National Concrete Consortium
Oklahoma City
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Portland-Limestone Cement:
Synergies that Enhance Concrete Performance

- New specification categories for PLC in ASTM C595 and AASHTO M240
- Basic PLC performance attributes
- Holcim (US) experiences with synergies in concrete
- Studies of PLC properties that influence performance synergies, with and without SCM's

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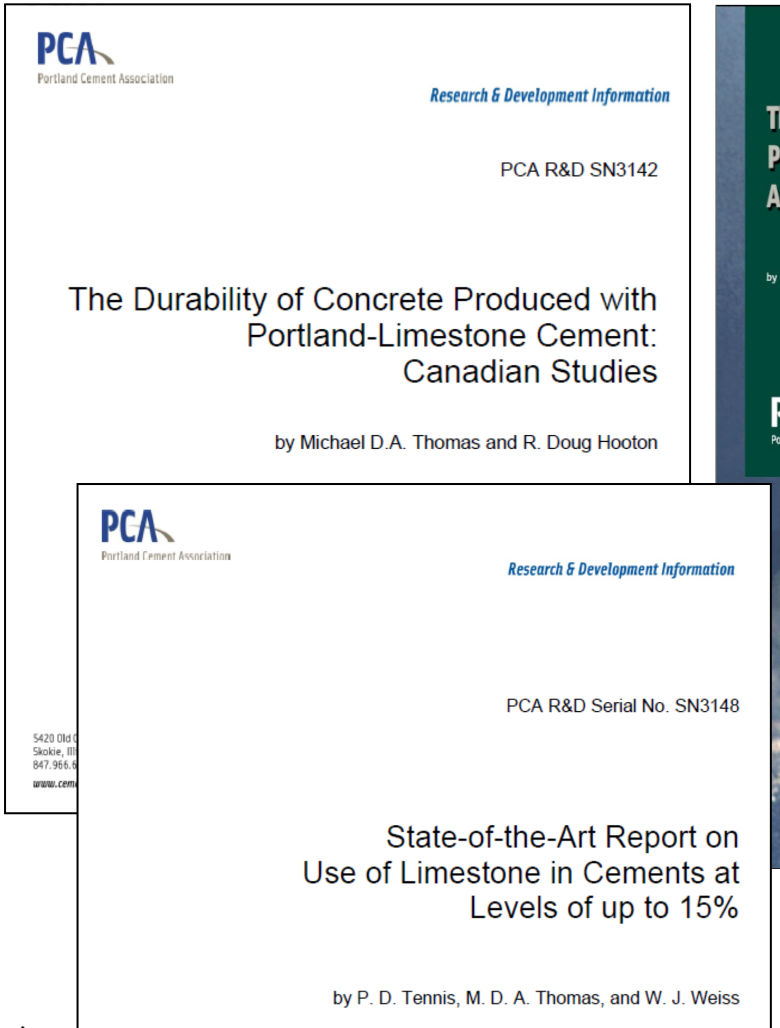
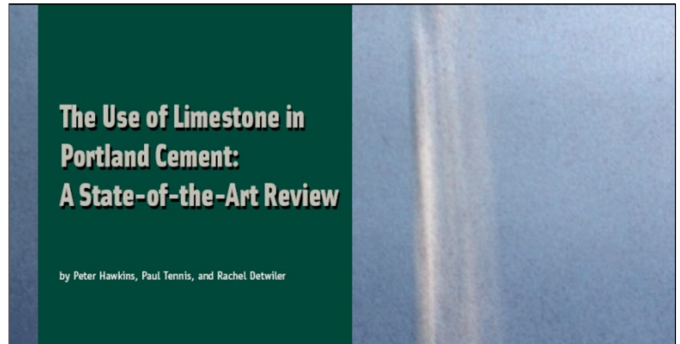
Recap, use of limestone in cement

- Experiences span several decades in many countries
  - Since 1970’s in Europe, now predominant with spec categories for up to 35% LS
  - Up to 5% LS allowed in Canada since early 1980’s
  - New CSA A3001 classification created for up to 15% LS in 2008 and was adopted by Canadian building code in 2010
- US experiences: up to 5% LS in portland cement
  - ASTM C150 in 2004
  - AASHTO M 85 in 2007
  - ASTM & AASHTO cement specs became “harmonized” in 2009
  - Practical limitations mean common LS% usually ≈ 3.5% or less
- ASTM ballot for 5% to 15% LS in C595 (Type IL portland-limestone cement) passed Dec. 2011, AASHTO parallel spec (M 240) changes pending
  - Includes types IS, IP, IL, and IT (combinations of S, P, L)
- Only US spec option for LS > 5% up to now has been ASTM C1157 (performance spec), no AASHTO equivalent
  - Several US producers have made 10% or more LS under C1157 since around 2004 to 2005; limited market in many AASHTO states

Literature review – PLC performance





- Significant sustainability impacts
- Performance in concrete equivalent to or better than OPC
  - Strength
  - Freeze-thaw resistance
  - Resistance to deicer salt scaling
  - Chloride permeability & diffusion
  - Heat of hydration
  - AAR potential
  - Shrinkage & creep
  - Reduced carbonation depth
  - Use of SCM's for sulfate resistance

PLC production, basic performance trends

- PLC is made by metering LS to the finish mill with clinker and gyp
- Blaine of PLC must be somewhat higher for equivalent performance
  - LS fraction is finer
  - Blaine must be increased as LS% is increased
- Grinding production is slowed somewhat
- Performance in concrete equivalent to or slightly better than cements without LS, both with and without SCM's at traditional rates, when Blaine fineness is controlled to about 100 m^2/kg higher than for traditional cements**
- Limestone "filler" is not entirely inert but contributes to hydration both physically and chemically

**Tennis, P. D., Thomas, M. D. A., and Weiss, W. J., "State-of-the-Art Report on Use of Limestone in Cements at Levels of up to 15%", PCA SN3148, 2011

What was that?

So ground limestone in cement is going to contribute to hydration? It's not just a filler?

Hmm…..

Holcim (US) experiences with ASTM C1157 Type GU cement containing higher LS proportions (usually ± 10%)

This product is identical to Type IL(10) cement under proposed ASTM C595 and AASHTO M 240 specs.

Holcim (US) has supplied over 800,000 tons to date

- 5 different US plants
  - **Lots of experience in UT and CO where DOT's approve ASTM C1157**
- General performance
  - Higher early strengths
  - Comparable or better later strengths
  - Similar or slightly longer set times
  - Excellent concrete finishing properties
  - Lower bleeding and slump loss
  - Highly successful in products plants
  - No differences in water demand
  - Excellent response with SCM's and chemical admixtures

Durability testing (±10% LS) – favorable data

- Production samples, 2005 – 2007
  - No issues indicated
  - Essentially equivalent performance to that of non-limestone cements from the same plants, some slight enhancements:

    ASTM C 1012 Length Change
    ASTM C 1260 and C1567 ASR Testing
    ASTM C 666 Freeze-Thaw
    ASTM C 672 Salt Scaling
    ASTM C 157 Drying Shrinkage
    ASTM C 39 Compressive Strength (500 lb. Mix)
    ASTM C 39 Compressive Strength (564 lb. Mix)
    ASTM C 1202 Permeability (500 lb. Mix)
    ASTM C 1202 Permeability (564 lb. Mix)
- Similar data from published references

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Performance-enhancing

Research shows ways of reducing concrete's footprint

One of the most extraordinary things about ASTM C1157 GU performance cements is how ordinary they are. Compared to ASTM C150/AASHTO M 85 portland cements, they have similar strength gain characteristics, can be used under identical environmental conditions, are indistinguishable during mixing and placement and have similar durability characteristics.

The only major difference between the two cements is what is missing. The energy and carbon-dioxide footprint may be decreased 10% or more for ASTM C1157 GU performance cement compared with ordinary portland cement . . . and that is something extraordinary.

This is extremely important, because sustainability and sustainable design continue to grow in significance as resources grow scarce, the cost of energy increases and environmental stewardship is integrated into all elements of transportation design and construction. As a result of its relatively low cost, local availability, versatility and hallmark longevity, portland cement concrete is the most widely used building material on the planet.

This article discusses testing conducted by an independent laboratory of two ASTM C1157 GU portland-limestone cements produced by Holcim (US) Inc. in Colorado and Utah and several projects constructed using these cements to illustrate how extraordinarily ordinary these cements are.

Clinker part of clincher

So why is the manufacture of portland cement so CO_2 intensive? There are two primary sources of CO_2 inherent in the manufacturing

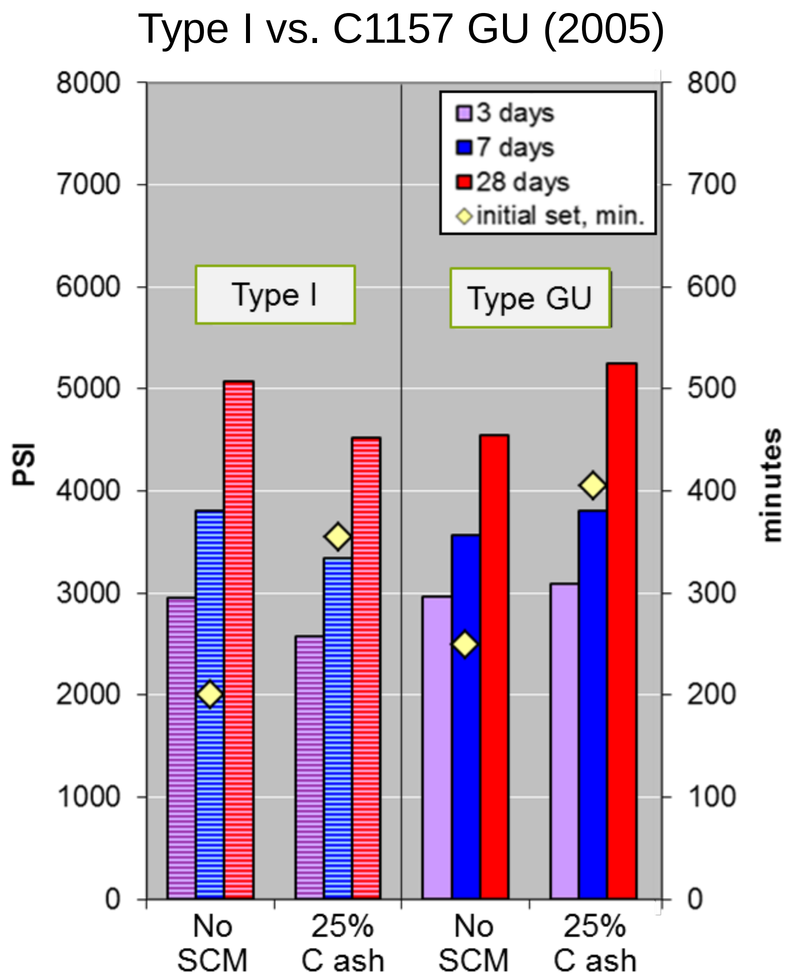
10% LS Paving in Colorado & Utah

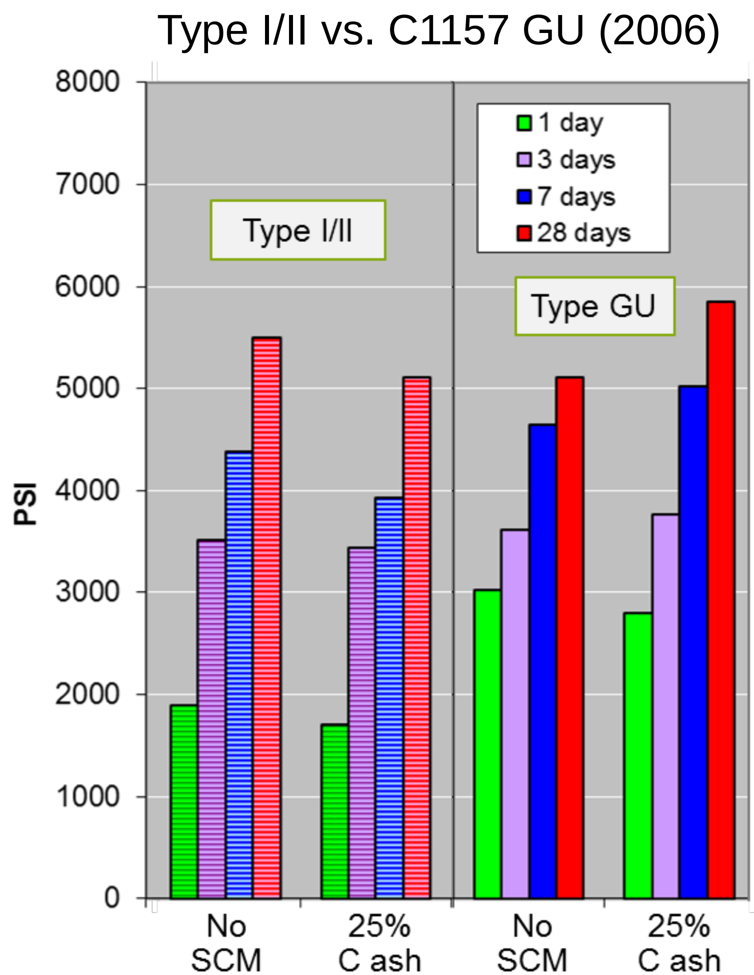
- DOT projects & urban
- Over 100 miles
- Excellent performance
- Documentation of durability w/ comparisons to C150 mixtures
- Topic of several papers, session presentations

First indications of unexpected “synergies”

- 10% LS ASTM C1157 Type GU cements, two HUS plants
  - Performance goals – slightly higher 1-day strengths (100 to 200 psi)
    - Fineness via blaine, typically 80 to 120 m^2/kg higher (nearer Type III)
    - Fineness via #325 sieve, similar or slightly higher % passing
- Concrete properties noted and reported:
  - Straight cement concrete mixtures trended with cement properties but <u>mixtures with SCM’s showed consistently enhanced strengths</u>
  - Very good finishing properties
  - Quite successful in concrete block and other products production

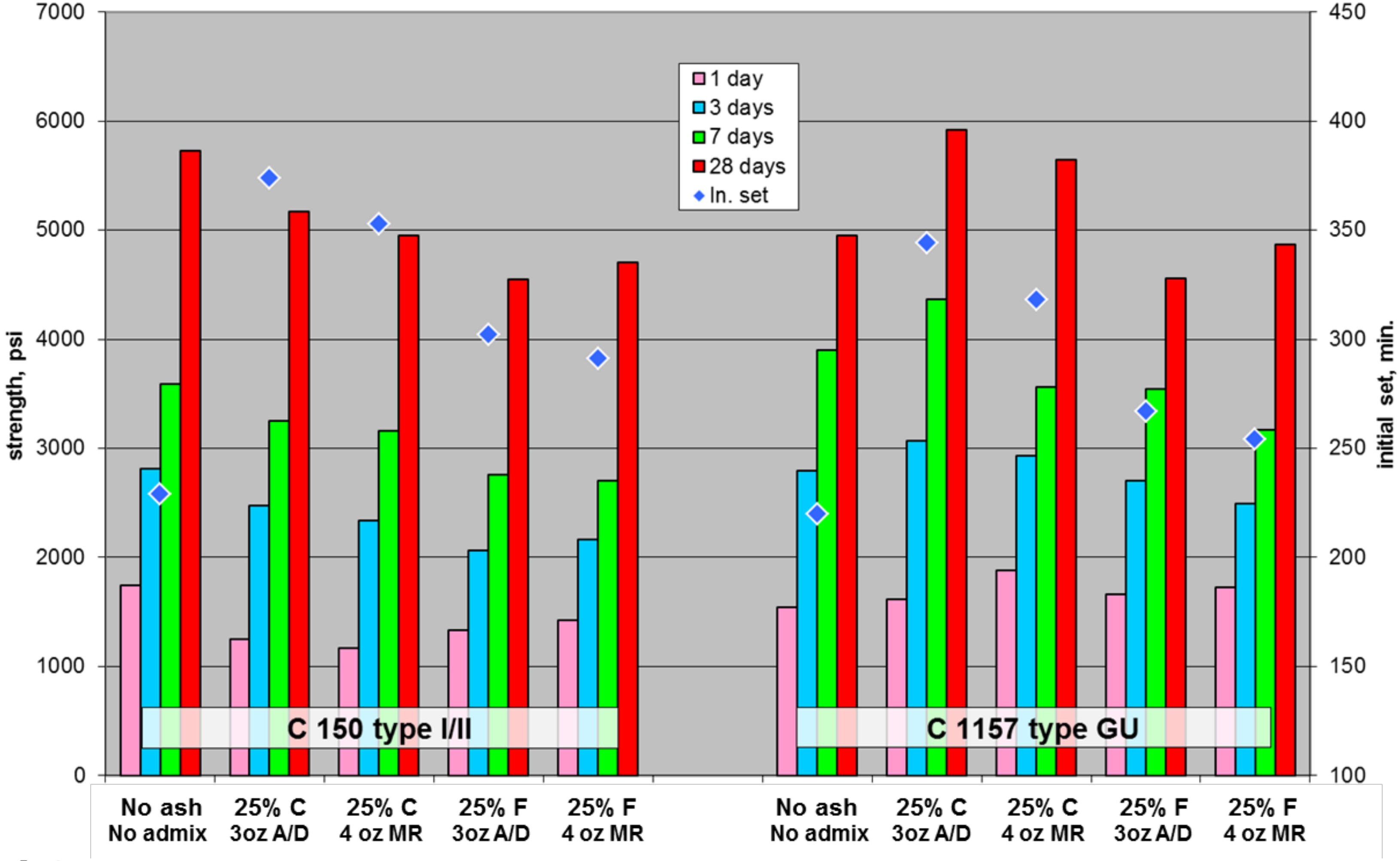
Example concrete data, enhanced synergy with fly ash



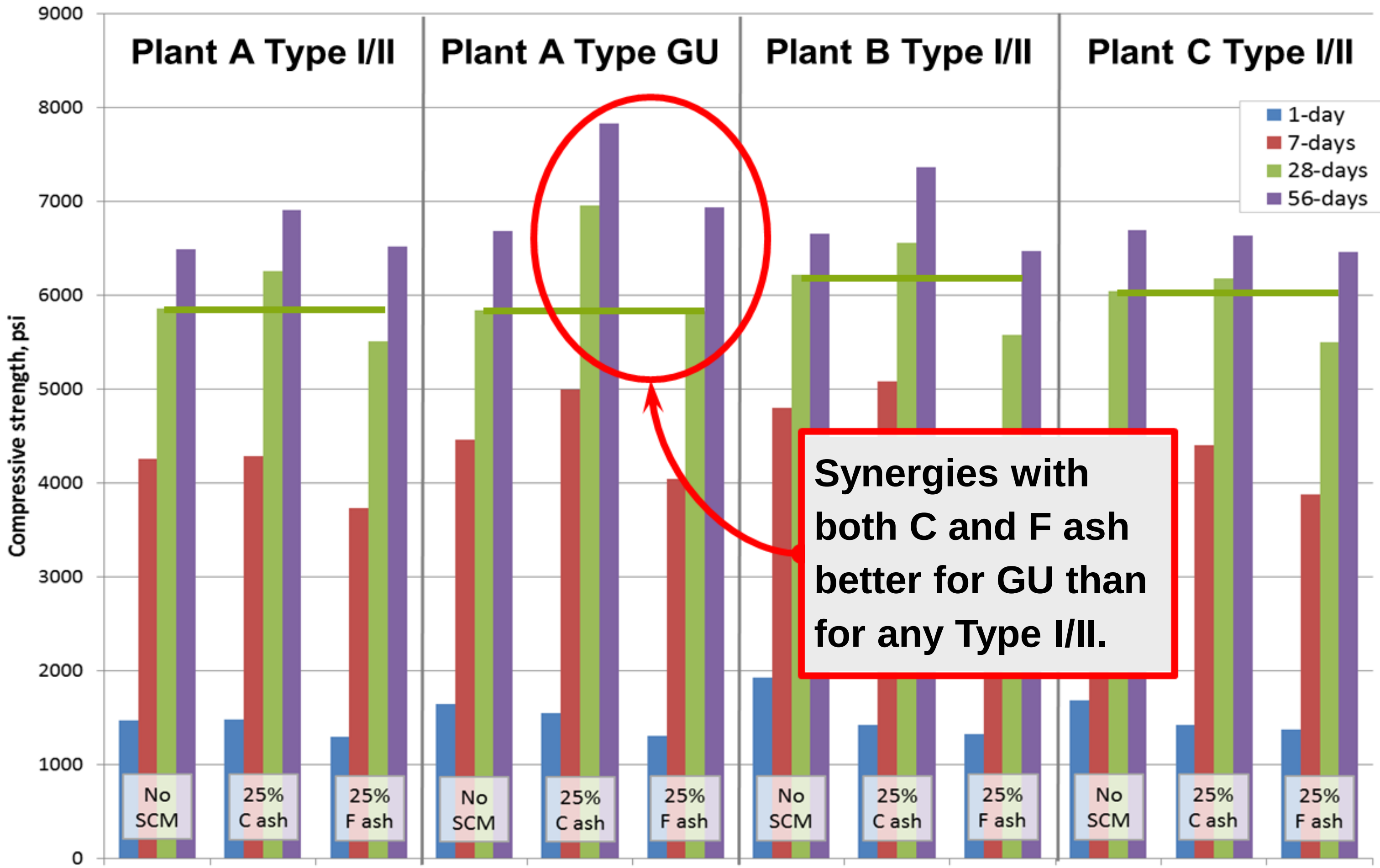


517 pcy concrete mixtures, gravel aggregates, C150 vs. C1157 cement comparisons

- Type I/II and 10% LS Type GU cements (2008) compared, concrete mixes w/ gravel CA, 517 pcy total cementitious, 5” slump
- 100% cement mixes w/o admix compared to 25% Class C ash and 25% Class F ash mixtures with mild dosages of 2 different WR’s



10% LS C1157 GU compared to Type I/II's from 3 plants for synergy effects with C and F ash, **averages of 3 samples, each mixture**



Shown are strength averages of 3 identical 517 pcy cementious, gravel agg. mixes with 3 different samples of each cement, March-June, 2011

Literature review on limestone synergies

References

Bentz, D. P.; Ferraris, C. F.; De la Varga, I.; Peltz, M. A.; and Winpigler, J. A., "Mixture Proportioning Options for Improving High Volume Fly Ash Concretes," *International Journal of Pavement Research and Technology*, V. 3, No. 5, 2010, 234-240.

Bentz, D. P., "Powder Additions to Mitigate Retardation in High-Volume Fly Ash Mixtures," *ACI Materials Journal*, V. 107, No. 5, September-October 2010, 506-514.

Bentz, D. P.; De la Varga, I.; Sato, T.; and Weiss, W. J., "Fine Limestone Additions to Regulate Setting in High Volume Fly Ash Mixtures," submitted to *Cement and Concrete Composites*, 2011.

De Weerdt, K.; Kjellsen, K. O.; Sellevold, E.; and Justnes, H., "Synergy Between Fly Ash and Limestone Powder in Ternary Cements," *Cement and Concrete Composites*, V. 33, No. 1, January 2011, 30-38.

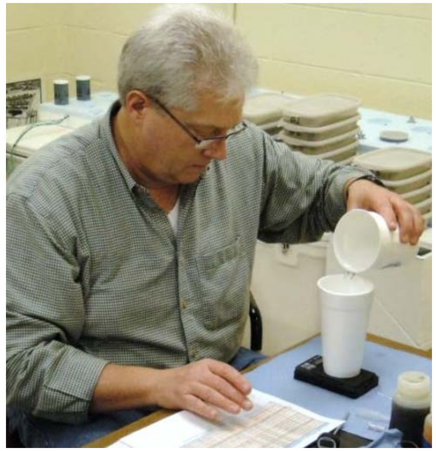
Gurney, L.; Bentz, D.P.; Sato, T.; and Weiss, W.J., "Using Limestone to Reduce Set Retardation in High Volume Fly Ash Mixtures: Improving Constructability for Sustainability," submitted for presentation to the Transportation Research Board annual conference, January, 2012.

Mehta, P. K., "High-Performance, High-Volume Fly Ash Concrete for Sustainable Development," Proceedings of the International Workshop on Sustainable Development and Concrete Technology, Beijing, China, 2004, 3–14.

Mounanga, P.; Khokhar, M.I.A.; Hachem, R. E.; and Loukili, A., "Improvement of the Early-Age Reactivity of Fly Ash and Blast Furnace Slag Cementitious Systems Using Limestone Filler. Materials and Structures, Vol. 44, 2011, 437-453.

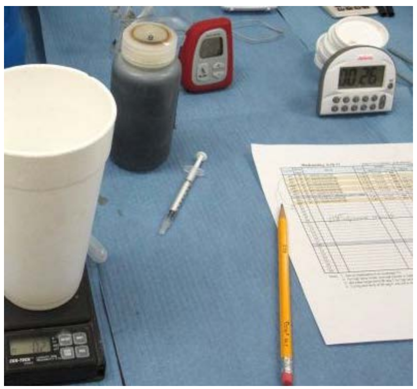
Sato, T., and Beaudoin, J. J., "The Effect of Nano-Sized $CaCO_3$ Addition on the Hydration of Cement Paste Containing High Volumes of Fly Ash," Proceedings of the 12th International Congress on the Chemistry of Cement, July 2007.

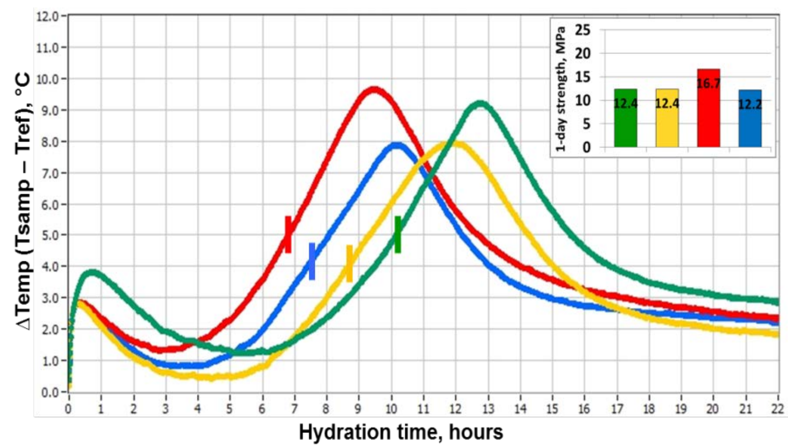
- A number of papers (esp. since 2010) report LS synergy with SCM's, in addition to known OPC interactions
- Reported beneficial LS interaction & synergy mechanisms include:
  - **A) Enhanced particle packing via improved overall PSD**
  - **B) Nucleation site phenomenon**
  - **C) Formation of carboaluminates from calcium carbonate reactions with aluminates (some from OPC but more from SCM's), increasing hydration products, decreasing porosity, and enhancing strength**.
- Synergies are reported to accelerate set as well as increase strength
- All related benefits improve as LS surface area (fineness) increases



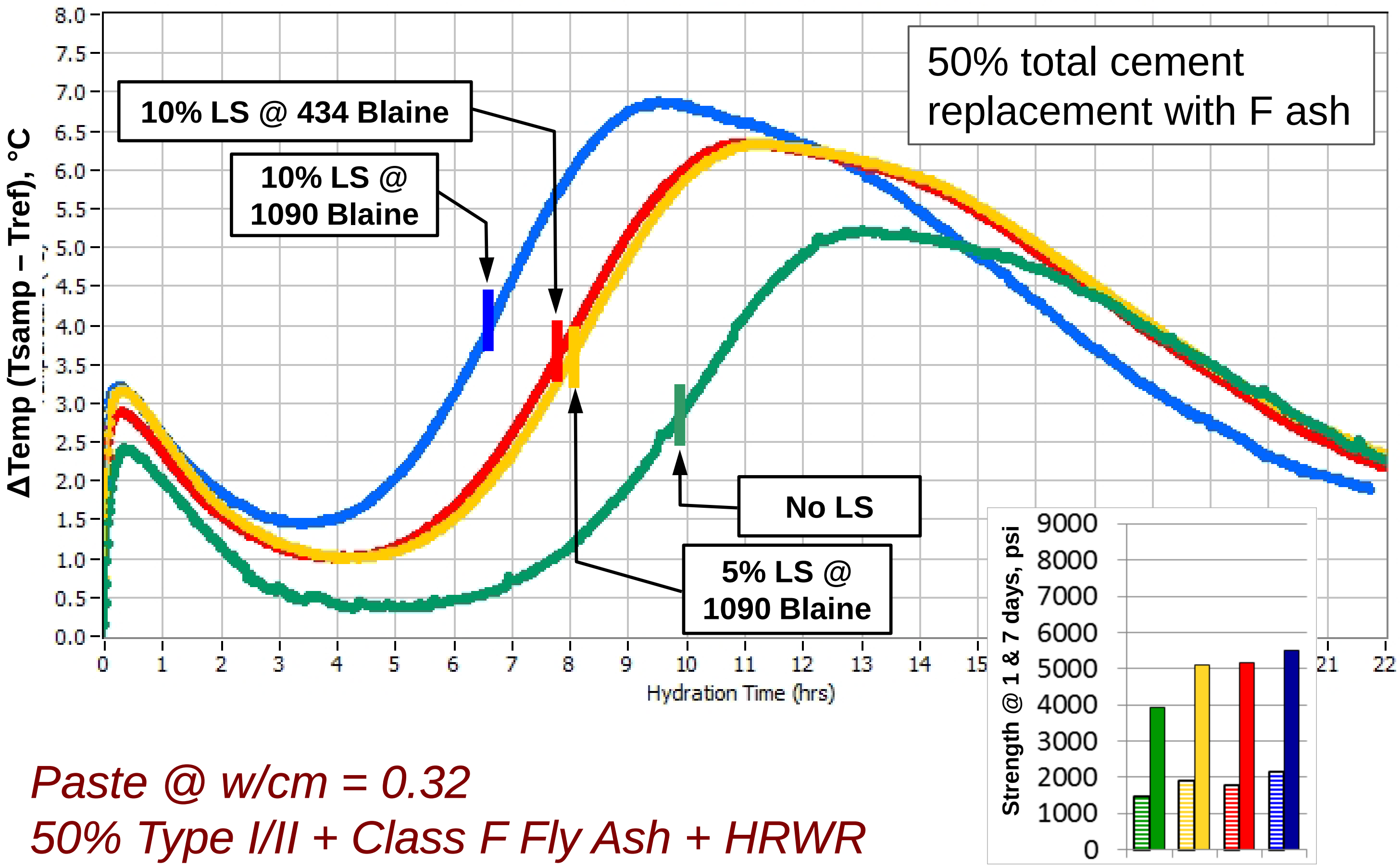
Thermal profile and strength testing of lab paste mixtures

for quick evaluation of multiple variables, investigation of trends





Thermal set and strength trends in paste (HVFA example) with 2 fineness levels of LS added as SCM



1- & 7-day strengths

Paste @ w/cm = 0.32
50% Type I/II + Class F Fly Ash + HRWR
with and without added ground LS (434 or 1090 Blaine)

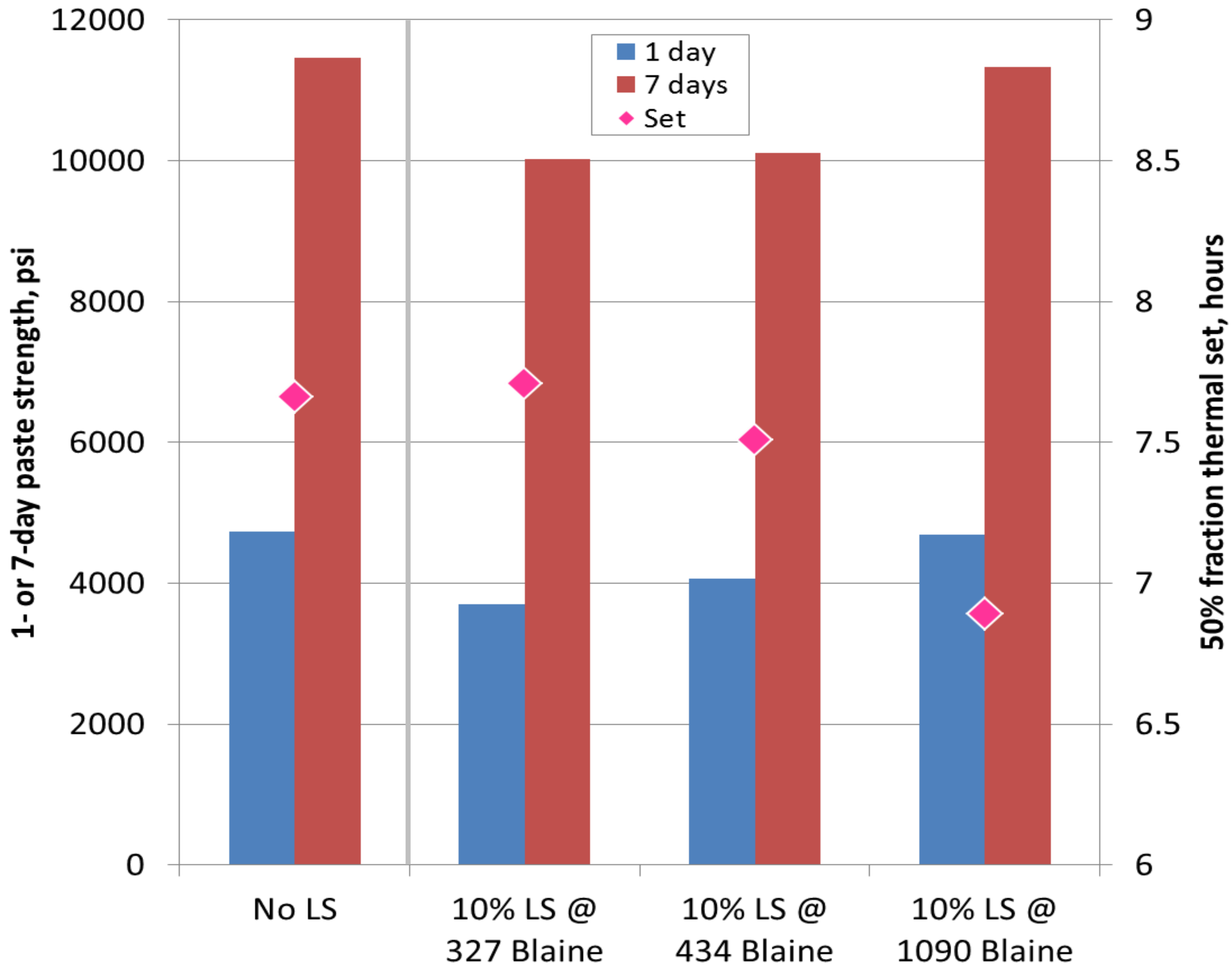
Constant w/c and OPC content – added LS replaced fly ash

Paste mixtures – evaluation of trends for thermal set and strengths, multiple PLC & SCM variables

- Objective: to help evaluate the fineness of limestone (& clinker) fractions, related performance impacts
- Simulations of PLC with separately added LS
  - Ground LS of 327 to 1090 m^2/kg Blaine
  - Typically 10% of OPC total, some 15%
  - Comparisons with 10% LS mill-ground samples
- SCM's at generally higher-than-normal proportions (C and F ash) to exaggerate trends:
  - 40% replacement of cement
    - Class C fly ash w/ aggressive properties
    - Class F fly ash, low Ca, pure pozzolan
    - Some slag cement, C989 Grade 100 (common, mild replacement rate, but consistent for comparison value)
    - 14 oz/cwt HRWR, w/cm = 0.32

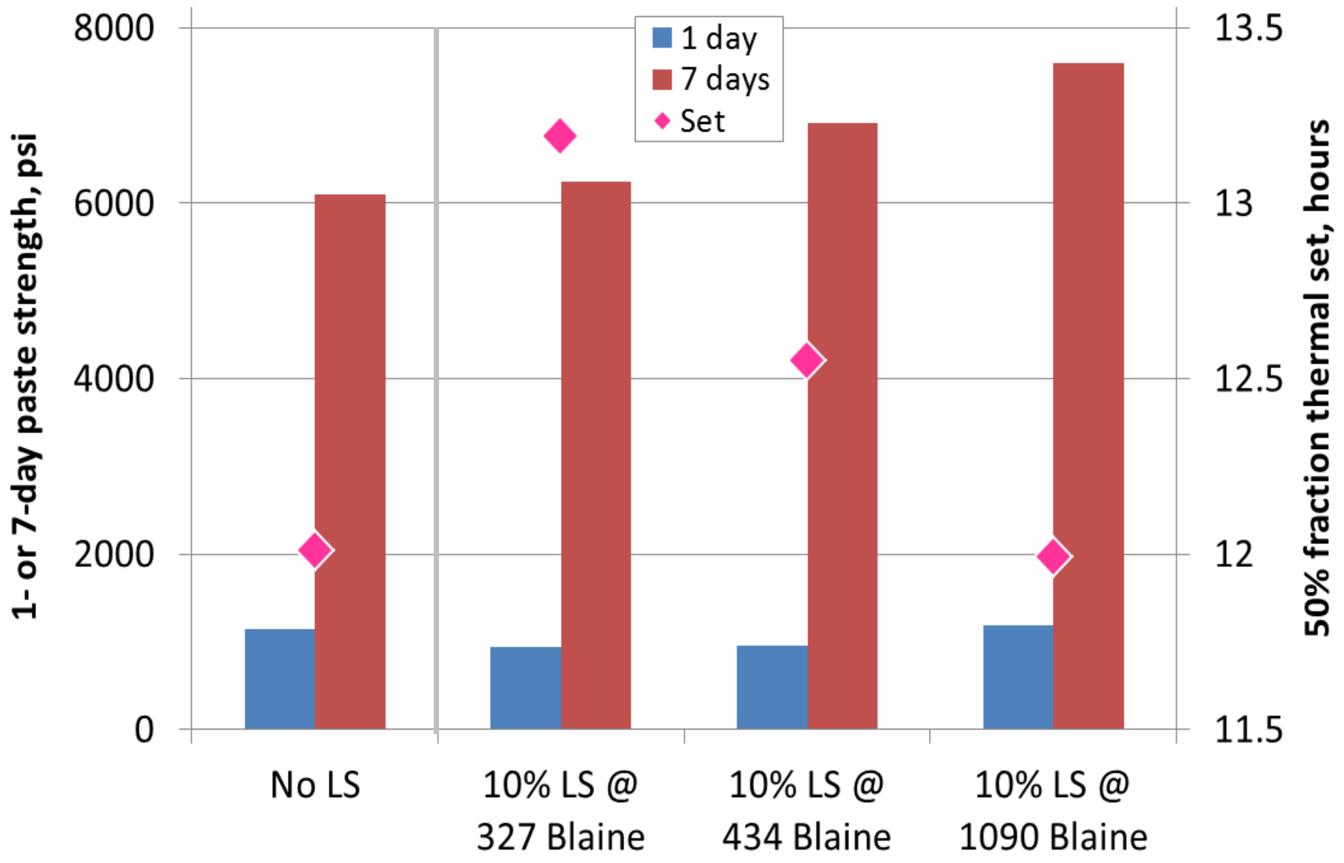
No SCM's, 10% LS @ 327 to 1090 Blaine

Type I/II cement, 360 Blaine



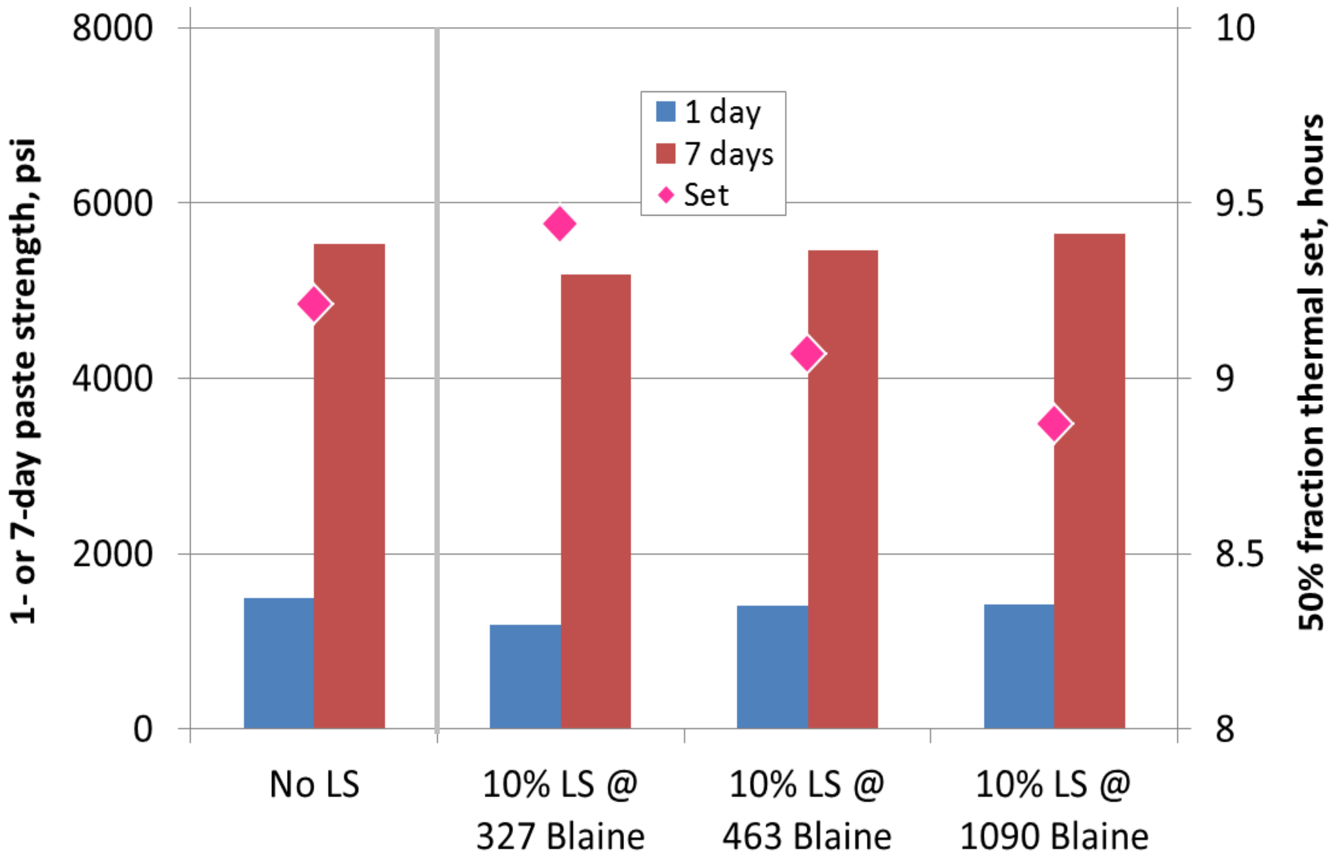
40% C ash, 10% LS @ 327 to 1090 Blaine

Type I/II cement, 360 Blaine



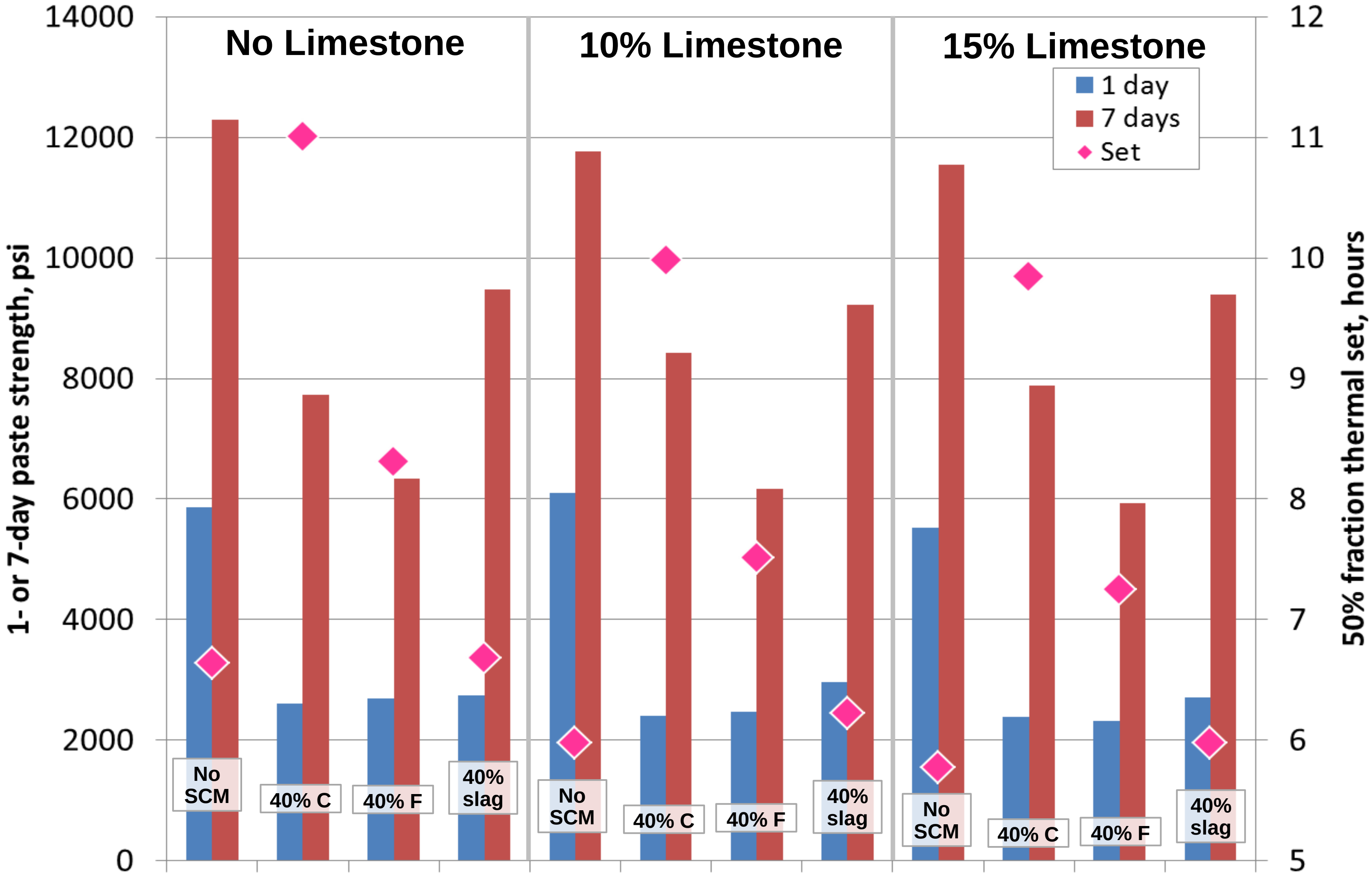
40% F ash, 10% LS @ 327 to 1090 Blaine

Type I/II
cement,
360 Blaine



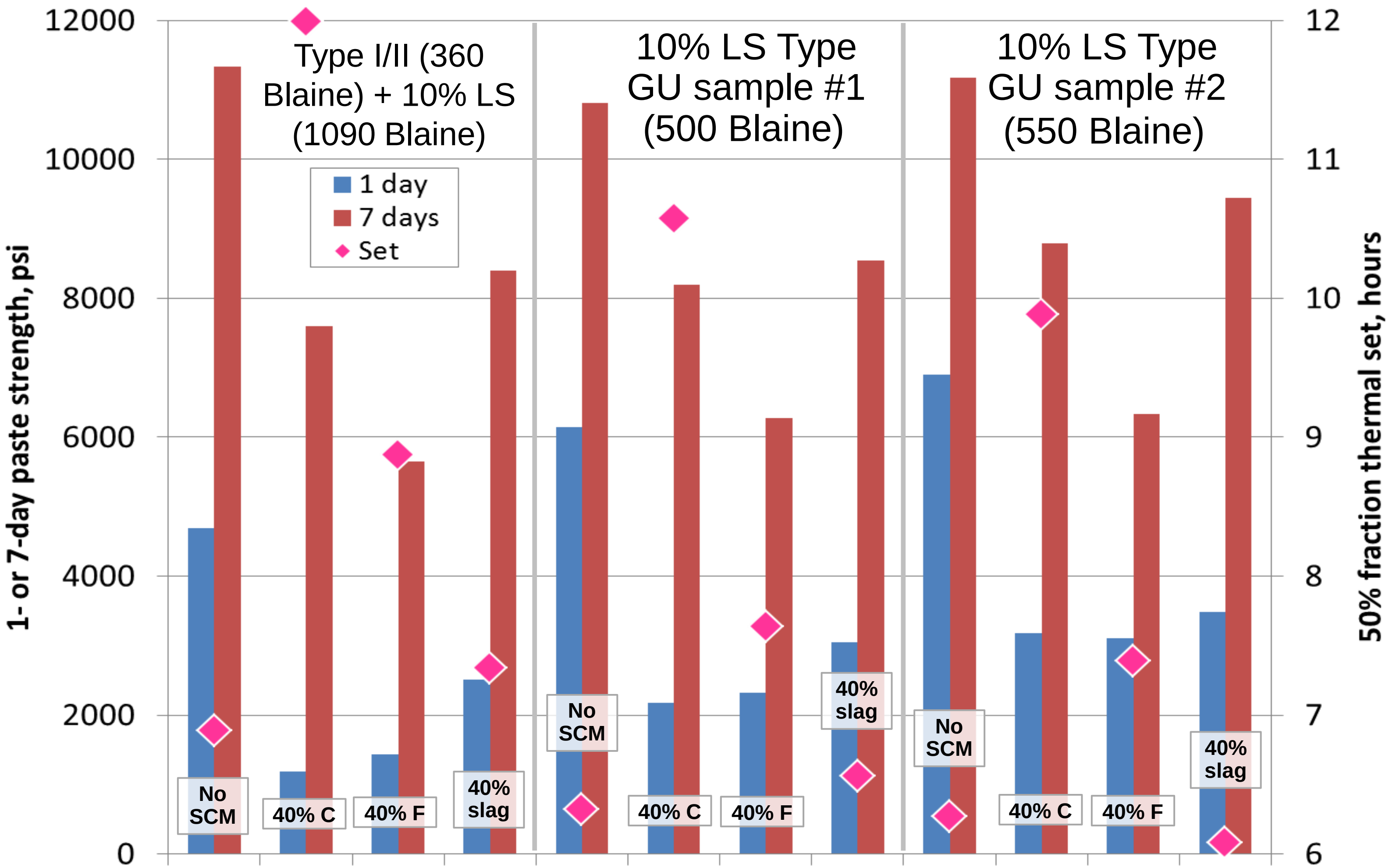
Type I/II cement, 400 Blaine

No SCM and 40% Class C ash, Class F ash, & slag mixtures with 0%, 10% and 15% LS (1090 Blaine)



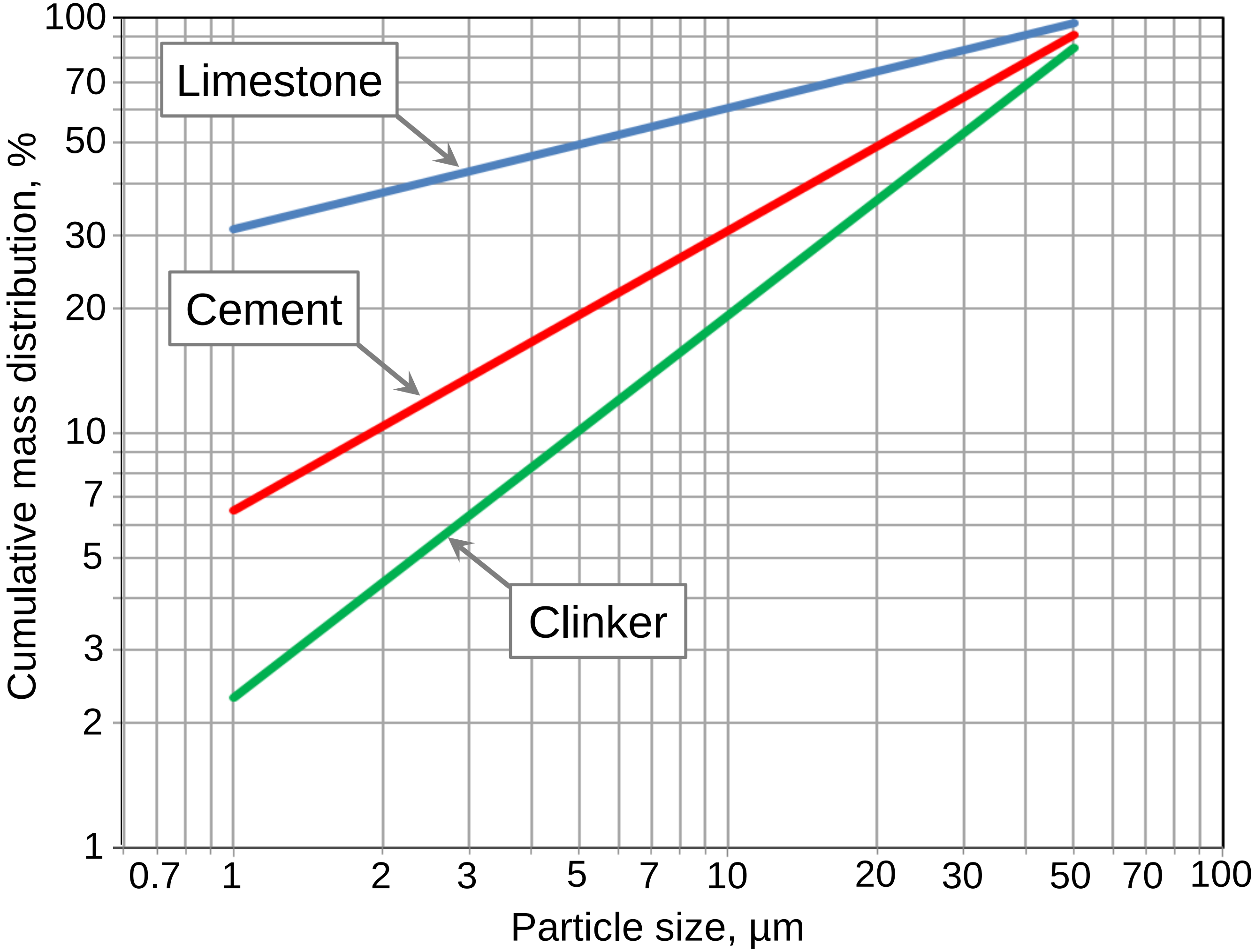
Holcim

10% added LS vs. 2 samples of mill-ground 10% LS GU



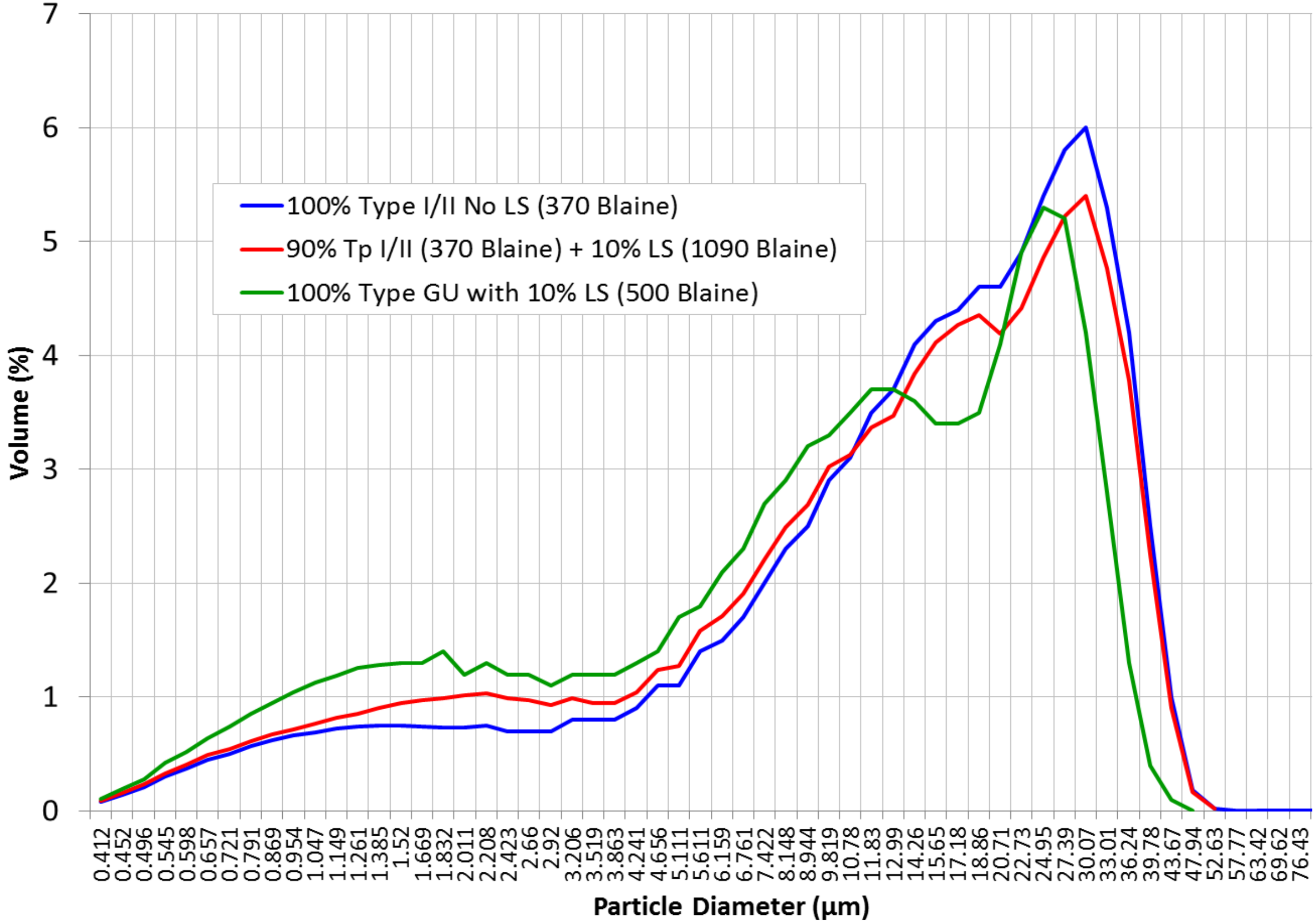
Fly ash "synergy" with mill-ground 10% LS cement samples slightly exceeds that with Type I/II + 10% separately-added LS of 1090 Blaine

Ball mill-ground PLC: fineness relationships of composite cement, LS and clinker fractions



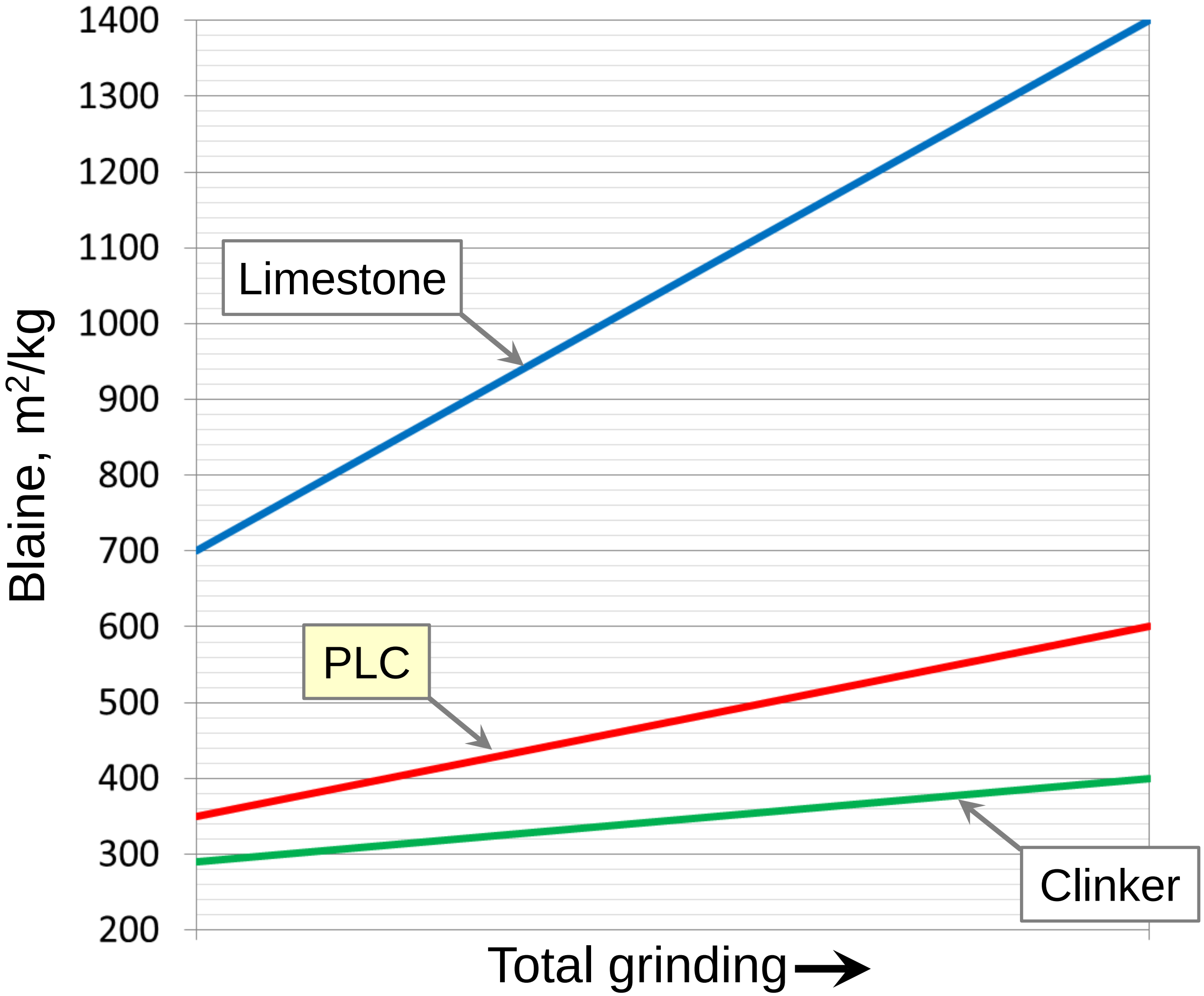
data from: Schiller, B., and Ellerbrock, H.-G., "The Grinding and Properties of Cement with Several Main Constituents, "*Zement-Kalk-Gips,* vol. 45, no. 7, July 1992, as discussed in *The Use of Limestone in Portland Cement: A State-of-the-Art Review,* PCA EB227, 2003.

PSD (differential volume) compared, Type I/II with and without 10% added LS vs. mill-ground 10% LS Type GU

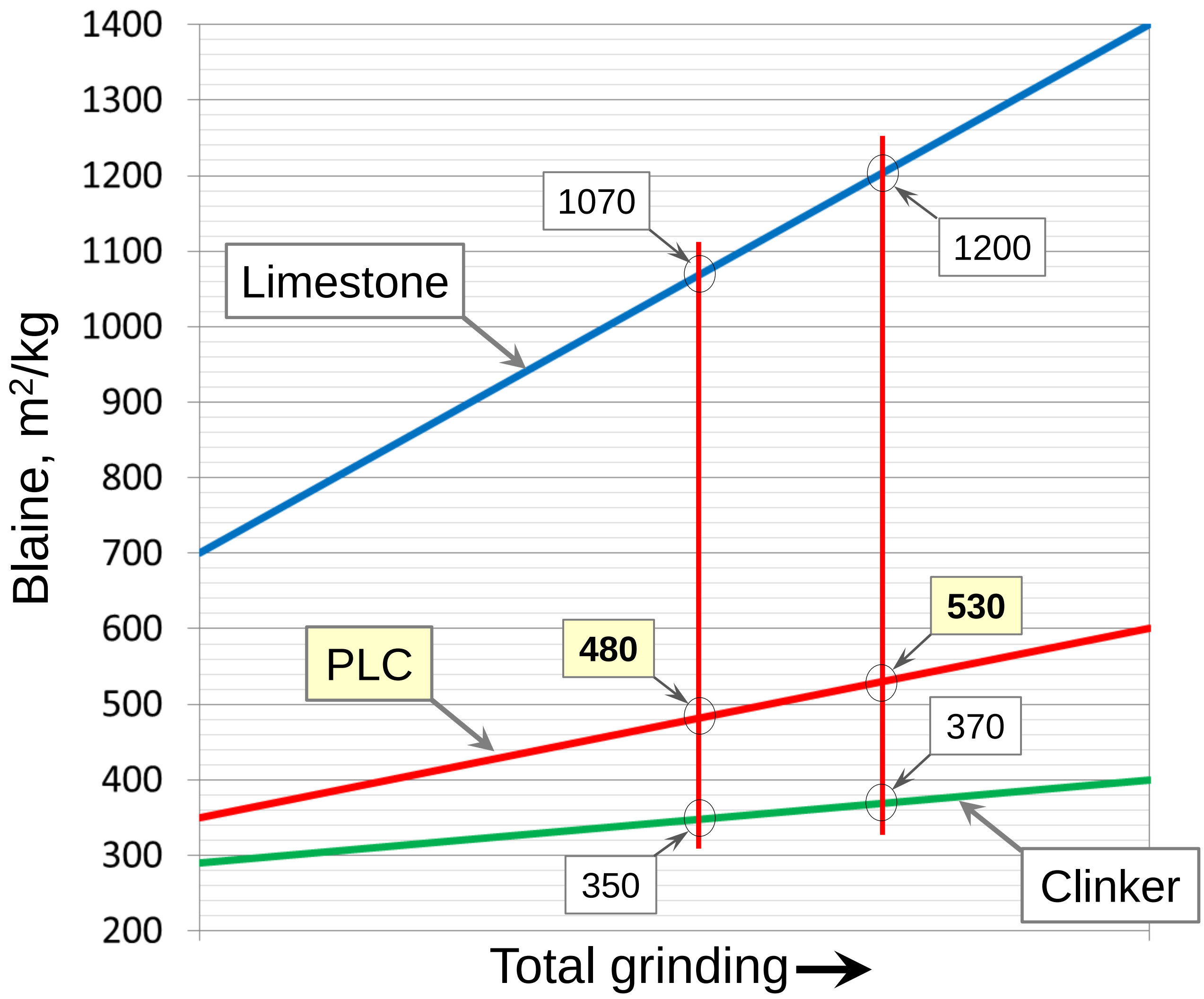


Particle size analyses of individual materials performed using a Beckman Coulter LS 13 320 laser diffraction PSA

Hypothetical Blaine relationships, LS / PLS / clinker, for a given mill system and set of materials



Example: suggested Blaine trends of component fractions for 2 Blaine levels of composite PLC



Summary / conclusions

- Portland-limestone cements produced at up to 15% LS have the potential to significantly improve concrete sustainability with performance equal to or better than C150 / M85 cements.
- Portland-limestone cements clearly hydrate with synergies contributed by limestone that enable enhanced setting and strength performance, especially in combination with SCM's.
- The extent of synergy benefits relates to LS fineness; clinker fineness similar to reference OPC's must be maintained in the composite PLC.
- The particle size distribution of PLC produced to optimum overall fineness in finish grinding ball mills appears well suited for synergy-driven performance enhancement.
- SCM replacement of cement as with traditionally-used C150 / M85 cements must be allowed and encouraged in order to achieve the maximum possible sustainability and performance benefits of PLC.
- Higher-than-traditional replacement rates with some SCM's appear possible without loss of performance, extending sustainability benefits.

Questions?

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