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# Zinc Oxide Retarder

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## Outline

- Background
- Testing at Inhibitor Dosage Levels
- Testing to Use in Mass Concrete
- Key Findings
- Future Areas of Interest



## Background

- ZnO is a readily available material (1,000,000 tons/y) that can have potentially positive effects on concrete
  - Corrosion inhibition in adverse environments
  - Increased strength
  - Lighter color
- Work was conducted to determine the concrete properties (mainly setting time and strength) associated with dosage rates needed to provide the above benefits.



## Testing at Corrosion Inhibitor Levels

- Corrosion literature reports that 1 to 3% ZnO by mass of cement significantly improves corrosion resistance of steel in concrete exposed to chloride ions.
- Dosage rate up to 2% in this study
- Two ZnO materials examined
  - Kadox 911—0.12 µm avg. D, and 9 $m^2/g$ surface area
  - Kadox 930—0.32 µm avg. D, and 3.2 $m^2/g$ surface area
- Some mixtures with calcium nitrite for set acceleration and additional corrosion protection
- Screening testing in mortars
- Concrete testing

## Mortar Testing

| Screening Mortar Matrix | | | |
|---|---|---|---|
| Mix | Flow(%) | Set Time (h) Initial | Final |
| Control | 90 | 3.42 | 5.12 |
| 2% ZnO[1] | 100 | >9 | >9 |
| 2% ZnO[2] | 82 | >9 | >9 |
| 1% ZnO[1] | 85 | >9 | >9 |
| 1% ZnO[2] | 85 | >9 | >9 |
| 1% $Ca(NO_2)_2$ | 86 | 3.27 | 4.85 |
| | | | |
| Note: w/cm=0.59 Sand/Cement=4.2 | | | |
| 1 is Kadox 930 | | | |
| 2 is Kadox 911 | | | |

- ZnO is a strong retarder at corrosion inhibitor dosage rates
- Finer product appears to have negative effects on flow at higher dosage
- Reduce ZnO dosage and add Corr. Inhibitor accelerator—$Ca(NO_2)_2$



## Mortar Testing Continued

- Repeated mortar testing with combinations of ZnO and $Ca(NO_2)_2$
  - Same design as before
  - 0.5 and 1% ZnO levels with 2%$Ca(NO_2)_2$
- Results
  - Flow reduced
  - All ZnO mixes over 12.5 h to final set
- Additional mixtures at lower 0.4 w/c with 1% ZnO and 2%$Ca(NO_2)_2$ and polycarboxylate superplasticizer for workability
  - Setting times ZnO mixes over 22 hours
  - Controls and nitrite alone under 4 hours for final set



## Concrete Testing

- 0.4 w/c
- Delayed addition of 0.5% ZnO after 1 h of mixing
  - Goal to get some cement reactions started
  - One mixture with 2% $Ca(NO_2)_2$ added in initial mixing

| Concrete Mixes | | | | |
|---|---|---|---|---|
| Mix | Slump (mm) | | Set Time (h) | |
| | 9 minutes | 1 h | Initial | Final |
| Control | 75 | | 3.3 | 4.5 |
| 0.5%ZnO delayed | 100 | 65 | 26.5 | 30.2 |
| 2%$Ca(NO_2)_2$ +0.5%ZnO delayed | 85 | 30 | 21.5 | 24.3 |
| Notes w/c= 0.40 polycarboxylate HRWR | | | | |



## Conclusions from Higher Dosage ZnO Work

- Retardation is excessive making product not practical for use as a corrosion inhibitor or whitening additive
- Strong retardation could have potential in several applications
  - Mass Concrete
  - Post-tensioned grout mixes
  - Long haul times



## Concrete Testing for Mass Concrete

- Screening
  - Normal and High Performance Concretes
  - With and without Calcium Nitrite
  - Dosage rates of ZnO under 0.5% on cementitious content
- Heat of Hydration Determination Based on Best Mixes from Screening



| Average Durable Concrete | | | | | | |
|---|---|---|---|---|---|---|
| | Mix # | | | | | |
| Component | 1 | 2 | 3 | 7 | 8 | 11 |
| Cement Type 1 (pcy) | 600 | 600 | 600 | 676 | 676 | 676 |
| Fly Ash Type F (pcy) | | | | | | |
| Silica Fume (pcy) | | | 50 | | | |
| Water (pcy) | 296 | 296 | 279 | 270 | 270 | 270 |
| Peastone (pcy) | 1709 | 1709 | 1709 | 1710 | 1710 | 1709 |
| Sand (pcy) | 1387 | 1387 | 1387 | 1401 | 1401 | 1401 |
| w/c | 0.49 | 0.49 | 0.43 | 0.4 | 0.4 | 0.4 |
| Admixtures | | | | | | |
| Adva 190 oz/cwt) | 3 | 4 | 9.2 | 8 | 10.75 | |
| Adva 575 (oz/cwt) | | | | | | 10.75 |
| ZnO (pcy) | | 4 | 3 | | 3 | 2.5 |
| ZnO (% on cement) | | 0.67% | 0.50% | 0.00% | 0.44% | 0.37% |
| ZnO (% on cementitious) | | | 0.46% | | | |
| DCI (gpy) | | | 2 | 3 | 3 | 3 |
| Recover (oz/cwt) | 3 | | | 4.5 | | |
| Results | | | | | | |
| Temperature (°F) | 92.1 | 99.1 | 102.7 | 102.4 | 102.9 | 103.5 |
| Slump (inches) | 3.25 | < 2.0 | 4.5 | 3.5 | 3.5 | 5.25 |
| Initial Set (h:min)) | 2:25 | 19:45 | 8:02 | 3:50 | 9:34 | 8:30 |
| Final Set (h:min)) | 3:12 | 44:45 | 34:32 | 4:46 | 18:10 | <21:00 |
| 28 Day Compressive Strength (psi) | 6395 | 7720 | 9655 | 9435 | 8870 | 9355 |
| | | | | | | |
| Notes: ZnO is Kadox 930. Adva admixtures are superplasticizers (575 is less retarding), Recover is a retarder, DCI is an acclerating corrosion inhibitor. | | | | | | |

**High Performance Concretes**

| | Mix # | | | | | |
|---|---|---|---|---|---|---|
| Component | 4 | 5 | 6 | 9 | 10 | 12 |
| Cement Type 1 (pcy) | 495 | 495 | 495 | 718 | 718 | 718 |
| Fly Ash Type F (pcy) | 211 | 211 | 211 | | | |
| Silica Fume (pcy) | 20 | 20 | 20 | 42 | 42 | 42 |
| Water (pcy) | 254 | 254 | 254 | 270 | 270 | 270 |
| Peastone (pcy) | 1682 | 1682 | 1682 | 1682 | 1682 | 1682 |
| Sand (pcy) | 1365 | 1365 | 1365 | 1379 | 1379 | 1379 |
| w/c | 0.35 | 0.35 | 0.35 | 0.36 | 0.36 | 0.36 |
| Admixtures | | | | | | |
| Adva 190 oz/cwt) | 10 | 10 | 15 | 13.75 | 14.5 | |
| Adva 575 (oz/cwt) | | | | | | 11 |
| ZnO (pcy) | | 4.95 | 2.5 | | 4 | 2.5 |
| ZnO (% on cement) | | 1.00% | 0.51% | | 0.56% | 0.35% |
| ZnO (% on cementitious) | | 0.68% | 0.34% | 0.00% | 0.53% | 0.33% |
| DCI (gpy) | 4 | 4 | 4 | 4 | 4 | 4 |
| Recover (oz/cwt) | 6 | | | 5 | | |
| Results | | | | | | |
| Temperature (°F) | 100.1 | 100.9 | 101.9 | 99.8 | 99.6 | 102.5 |
| Slump (inches) | 5 | 4.5 | 8 | 4.5 | 4.0 | 7.5 |
| Initial Set (h:min)) | 4:21 | 22:38 | 26:30 | 3:44 | 10:56 | 19:54 |
| Final Set (h:min)) | 5:01 | 29:08 | 31:30 | 4:32 | 35:05 | 23:34 |
| 28 Day Compressive Strength (psi) | 10005 | 8895 | 9635 | 11910 | 11435 | 10460 |

Notes: ZnO is Kadox 930. Adva admixtures are superplasticizers (575 is less retarding), Recover is a retarder, DCI is an accelerating corrosion inhibitor.

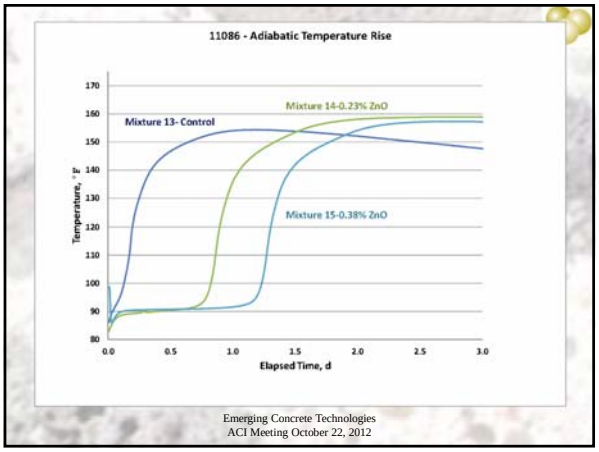


**Adiabatic Heat Determination Mixes**

| | Mix # | | |
|---|---|---|---|
| Component | 13 | 14 | 15 |
| Cement Type 1 (pcy) | 658 | 658 | 658 |
| Water (pcy) | 263 | 263 | 263 |
| Peastone (pcy) | 1725 | 1725 | 1725 |
| Sand (pcy) | 1410 | 1410 | 1410 |
| w/c | 0.4 | 0.4 | 0.4 |
| Admixtures | | | |
| Adva 575 (oz/cwt) | 7.5 | 8.6 | 7 |
| ZnO (pcy) | | 1.5 | 2.5 |
| ZnO (% on Cement) | | 0.23% | 0.38% |
| DCI (gpy) | 4 | 4 | 4 |
| Results | | | |
| Temperature (°F) | 86 | 86 | 86 |
| Slump (inches) | 5 | 4.5 | 8 |
| Initial Set (h:min)) | | | |
| Final Set (h) | < 3 | < 22 | 31:20 |
| 3 Day Compressive Strength (psi) | 7715 | 7250 | 6850 |
| 28 Day Compressive Strength (psi) | 9730 | 9660 | 9890 |

Notes: ZnO is Kadox 930. Adva 575 is a superplasticizer, DCI is an accelerating corrosion








## Key Findings

- ZnO Is a Very Effective Retarder
  - At low dosage rates should behave similar to conventional retarders
  - At slightly higher rates can be used for long delays in setting
- Strength
  - Appear to be improved significantly at higher w/c values
  - Only minor reduction at lower w/cm or in high performance concretes
- Heat Development
  - Delay in set and time for development
  - Actual heat production not reduced, just occurs later
    - Still need to protect against thermal cracking
    - But improved scheduling as more time available before cooling needs to be turned on
    - Large pour or long hauling distance without need for ice is possible
- Works in Delayed Addition



## Future Areas of Interest

- Use at lower dosage as nonorganic retarder
  - Easily added to bag mixes
  - No microbiological growth (most retarders are food for microorganisms)
  - Could be cost effective especially in hot climates
- Use to stop concrete from setting
  - Long haul times to remote sites
  - Unexpected delays in construction
  - Keep concrete overnight
- Grout mixes
  - Long pump distances without setting
  - Lower dosages need to be explored



## Mold with Organic Retarder

## Long Haul Times on Hot Days



## Thank You!
## Questions?