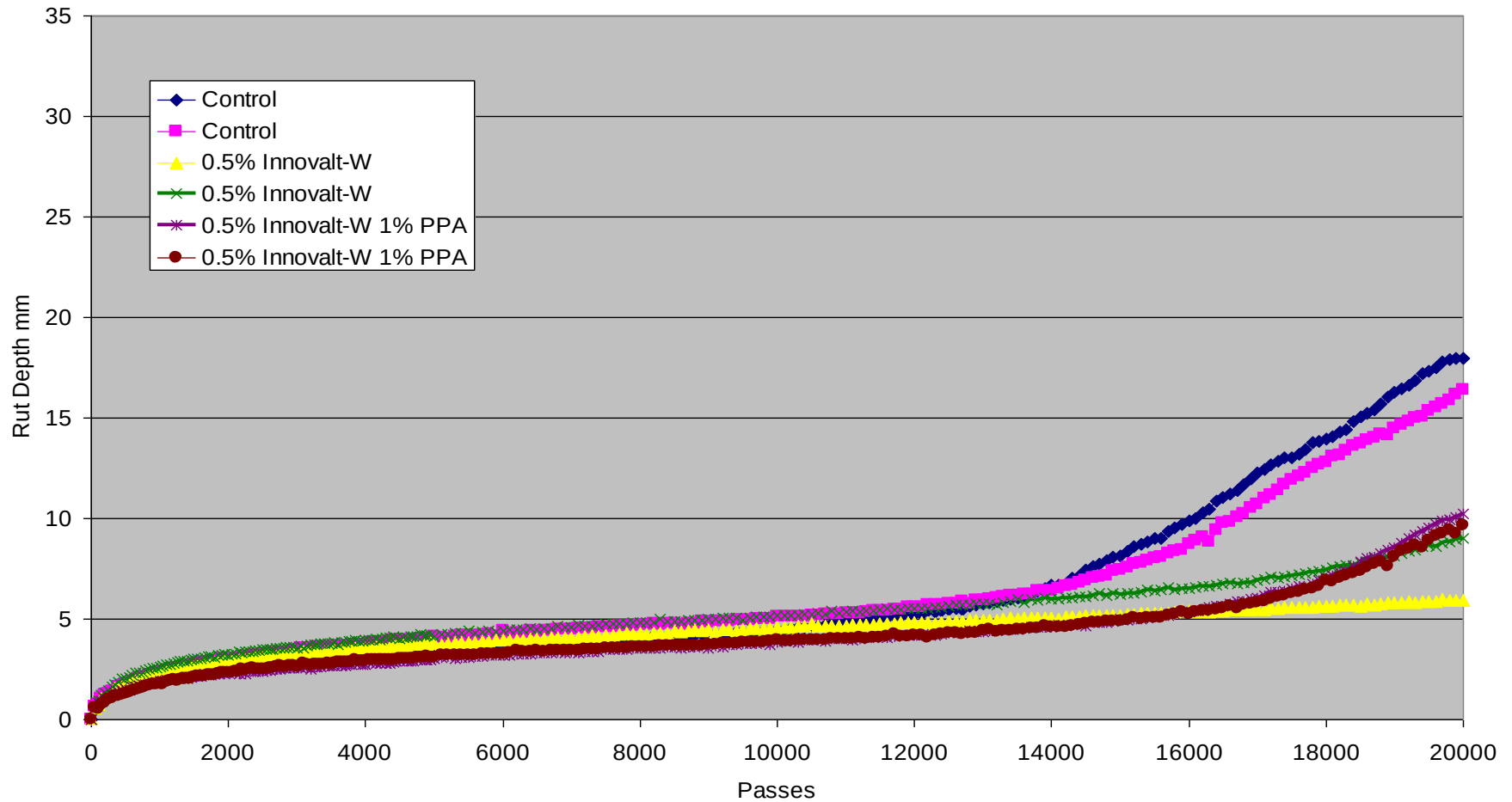
Hamburg 50degC Citgo Asphalt Limestone Aggregate

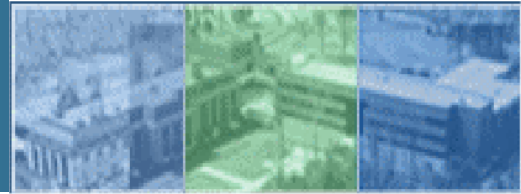


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Hamburg 50degC Citgo Asphalt GA Granite Aggregate

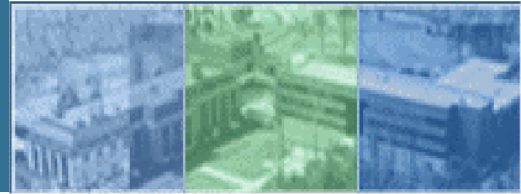




Innovalt –W (2-Ethylhexyl phosphate)

- A phosphate ester and not expected to be affected by PPA
- Additive worked well with sandstone
- PPA modification made it a lot worse
- Additive did not work well with limestone
- PPA improved it slightly
- Additive worked well with granite and was not affected by PPA modification

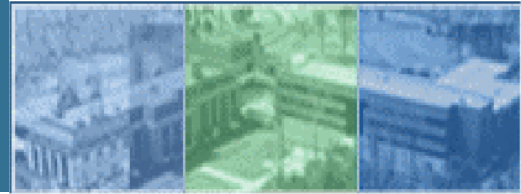




Conclusions – Hamburg Testing

- Test is only an indication and was with a single asphalt
- PPA increased moisture sensitivity of the neat binders
- Action of amine and phosphate ester antistrips is aggregate specific- PPA generally increases moisture sensitivity
- With lime treated aggregates the moisture sensitivity is unaffected by PPA modification
- Users need to test each asphalt/aggregate/antistrip combination.

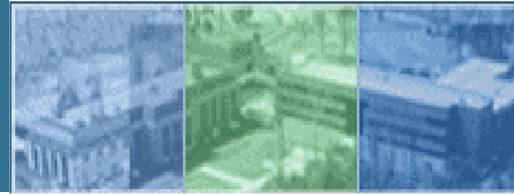




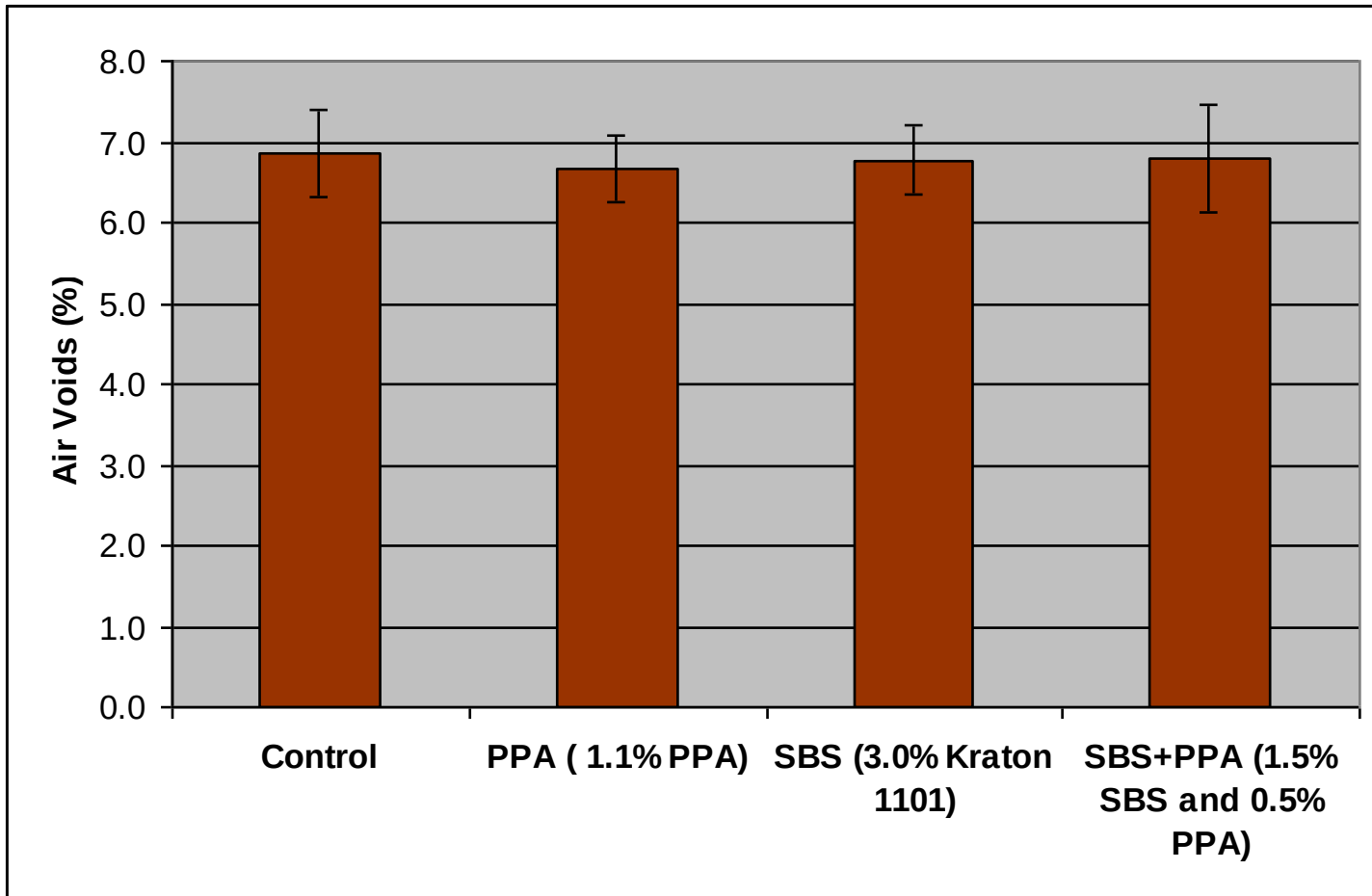
Fatigue Testing

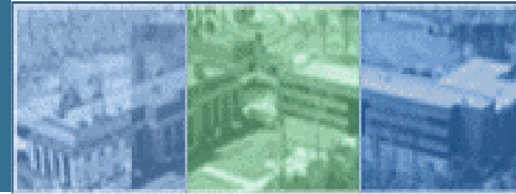
Binder	Lab Ref	Modification	PG Grade
Citgo	B-6362	Control	64
Citgo	B6362	1.1% PPA	76.2
Citgo	B6362	3% Kraton 1101	74.3
Citgo	B6362	1.5% Kraton 1101 + 0.5%PPA	74.6



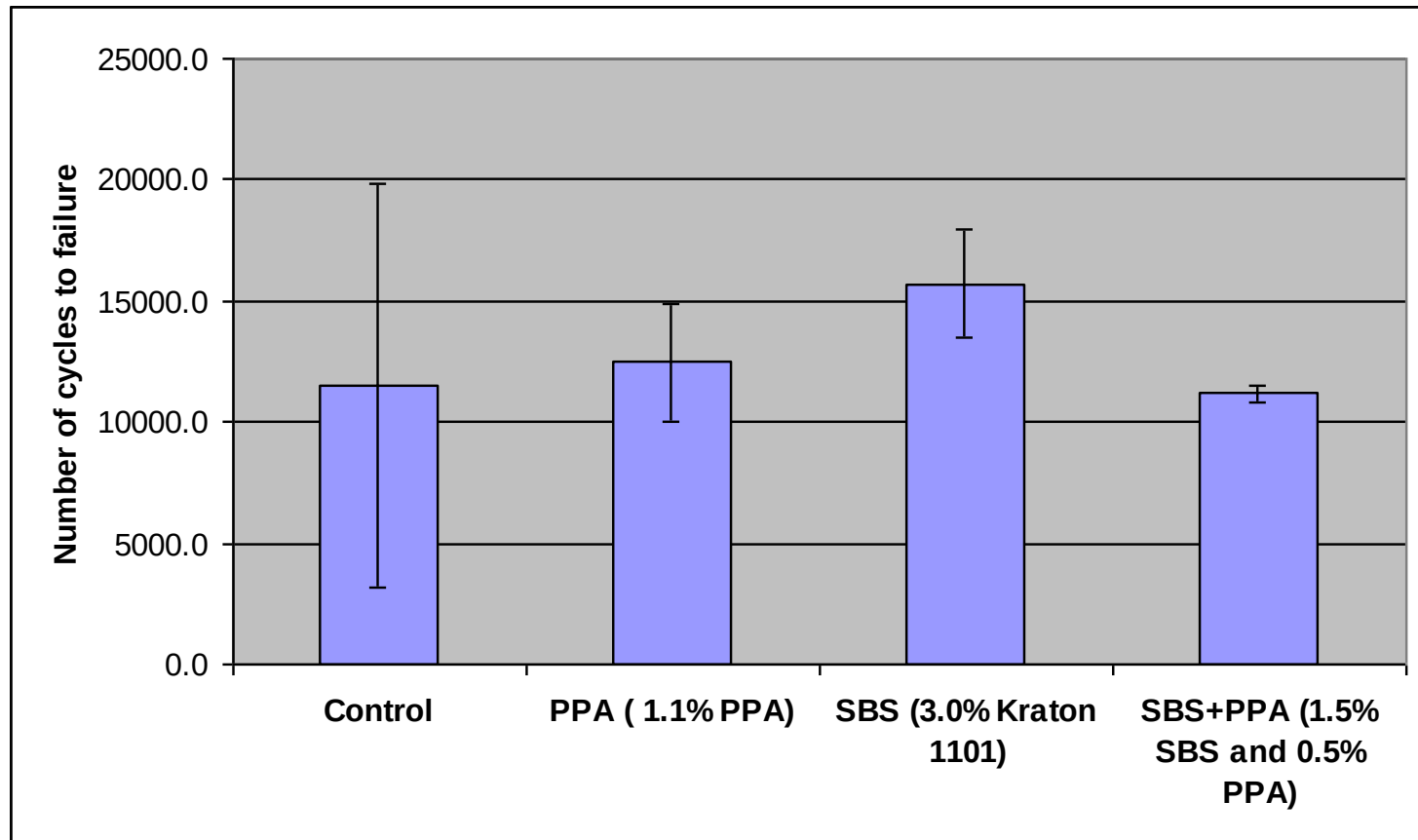


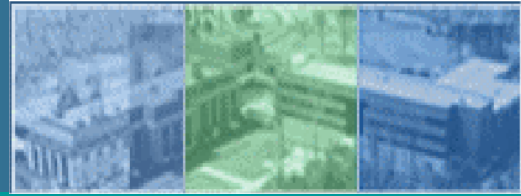
Air Voids





Cycles to Failure





Questions?

