Simple Oxidation Kinetics

• Assume simple second order kinetics for oxidation of both polymer and bitumen:

\[
\frac{d[AC]}{dt} = k_{2a}[AC][O_2]
\]
\[
\frac{d[poly]}{dt} = k_{2p}[poly][O_2]
\]

• Also assume oxygen diffusion is not an issue:

\[
\frac{d[AC]}{dt} = k_{2a}[AC]
\]
\[
\frac{d[poly]}{dt} = k_{2p}[poly]
\]
Simple Oxidation Kinetics

• The second order rate constant $k_2$ can be expressed as an Arrhenius relationship:

$$K_{2a} = Ae^{-(E_a/RT)}$$

• What is $E_a$ for the various components of PMB?
Typical Activation Energies

- **Typical $E_a$ for oxidative degradation of diene elastomers** – 125 kJ/mol
  
  D. W. van Krevelen, Properties of Polymers p. 472

- **Typical $E_a$ for diene elastomers** - 24-26 kcal/mole ~ 105 kJ/mol
- **Typical $E_a$ for olefinic plastics** - 33-55 kcal/mole ~ 188 kJ/mol
  
  Robert W. Lenz, Organic Chemistry of Synthetic High Polymers p. 762

- **Typical $E_a$ for bitumen oxidation** – 17 kcal/mol or 73 kJ/mol
  
  SHRP A-367 pp38, 64
Acceleration from 60°C to 100°C for Bitumen Versus Rubber Versus Plastic

- $k_{AC} (60°C)$
- $k_{AC} (100°C)$
- $k_{AC} (100°C)/k_{AC} (60°C)$

- $k_{elastomer} (60°C)$
- $k_{elastomer} (100°C)$
- $k_{elastomer} (100°C)/k_{elastomer} (60°C)$

- $k_{plastomer} (60°C)$
- $k_{plastomer} (100°C)$
- $k_{plastomer} (100°C)/k_{plastomer} (60°C)$

- $4 \times 10^{-12}$
- $7 \times 10^{-11}$
- $17 \times$

- $2.5 \times 10^{-20}$
- $3.2 \times 10^{-18}$
- $126 \times$

- $2.9 \times 10^{-30}$
- $4.2 \times 10^{-27}$
- $1470 \times$
Long Term Mixture Aging

Is there a way to get around it?
Long Term Mixture Aging

• The 9-54 Final Report recommends long term aging at 95 °C for variable times that can be longer than two weeks.
• This will be onerous, at best, for mix design work during project development.
• It will not be possible for QC work.
• Add to that, long term aged specimens are usually brittle so there is little discrimination.
Long Term Mixture Aging

• So is there a way around this dilemma?
• A consideration and possible solution–
• Since aging occurs dominantly in the binder, is it possible to do:
  – Mixture short term aging
  – Binder alone “long term” aging
  – Extrapolate long term mixture aging behavior?
• Thoughts?