Advantages of Slag-Silica Fume Ternary Binders for Production of Durable Concrete

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DEPARTMENT OF CIVIL ENGINEERING
General Advantages of SCM’s

The advantages of properly designed and cured concretes containing SCM’s are that lower permeability and chloride diffusion can be achieved:

1. There is more C-S-H formed which uses up Ca(OH)$_2$ and fills more space.
2. The reactions happen later, so that the new C-S-H subdivides and blocks the initial capillary pore system.
3. The porous aggregate transition zones (ITZ) become filled with C-S-H, reducing their influence.
4. With SCM's, the C-S-H which forms has lower Ca/Si. To make up for this, the C-S-H incorporates more alkalies (substituting for Ca). This reduces the alkalinity of the pore solution, making it less likely to attack reactive aggregates.

5. SCM’s with higher $\text{Al}_2\text{O}_3$ contents will also form C-A-S-H, ($\text{Al}_2\text{O}_3$ substituting for $\text{SiO}_2$) and other aluminate hydrates which will bind more chlorides and alkali.
Concerns with SCMs

- Often the initial rate of reaction is slower, especially at high replacement levels and at lower temperatures.
- This can be overcome by re-designing mixes to get early age properties, or by use of ternary mixtures—e.g. Silica fume with slag or ash; or slag mixed with high-alkali Class C fly ash.
- Rates of reaction increase with increasing temperature, so replacement levels often have to change with seasons.
Slag and Silica Fume Use in Ontario, Canada

- Ground Granulated Blast-Furnace Slag has been produced since 1976 and is used by most concrete producers.
- Silica Fume has been available since 1978 and Type GUb8SF blended cement since 1982.
- Slag-Silica Fume Ternary systems have been used since 1986 and are commonly whenever Silica Fume is used.
Slag Uses and Concerns

- Typically 25% cement replacement is used for general purpose use in concrete and also in ternary systems with silica fume.
- Slag can also provide improved resistance to chlorides, sulfates, and ASR when used at replacement levels of 35 to 50%.
- However, setting times and early age properties may be retarded at high replacement levels or in cold weather.
SF Blended Cement

- Type Gub-8SF cement typically contains 7 to 9% Silica Fume (±0.5%)
- Makes SF easier to transport
- This reduces SF handling problems at the concrete plant
- This makes SF easier to disperse in concrete
Concerns with Silica Fume

- Silica Fume is often specified for High Strength or High Performance Concrete but requires high-dose rates of HRWR.
- Construction concerns have included finishing problems and plastic cracking.
- Strength development is fast but not much beyond 28 days.
Early-age advantages:

- Lower HRWR doses needed
- Easier to place
- Less “sticky” to finish
- Fewer contractor complaints
- Good early age properties (strength and chloride resistance) due to SF, and continued later-age improvement due to Slag
- Lower heat rise
Admixtures add to cost of HPC
Improved Resistance to Fluid Ingress

• Silica Fume results in improved resistance to fluid penetration at early ages, but has less effect at later ages.

• Slag results in improved resistance to fluid penetration at ages beyond ~14 days that continues to further improve for along time.

• Using ternary mixtures gives the benefit of improved resistance at early ages combined with continued long-term improvements.
REDUCTION IN EARLY AGE WATER PERMEABILITY
of w/cm=0.45 Mortars

PERMEABILITY, K (m/s)

TIME (days)

OPC Control

25% Slag

8% Silica Fume

(McGrath, 1996)
## Effect of Slag on Concrete ( = [W] and w/cm)

<table>
<thead>
<tr>
<th>Slag %</th>
<th>Water</th>
<th>W/CM</th>
<th>91-day Strength (MPa)</th>
<th>RCPT (coulombs)</th>
<th>Permeability H$_2$O 10$^{-13}$ m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>200</td>
<td>0.45</td>
<td>35.8</td>
<td>5200</td>
<td>10.1</td>
</tr>
<tr>
<td>25</td>
<td>200</td>
<td>0.45</td>
<td>42.7</td>
<td>2450</td>
<td>5.4</td>
</tr>
<tr>
<td>50</td>
<td>200</td>
<td>0.45</td>
<td>42.8</td>
<td>1020</td>
<td>2.3</td>
</tr>
</tbody>
</table>

R. Bin Ahmad, 1991
Early-Age Concrete Permeability Results: Effect of Slag (calculated on inflow up to 7 days)

Nokken and Hooton, 2003

- Equivalent at 7 Days
- 35% Slag
- 10x better at 50 Days

0.40 OPC (135)
0.40 35% SG
Bulk Conductivity to 28 days

HPC mix has 6% SF and 25% Slag

Nokken & Hooton 2004
Diffusion rates decrease with time

\[ D(t) = D_{REF} \left( \frac{t_{REF}}{t} \right)^m \]

**Graph:**
- **Y-axis:** Diffusion Value [m²/s]
- **X-axis:** Age [Days]
- **Graph Line:** Decreasing trend from 1E-13 to 1E-11
- **Points:**
  - \( t_1 \)
  - \( t_2 \)
- **Equation:**
  - \( D_{AVE} \)
Ternary Blends – Time-Dependant Diffusion

Thomas, 2000
ASTM C1202 Chloride Penetration Resistance -
Chloride Bulk Diffusion

![Graph showing chloride bulk diffusion values over age in days. Legend includes lines for 0.35, Plain, 0.35, 8 % SF, and 0.35, 8 %SF, 35 % SG.]
### Water Permeability of Concretes at 90 days (cured 4 days)

<table>
<thead>
<tr>
<th>Cement</th>
<th>w/cm</th>
<th>K (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>0.69</td>
<td>3.7 \times 10^{-12}</td>
</tr>
<tr>
<td>OPC</td>
<td>0.49</td>
<td>2.8 \times 10^{-13}</td>
</tr>
<tr>
<td>8% SF + 25% Slag</td>
<td>0.29</td>
<td>2.0 \times 10^{-16}</td>
</tr>
</tbody>
</table>

El-Dieb & Hooton
1995, CCR
Effect of Alumina in SCMs on chloride binding

- \( w/cm = 0.5 \) @ 56d
- 25% Slag or Fly Ash increases binding
- 8% Silica Fume decreases chloride binding
- Ternary mixes result in increased levels of binding.

H. Zibara, PhD Thesis, U of T
Scotia Plaza Toronto

- Built in 1986-87.
- The first of >10 towers in Toronto to use silica fume plus slag (7.8%+25%).
- 70MPa specified strength (later ones were 85 Mpa)
- All concrete was truck mixed, cooled with liquid nitrogen, and pumped.
- Slumps were >200mm and 90d strengths >90MPa at w/cm=0.31.
## High Strength Concrete in Toronto (70 MPa)

<table>
<thead>
<tr>
<th></th>
<th>Scotia Plaza</th>
<th>BCE Place Phase I</th>
<th>BCE Place Phase II</th>
<th>Bay Adelaide</th>
<th>Simcoe Place</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. Tests</td>
<td>143</td>
<td>287</td>
<td>294</td>
<td>93</td>
<td>139</td>
</tr>
<tr>
<td>91 day strength</td>
<td>93</td>
<td>87</td>
<td>94</td>
<td>95</td>
<td>93</td>
</tr>
<tr>
<td>Std. dev. (MPa)</td>
<td>6.8</td>
<td>8.1</td>
<td>6.0</td>
<td>5.8</td>
<td>5.1</td>
</tr>
<tr>
<td>C.V. (%)</td>
<td>7.3</td>
<td>9.3</td>
<td>6.4</td>
<td>6.1</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Before SF-blended cements
## High Strength Concrete in Toronto (85 MPa)

<table>
<thead>
<tr>
<th></th>
<th>BCE Place Phase II</th>
<th>Bay Adelaide</th>
<th>Simcoe Place</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. Tests</td>
<td>281</td>
<td>137</td>
<td>97</td>
</tr>
<tr>
<td>91 day strength</td>
<td>99</td>
<td>97</td>
<td>105</td>
</tr>
<tr>
<td>Std. dev. (MPa)</td>
<td>5.6</td>
<td>5.3</td>
<td>5.2</td>
</tr>
<tr>
<td>C.V. (%)</td>
<td>5.7</td>
<td>5.4</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Courtesy of J. Ryell
Ternary Cements for Pre-Cast Concrete

- Ternary systems can develop high-early strength in accelerated curing and help prevent ASR and chloride penetration.
- 18h strengths are similar to Type HE cements for release of PT wires.
- Chloride resistance of 65°C-cured ternary concrete is not adversely affected, unlike Type HE portland cement.
Concretes
W/CM=0.3, CM=460kg/m³, 5-8%Air, Slump=150-200mm

Accelerated Curing Program

- 23°C until initial set (6-8 h)
- 20°C/h rise to 65°C
- Hold at 65°C for 9 h
- Cool at 20°C/h

Results compared to moist curing at 23°C
# Strength after 65°C Cure (MPa)
(7.5% Air, 150-200mm Slump)

<table>
<thead>
<tr>
<th>Concrete</th>
<th>18 Hour</th>
<th>28 Day</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>31.2</td>
<td>45.4</td>
</tr>
<tr>
<td>4% SF</td>
<td>40.9</td>
<td>55.8</td>
</tr>
<tr>
<td>8% SF</td>
<td>45.4</td>
<td>54.1</td>
</tr>
<tr>
<td>8% SF+ 25% Slag</td>
<td>40.5</td>
<td>58.1</td>
</tr>
</tbody>
</table>
### RCPT (coulombs) at 28days

<table>
<thead>
<tr>
<th>Cementing Materials</th>
<th>23C 6 days moist</th>
<th>65C heat + air cured</th>
<th>RCPT 65C/RCPT 23C</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>2280</td>
<td>3120</td>
<td>1.4x</td>
</tr>
<tr>
<td>4% SF</td>
<td>520</td>
<td>1050</td>
<td>2.0x</td>
</tr>
<tr>
<td>8% SF</td>
<td>270</td>
<td>230</td>
<td>0.9x</td>
</tr>
<tr>
<td>4% SF + 25% slag</td>
<td>310</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8% SF + 25% slag</td>
<td>170</td>
<td>130</td>
<td>0.8x</td>
</tr>
<tr>
<td>T10 SF + 25% slag</td>
<td>260</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
### 120 Day Chloride Bulk Diffusion

<table>
<thead>
<tr>
<th>Concrete</th>
<th>$D_a \times 10^{-12}$ m$^2$/s (23°C Cure)</th>
<th>$D_a \times 10^{-12}$ m$^2$/s (65°C Cure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU Cement</td>
<td>32.7</td>
<td>61.4</td>
</tr>
<tr>
<td>4% SF</td>
<td>4.3</td>
<td>13.4</td>
</tr>
<tr>
<td>8% SF</td>
<td>2.4</td>
<td>3.8</td>
</tr>
<tr>
<td>4% SF+25% S</td>
<td>4.4</td>
<td>-</td>
</tr>
<tr>
<td>8% SF+25% S</td>
<td>2.7</td>
<td>3.3</td>
</tr>
<tr>
<td>GUUbSF+25%S</td>
<td>4.5</td>
<td>-</td>
</tr>
</tbody>
</table>

Titherington & Hooton 2004

w/cm = 0.30 air-entrained mixes
120 Day, 5M, 40°C Chloride Diffusion

![Diffusion Coefficient Graph]

- **OPC**
- **4%SF**
- **8%SF**
- **4%SF + 25%SL**
- **8%SF + 25%SL**
- **T10SF + 25%SL**

**Graph Details:**
- **Y-axis:** Diffusion Coefficient [m^2/s x 10^-12]
- **X-axis:** Layers and Conditions

**Legend:**
- **Black:** AMBIENT
- **Gray:** STEAM
- **White:** STEAM+MOIST
TTC - Subway Toronto

<table>
<thead>
<tr>
<th></th>
<th>Actual</th>
<th>Specified</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 10SF (kg/m³)</td>
<td>305</td>
<td>400 min</td>
</tr>
<tr>
<td>Slag (kg/m³)</td>
<td>145</td>
<td></td>
</tr>
<tr>
<td>W/CM</td>
<td>0.31</td>
<td>0.35 max</td>
</tr>
<tr>
<td>28-day Strength (MPa)</td>
<td>74.9</td>
<td>60 min</td>
</tr>
<tr>
<td>$D_a \times 10^{-15}$ m²/s</td>
<td>621</td>
<td>1500 max</td>
</tr>
<tr>
<td>$k \times 10^{-15}$ m/s</td>
<td>1.34</td>
<td>100 max</td>
</tr>
</tbody>
</table>
# Summary of Diffusion Coefficients and ASTM C1202 Rapid Chloride Permeability Values for TTC Subway Project

<table>
<thead>
<tr>
<th>Die Cast</th>
<th>Chloride Diffusion $x10^{15}$ m$^2$/s</th>
<th>Rapid Chloride Permeability</th>
<th>Charge Passed after 6 hours (Coulombs)*</th>
<th>Age at Test (months)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40D</td>
<td>80D</td>
<td>120D</td>
<td></td>
</tr>
<tr>
<td>April 30/96</td>
<td>1,087</td>
<td>480</td>
<td>783</td>
<td>434</td>
</tr>
<tr>
<td>June 11/96</td>
<td>583</td>
<td>574</td>
<td>784</td>
<td>484</td>
</tr>
<tr>
<td>July 23/96</td>
<td>604</td>
<td>1,030</td>
<td>590</td>
<td>443</td>
</tr>
<tr>
<td>Sept. 12/96</td>
<td>1,320</td>
<td>1,112</td>
<td>517</td>
<td>515</td>
</tr>
<tr>
<td>Oct. 24/96</td>
<td>510</td>
<td>464</td>
<td>325</td>
<td>394</td>
</tr>
<tr>
<td>Dec. 5/96</td>
<td>499</td>
<td>429</td>
<td>972</td>
<td>91</td>
</tr>
</tbody>
</table>

*Cores stored moist for initial 28 days, then in air until tested.*

Ref. Hart, Ryell, and Thomas, 1997
Bridge Decks at Toronto Airport

- In 1999, 4 bridge decks were placed using Type GUbSF cement + 25% Slag at 0.40 w/cm using the MTO High Performance Concrete Spec. but spec’d at 35MPa (but >50MPA achieved)
- High corrosion resistance was required.
- The concretes were placed in cold weather in 16h continuous placements of 1200m³.
- After that, 40 bridge structures and terminal decks at the airport used similar concrete mixtures. The bridges have been recently inspected and all are performing well.
• Slump: 170 ± 40mm (7 ± 1.5in.)
• Air: 6.9%, Spacing: 0.202mm
• Strength: 50.5MPa (7300psi),
  std.dev. = 3.5MPa (500psi)
• RCPT: 590 coulombs
• Bulk Diffusion \((D_a) = 2.5 \times 10^{-12} \text{ m}^2/\text{s}\)
2900m² (96,000SF) top level parking deck exposed to de-icing salts and freezing.

395kg/m³ (658pcy) of Type 10SF cement and 30% slag = 36% SCM
W/CM = 0.37
45 MPa (6500psi), air-entrained.
Pumped
185 coulombs at 60 days
Dcl = 2.5 × 10⁻¹² m²/s
ASR
Reduction in Pore Solution Alkalinity with SCMs (Slag + SF)

When pore solution alkalinity was < 0.3 M, no ASR expansion in ASTM C1293 Concrete prism tests after 2 years.
2-Year Paste Specimen Pore Solution Alkalinity

Bleszynski 2002

Theoretical Effect of an Inert Diluent

Hydroxyl Ion Concentration [mM/l]

Level of Slag Replacement (% Mass)

ASR Threshold
But without Alumina to stabilize the alkali in the C-S-H, alkali is slowly released to the pore solution.
Concrete Prism Expansion
Spratt Aggregate - Silica Fume or Slag

Bleszynski et al
Concrete Prism Expansion
Spratt Aggregate - Ternary Blends

Expansion [%] vs Time (days)

- Control
- Silica Fume/Slag

CSA LIMIT


Time (days) 0 300 600 900
1991 MTO Site
Kingston, Ont.

6 Concretes: 420kg/m³, Spratt Agg.
HAPC
LAPC
25% slag
50% slag
18% fly ash
25% slag + 3.8% silica fume
20-year old 0.6x0.6x2.0 m concrete beams exposed outdoors in Kingston (mixes: 420kg/m\(^3\))

Hooton, Rogers et al, 2013
## Strengths of Air-entrained Concretes cured at 23 °C with limestone and SCMs

<table>
<thead>
<tr>
<th>Mix Identification (all 400 kg/m3 (666 pcy mixes))</th>
<th>% clinker in binder</th>
<th>w/cm</th>
<th>Compressive Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>7 day</td>
</tr>
<tr>
<td>GU Cement Control</td>
<td>89*</td>
<td>0.40</td>
<td>39.3</td>
</tr>
<tr>
<td>GU + 40% Slag</td>
<td>53</td>
<td>0.40</td>
<td>32.8</td>
</tr>
<tr>
<td>GUL9 + 40% Slag</td>
<td>50</td>
<td>0.40</td>
<td>36.1</td>
</tr>
<tr>
<td>GUL9 + 50% Slag</td>
<td>41</td>
<td>0.40</td>
<td>34.6</td>
</tr>
<tr>
<td>GUL15 + 40% Slag</td>
<td>46</td>
<td>0.40</td>
<td>37.1</td>
</tr>
<tr>
<td>GUL15 + 50% Slag</td>
<td>38</td>
<td>0.40</td>
<td>36.3</td>
</tr>
<tr>
<td>GUL15+ 6% Silica Fume + 25% Slag</td>
<td>53</td>
<td>0.40</td>
<td>46.0</td>
</tr>
</tbody>
</table>

* 3.5% limestone and 8% gypsum

U. of Toronto Field site data
## Permeability Index of Air-entrained Concretes Cured at 23 °C with Limestone and SCMs

### Mix Identification (all 400 kg/m³ (666 pcy mixes))

<table>
<thead>
<tr>
<th>Mix Identification</th>
<th>% Clinker in Binder</th>
<th>w/cm</th>
<th>Rapid Chloride Permeability ASTM C1202 (Coulombs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU Cement Control</td>
<td>89</td>
<td>0.40</td>
<td>2384, 2042, 1192</td>
</tr>
<tr>
<td>GU + 40% Slag</td>
<td>53</td>
<td>0.40</td>
<td>800, 766, 510</td>
</tr>
<tr>
<td>PLC 9% + 40% Slag</td>
<td>50</td>
<td>0.40</td>
<td>867, 693, 499</td>
</tr>
<tr>
<td>PLC 9% + 50% Slag</td>
<td>41</td>
<td>0.40</td>
<td>625, 553, 419</td>
</tr>
<tr>
<td>PLC 15% + 40% Slag</td>
<td>46</td>
<td>0.40</td>
<td>749, 581, 441</td>
</tr>
<tr>
<td>PLC 15% + 50% Slag</td>
<td>38</td>
<td>0.40</td>
<td>525, 438, 347</td>
</tr>
<tr>
<td>PLC 15% + 6% Silica Fume + 25% Slag</td>
<td>53</td>
<td>0.40</td>
<td>357, 296, 300</td>
</tr>
</tbody>
</table>

CSA A23.1 limit is 1500 coulombs @ 56d for C-1 Exposure
Summary

• Ternary cementitious systems work synergistically to combine the best properties of both Slag and Silica Fume.

• High-Performance Concretes are easier to produce, place, and finish with ternary systems.

• Physical properties and durability are also enhanced at both early and later ages.
Conclusions

Appropriate ternary blend combinations exhibit greater performance than the control mix or mixes with a single SCM in terms of:

- Compressive strength (early and late age)
- Controlling damaging expansion due to ASR
- Resistance to the ingress of chlorides
- Resistance to sulfate attack

The de-icer salt scaling field performance of ternary mixes is also good.