Simple Oxidation Kinetics

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

$$d[AC]/dt = k_{2a}[AC][O_2]$$
$$d[poly]/dt = k_{2p}[poly][O_2]$$

- Also assume oxygen diffusion is not an issue:

$$d[AC]/dt = k_{2a}[AC]$$
$$d[poly]/dt = k_{2p}[poly]$$

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 – 17kcal/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)**

- **4 E-12**
- **7 E-11**
- **17X**

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

- **2.5 E-20**
- **3.2 E-18**
- **126X**

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

- **2.9 E-30**
- **4.2 E-27**
- **1470X**

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?