Reactions Between Atmospheric Water and Phosphate Glass Surfaces

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Contradictory Results

Aqueous Corrosion

Humid Weathering
Outline of Discussion

Can we see structural differences in glasses of similar phosphate compositions before and after weathering that allow us to characterize the structural changes and differences?

Glass compositions and weathering conditions

- $^{31}$P MAS characterization
- $^{31}$P-$^1$H cp experiments
- $^{27}$Al MAS
- $^{27}$Al-$^{31}$P REDOR
- Conclusions
Glass Compositions

- Alumino-metaphosphate glasses have the general composition $30R_{2}O \cdot 10Al_{2}O_{3} \cdot 60P_{2}O_{5}$.

- Two series III glasses were also prepared with increased $Al_{2}O_{3}$.

<table>
<thead>
<tr>
<th></th>
<th>$K_2O$</th>
<th>$BaO$</th>
<th>$MgO$</th>
<th>$Al_{2}O_{3}$</th>
<th>$P_2O_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAP</td>
<td>30</td>
<td></td>
<td></td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>KBAP</td>
<td>15</td>
<td>15</td>
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<td>45-10-45</td>
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<td>40-20-40</td>
<td>40</td>
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<td>20</td>
<td>40</td>
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</table>
Weathering Conditions

- Annealed glass was ground and the 45-63µm fraction collected.

- Small amounts of powder were placed into teflon petri dishes and weathered at 50°C and 80%RH.

- Samples were removed after 0, 1, and 7 days and the change in structure was studied via NMR.
$^{31}$P MAS Data

- All three metaphosphate glasses appear to have nearly the same structure consisting entirely of $Q^2$ units.
$^{31}$P MAS Data after Weathering for 7 Days

- KAP and KMAP glasses show significant changes in the phosphate network after 1 week of corrosion.
- KBAP does not appear to show the same reactivity.

50°C / 80% RH

$Q^1$(OH) $Q^2$(OH) $Q^0$(OH) $Q^2$

ppm
$^{31}$P-$^1$H CP Experiments

- All of the new phosphate species that show up in the MAS spectra correlated to $^1$H.
- While $^1$H is present in the KBAP glass, it has no obvious effect on the phosphate network.
Series III $^{31}$P MAS Spectra

- Show the transition from Entirely $Q^2$ to entirely $Q^1$ units as we increase the $Al_2O_3$ fraction at the expense of $P_2O_5$.
Series III $^{31}$P MAS after weathering 1 Day

- Time constraints only allowed 1 day of corrosion.
- See increasing reaction rates as approach the metaphosphate composition.
- 2 variables
Series III CP Experiments

50°C / 80%RH

KAP (40-20-40)

KAP (45-10-45)

KAP (30-10-60)

- Again all new species are correlated to $^1$H.
- There does appear to be water present in the 40-20-40 glass, just not affecting the structure.
### $^{27}$Al MAS Data

<table>
<thead>
<tr>
<th>Glass</th>
<th>6</th>
<th>5</th>
<th>4</th>
<th>Avg.</th>
</tr>
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<tbody>
<tr>
<td>KMAP</td>
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<td>5.17</td>
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<td>40-20-40</td>
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<td>0.22</td>
<td>0.68</td>
<td>4.42</td>
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![Graph showing $^{27}$Al MAS data for different glasses](image-url)
Structural Differences

- Initial $^{31}$P and $^{27}$Al data show little structural differences to account for the difference in reactivity between KMAP and KBAP glasses.

- Looking for other methods to probe the structural order and find differences.

- Al is known to be a stabilizing species, can we probe Al-P connectivities?
Explanation of Redor Measurements

\[ \frac{\Delta S}{S_0} = \frac{f}{I(I+1)\pi^2} (NT_r)^2 M_2^{IS} \]

\[ a = \frac{f}{I(I+1)\pi^2} M_2^{IS} \]


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Redor Results

- The second dipole moment is based on the Al coordination with Al-P distance.
- 1-D data shows that KMAP-KBAP have same coordination distribution.

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<th>Glass</th>
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</tr>
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<tbody>
<tr>
<td>KMAP</td>
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<tr>
<td>5.4</td>
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</tr>
<tr>
<td>3.5</td>
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</tr>
<tr>
<td>3.0</td>
<td></td>
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Conclusions

- $^{31}$P MAS NMR provides details about the attack of water on the phosphate glass structure.
  - Including the differences in reactivity of different glass compositions.
- $^{31}$P and $^{27}$Al NMR, however, show little structural difference in the glasses prior to weathering.
- $^{27}$Al - $^{31}$P Redor measurements appears to show small differences in Al-P coordination environments in the different glass species.
Acknowledgements

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- Joe Hayden of Schott Glass Technologies