

# Interactions between $\text{BaCO}_3$ and OPC/BFS composite cements at $20^\circ\text{C}$ and $60^\circ\text{C}$

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# Outline

- Introduction
  - Why  $\text{BaCO}_3$ ?
  - Earlier work
- Experimental work
- Results and Discussion
- Conclusions
- Acknowledgments



## THORP Plant and BaCO<sub>3</sub>

THORP process for fuel reprocessing dissolves spent fuel in HNO<sub>3</sub> releasing <sup>14</sup>CO<sub>2</sub>. Gases are caustic scrubbed to remove <sup>14</sup>CO<sub>2</sub> forming sodium carbonate. Solution is treated with Ba(NO<sub>3</sub>)<sub>2</sub>, precipitating Ba<sup>14</sup>CO<sub>3</sub>, Final waste stream contains 20-30wt% Ba<sup>14</sup>CO<sub>3</sub> in a salt solution.

**<sup>14</sup>C t<sub>1/2</sub> = 5730 years**



## BaCO<sub>3</sub> slurry

- Classified as Intermediate level waste (ILW)
- Dewatered to about 20% BaCO<sub>3</sub> solids in a alkaline solution containing ~ 10% sodium nitrate/sodium nitrite
- Encapsulated in a BFS:OPC composite cement and stored in 500l drums
- What reactions might occur?
- What is likely durability?



# What happens to the $\text{BaCO}_3$ in cement?

- Literature information on Ba salts in OPC is sparse
  - $\text{BaCO}_3$  added to  $\text{C}_3\text{A}$  slows hydration with formation of hemicarbonatite  
 $\text{C}_3\text{A} \cdot 0.5\text{CaCO}_3 \cdot 0.5\text{Ca}(\text{OH})_2 \cdot 11.5\text{H}_2\text{O}$   
containing 6% Ba<sup>(1)</sup>
  - $\text{Ba}(\text{NO}_3)_2$  reduces degree of hydration<sup>(2)</sup>
  - $\text{BaSO}_4$  was formed along with  $\text{BaCO}_3$ <sup>(2,3)</sup>

1. Dumitru et al. 10th ICCG Gothenburg, 1997, 3, 5-9.

2 Ouki & Hills, Waste Manage., 2002, 22(2), 147-151.

3 McWhinney et al. J. Environ. Sci. Health, 1990, A25(5), 463-477.

# Any similarities with $\text{CaCO}_3$ ?

- OPC hydrated with  $\text{CaCO}_3$ , produces an AFm phase, calcium monocarboaluminate,  $\text{C}_4\text{A}\hat{\text{C}}\text{H}_{11}$  (Mc), which controls hydration<sup>(1)</sup>
- Accelerates hydration of  $\text{C}_3\text{S}$ <sup>(2-4)</sup>
- Some  $\text{CaCO}_3$  incorporated in  $\text{C}_3\text{S}$ <sup>(4)</sup>
- Maximum amount of  $\text{CaCO}_3$  reacted is low  
~ 2-3%

1 Feldman et al., J. Am. Ceram. Soc., 1965, 48(1), 25-30.

2 Ramachandran, 8th ICCO, Rio de Janeiro, 1986, 5, 178-182

3 Ramachandran, Thermochem. Acta, 1988, 127, 385-394

4 Ramachandran & Zhang, Il Cemento, 1986, 83(3), 129-152.



# Group II Compound Solubilities



The University  
Of  
Sheffield.

	Solubility (°C) g/100cc		Ksp(25°C)
Ca(OH) <sub>2</sub>	0.160 <sup>20</sup>	0.077 <sup>100</sup>	5.02 x 10 <sup>-6</sup>
CaCO <sub>3</sub>	0.00066 <sup>20</sup>	0.0018 <sup>75</sup>	3.36 x 10 <sup>-9</sup>
CaSO <sub>4</sub> .2H <sub>2</sub> O	0.241 <sup>20</sup>	0.222 <sup>100</sup>	1.96 x 10 <sup>-5</sup>
CaSO <sub>4</sub> .0.5H <sub>2</sub> O	0.30 <sup>20</sup>		4.27 x 10 <sup>-5</sup>
CaSO <sub>4</sub>	0.209 <sup>30</sup>	0.162 <sup>100</sup>	2.36 x 10 <sup>-5</sup>
Sr(OH) <sub>2</sub>	2.25 <sup>25</sup>	21.83 <sup>100</sup>	6.40 x 10 <sup>-3</sup>
SrCO <sub>3</sub>	0.00034 <sup>20</sup>	0.065 <sup>100</sup>	5.60 x 10 <sup>-10</sup>
SrSO <sub>4</sub>	0.0135 <sup>25</sup>		3.44 x 10 <sup>-7</sup>
Ba(OH) <sub>2</sub> .8H <sub>2</sub> O	4.91 <sup>25</sup>	94.778	2.55 x 10 <sup>-4</sup>
BaCO <sub>3</sub>	0.0014 <sup>20</sup>	0.006 <sup>100</sup>	2.58 x 10 <sup>-9</sup>
BaSO <sub>4</sub>	0.00031 <sup>20</sup>	0.000336 <sup>50</sup>	1.08 x 10 <sup>-10</sup>



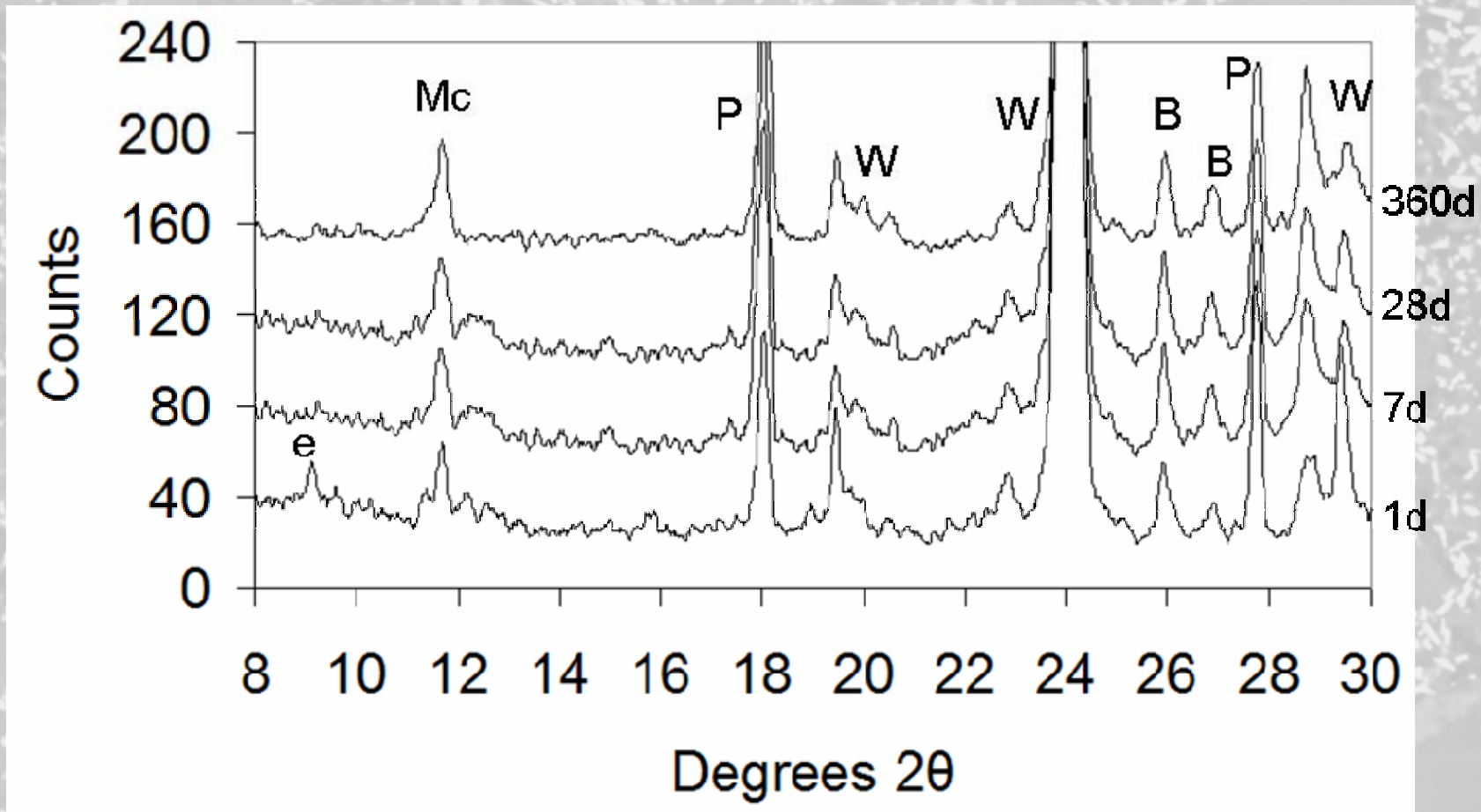
# Experimental

- OPC and BFS:OPC 9:1 mixed with 0 and 30%  $\text{BaCO}_3$  at w/s ratio of 0.37 hydrated at 20 and 60°C, 95% RH for times up to 2 years
- Examined by SEM/EDS, XRD and ICC (up to 72 hrs)
- $\text{C}_3\text{A}$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{BaCO}_3$  in 1:1:1 ratio mixed and examined at 2 and 24 hours



# Results

## BaCO<sub>3</sub> in OPC

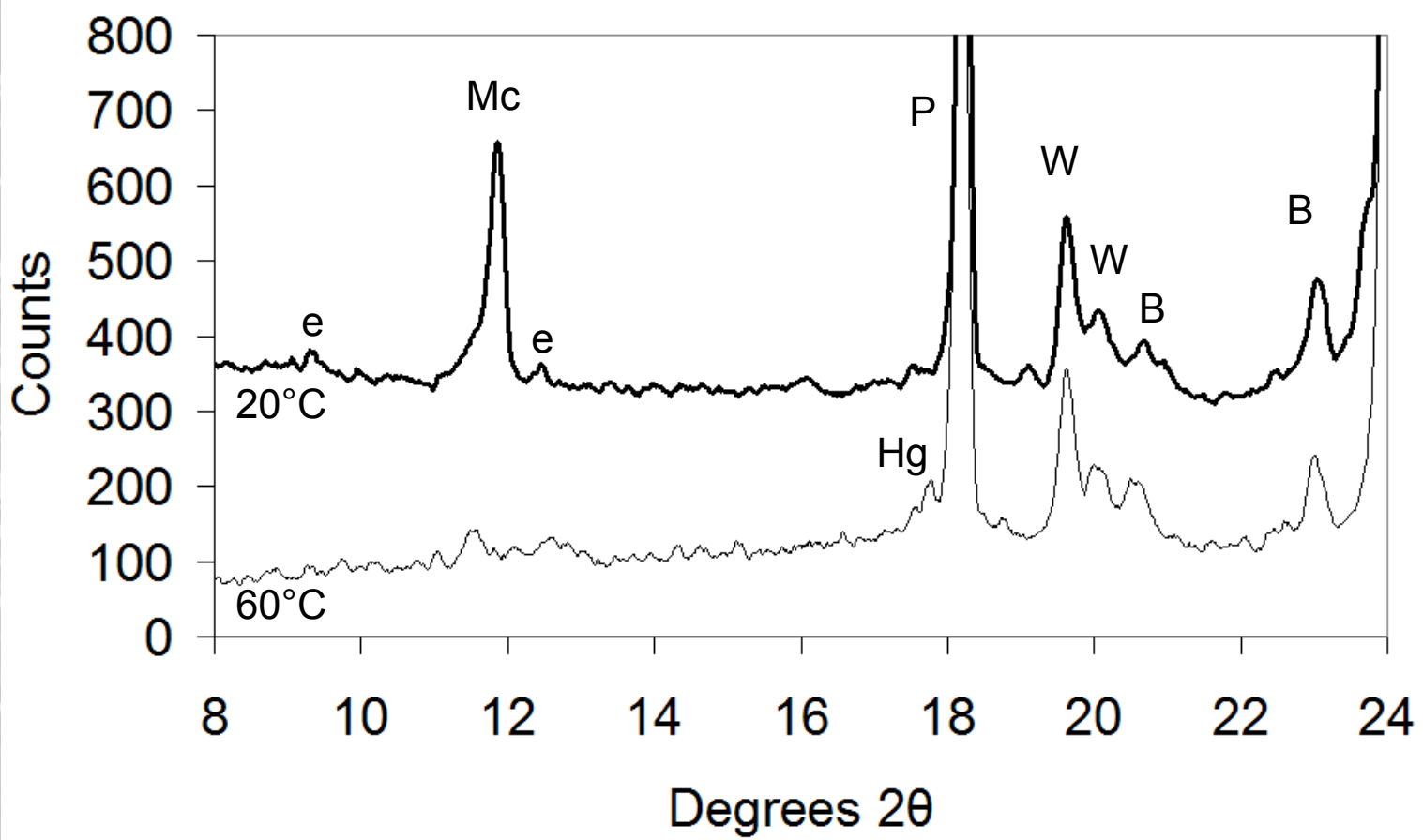


OPC with 30wt% BaCO<sub>3</sub> w/s 0.37 cured at 20°C between 24 hours and 360 days

Mc – Calcium monocarboaluminate, P – Ca(OH)<sub>2</sub>, W – BaCO<sub>3</sub>, B – BaSO<sub>4</sub>,

e – ettringite





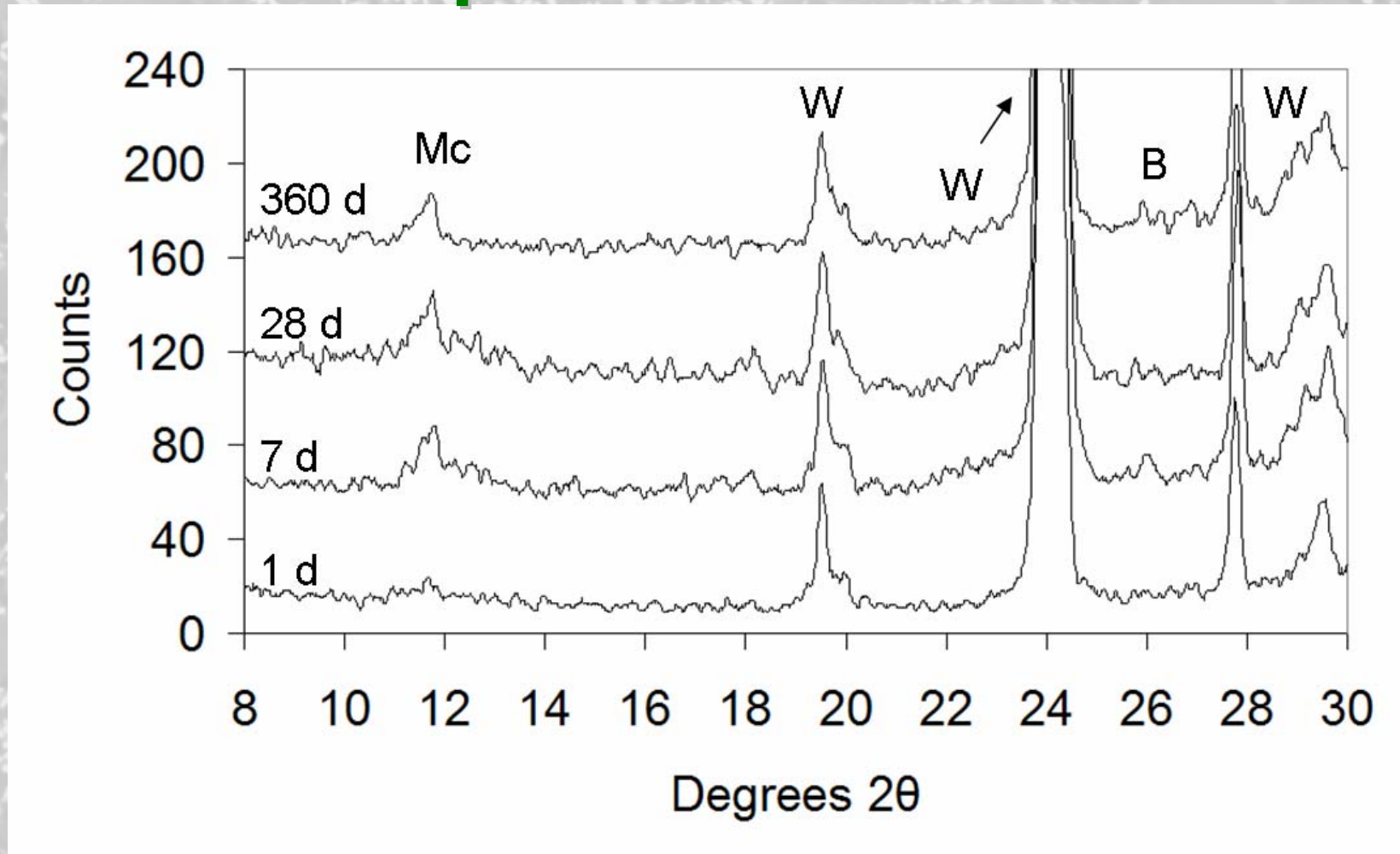
**100% OPC with 30wt% BaCO<sub>3</sub> w/s 0.37 cured at 20 and 60°C 360 days**

**e – ettringite, Mc – Calcium monocarboaluminate, P – Ca(OH)<sub>2</sub>, W – BaCO<sub>3</sub>,  
B – BaSO<sub>4</sub>, Hg – Hydrogarnet-type phase**

# BaCO<sub>3</sub> in OPC

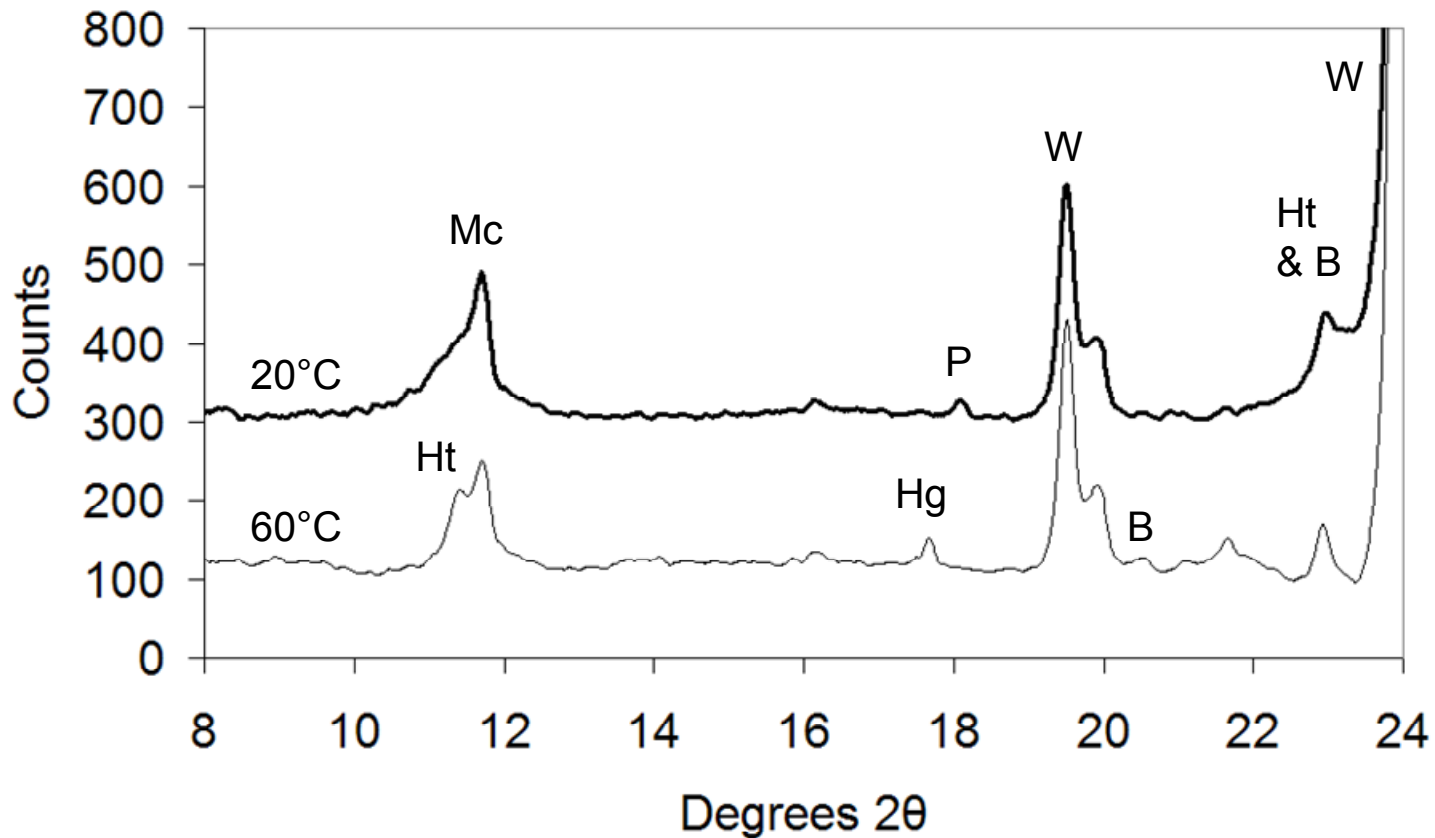
- Crystalline hydration products formed at 20°C were Ca(OH)<sub>2</sub>, C<sub>3</sub>A.3CaSO<sub>4</sub>.32H<sub>2</sub>O and C<sub>3</sub>A.CaCO<sub>3</sub>.12H<sub>2</sub>O
- BaSO<sub>4</sub> formed from BaCO<sub>3</sub> and SO<sub>4</sub><sup>2-</sup> ions from OPC releasing CO<sub>3</sub><sup>2-</sup>
- Ettringite slowly converts to BaSO<sub>4</sub> and Mc.
- An increase in temperature sees loss of Mc and formation of a hydrogarnet phase
- No specific carbonate phase observed at 60°C





9:1 BFS:OPC with 30wt% BaCO<sub>3</sub> cured at 60°C between 24 hours and 360 days

Mc – Calcium monocarboaluminate, W – BaCO<sub>3</sub>, B – BaSO<sub>4</sub>



9:1 BFS:OPC 30wt% BaCO<sub>3</sub> cured at 20°C and 60°C 360 days

Mc – Calcium monocarboaluminate, W – BaCO<sub>3</sub>, B – BaSO<sub>4</sub>, P- Ca(OH)<sub>2</sub>, Ht – Hydrotalcite, Hg - Hydrogarnet

# BaCO<sub>3</sub> in BFS:OPC composite

- Similar products to OPC but with much less Ca(OH)<sub>2</sub>.
- Mc is stable at 60°C, possibly due to lower pH and increased aluminium availability.
- Smaller amounts of BaSO<sub>4</sub> formed reflecting lower SO<sub>4</sub><sup>2-</sup> available.
- Hydrotalcite formed from slag
- Hydrogarnet still formed as Mc decomposes.



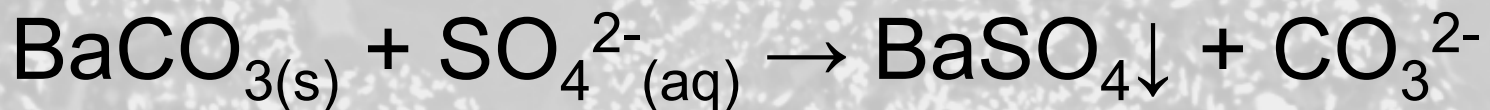




1:1:1

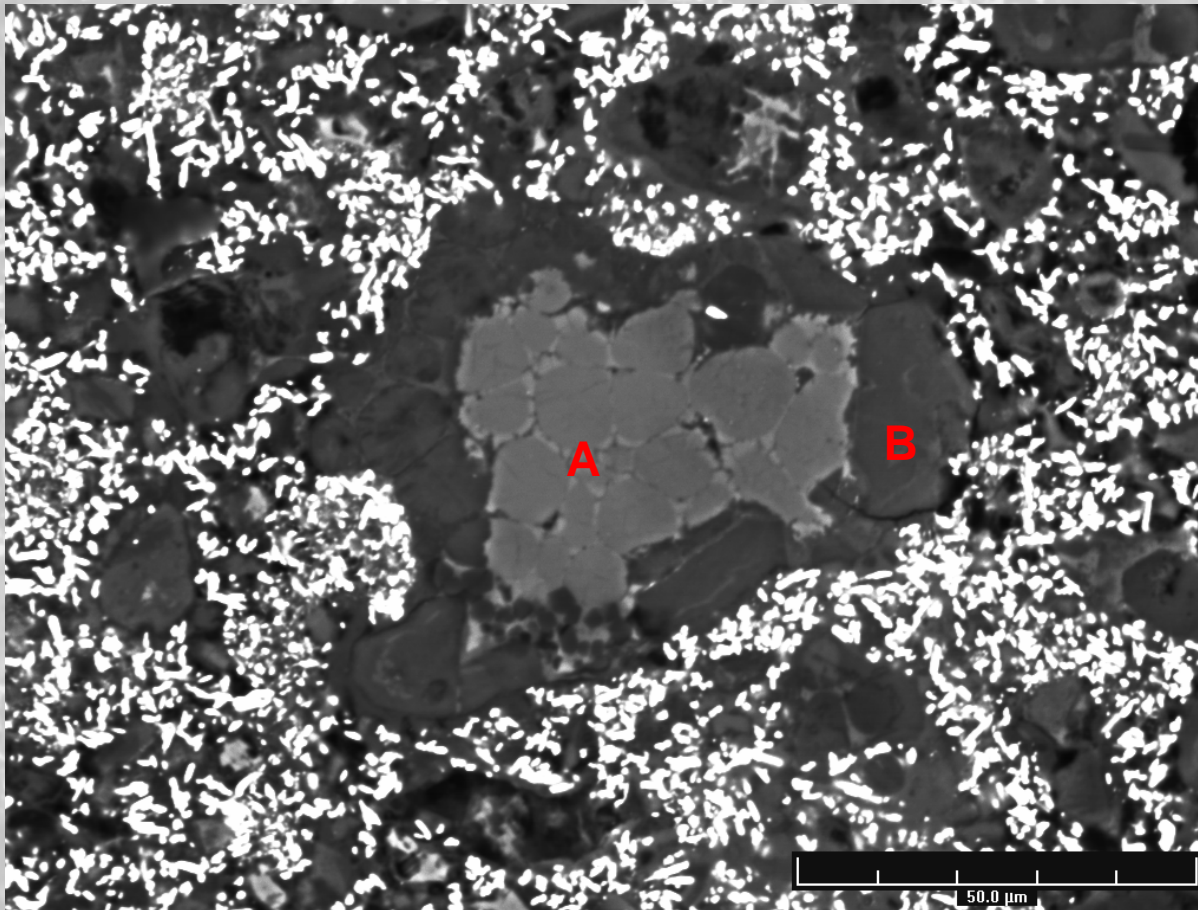
 $C_3A:CaSO_4 \cdot 2H_2O:BaCO_3$ 

- Both ettringite and  $BaSO_4$  formed initially as  $C_3A$  reacted rapidly
- With time, intensity of  $BaCO_3$  peaks decreases with increase of  $BaSO_4$ .  $Mc$  forms as more available  $CO_3^{2-}$  in solution.
- Almost all gypsum has disappeared by 24 hours.





# Microstructure in OPC with $\text{BaCO}_3$

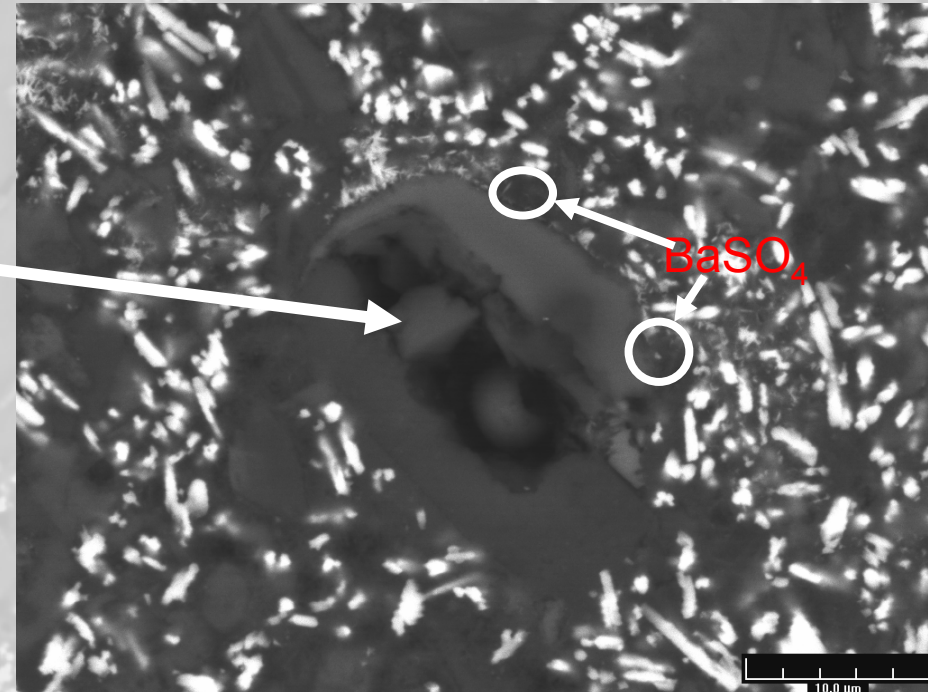
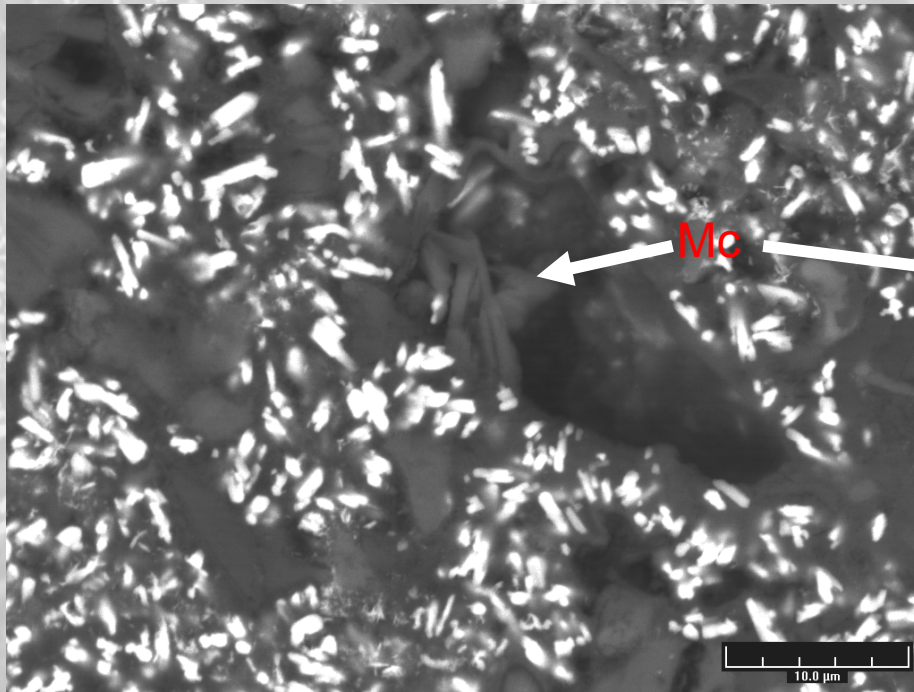


OPC with  $\text{BaCO}_3$  cured for 720 days at 20°C

A – anhydrous OPC, B – hydration rim containing traces of barium



# Voids are formed as OPC grains fully react

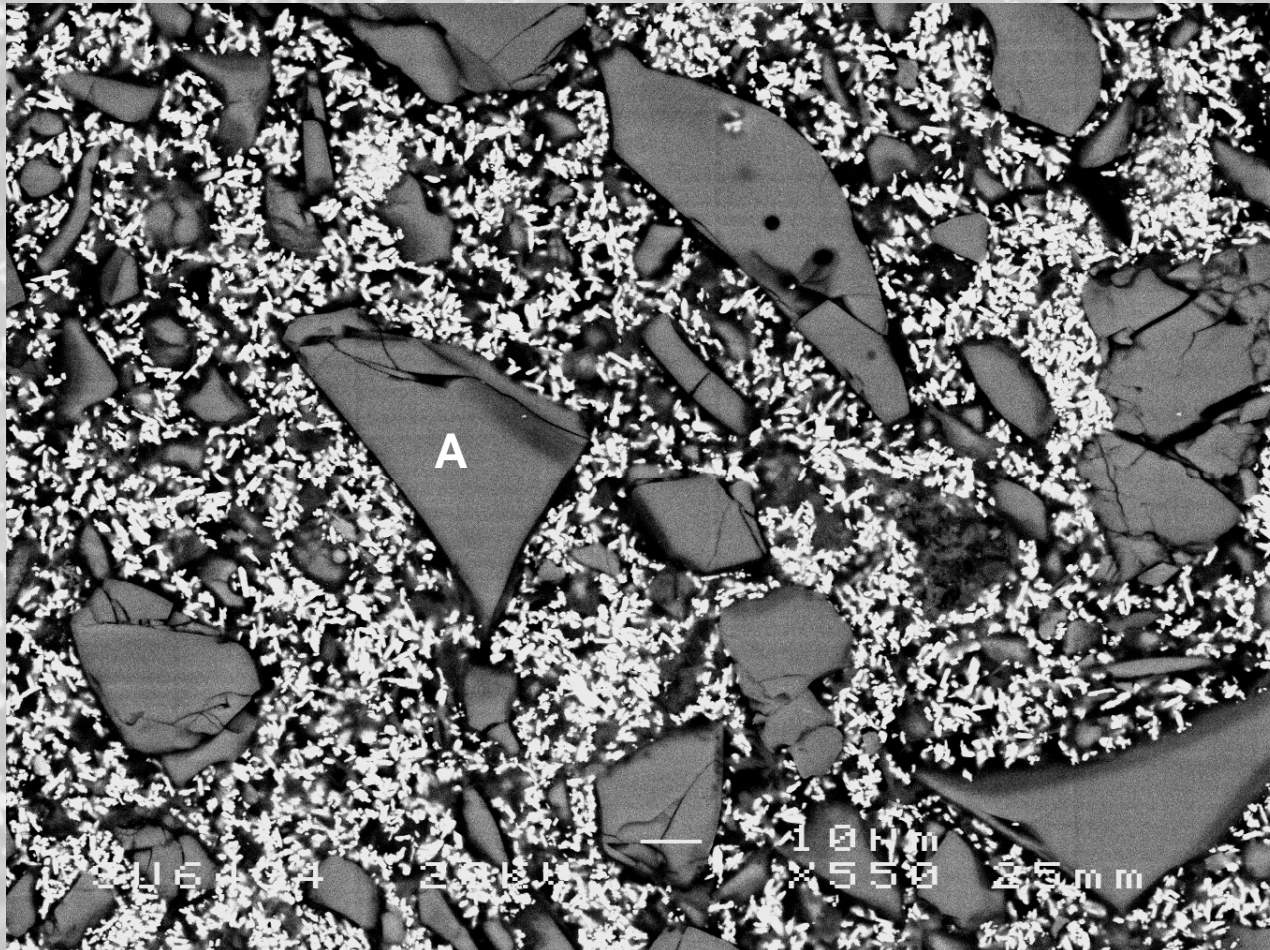


OPC with BaCO<sub>3</sub> cured for 720 days at 20°C. Voids contain precipitated Mc identified using EDX and fine particulates of BaSO<sub>4</sub>





# BaCO<sub>3</sub> in BFS composite



9:1 BFS:OPC 30wt% BaCO<sub>3</sub> 20°C 720 days

A – unreacted BFS particle



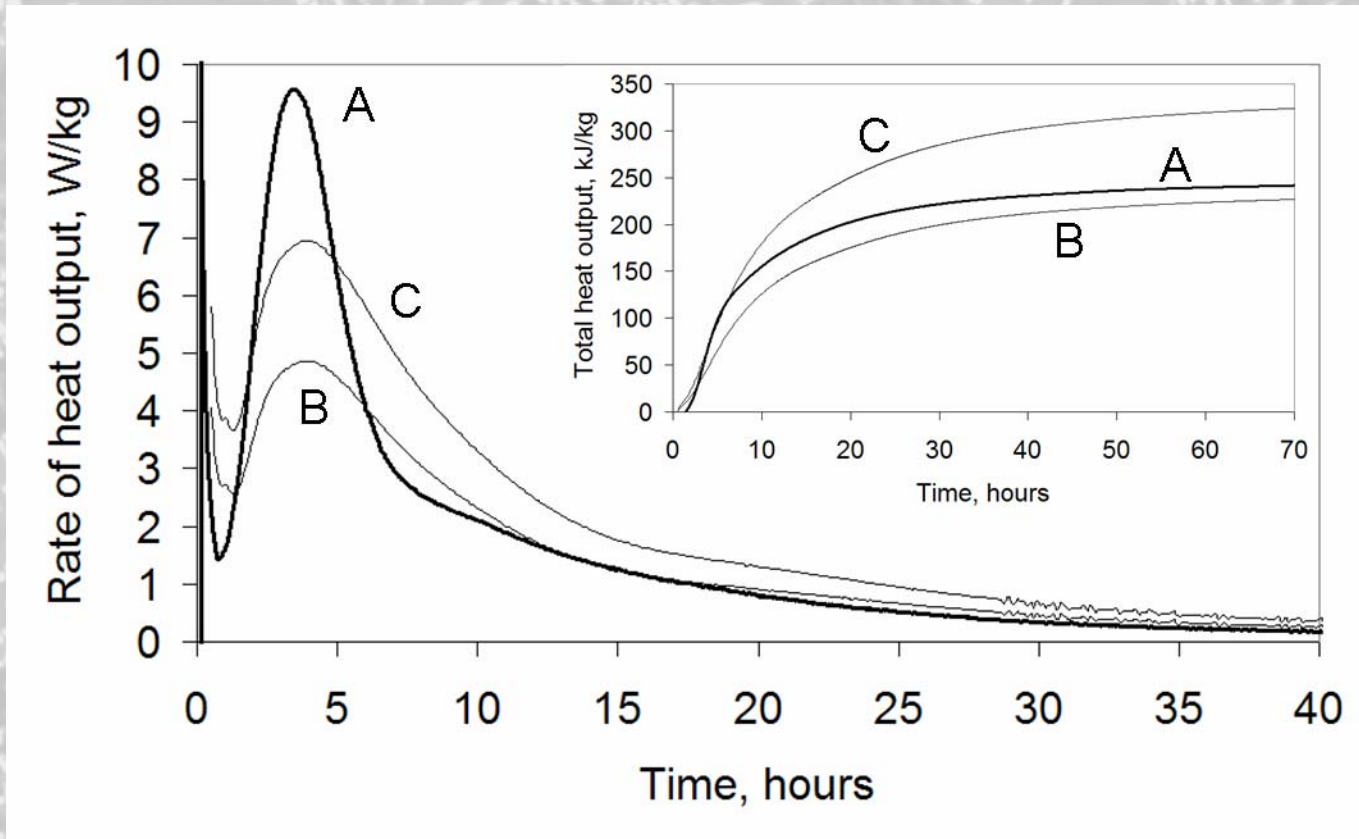


# BaCO<sub>3</sub> in OPC composites

- Ettringite and BaSO<sub>4</sub> are formed simultaneously initially and compete for SO<sub>4</sub><sup>2-</sup> (aq)
- Small amount of Ba<sup>2+</sup> incorporated in C-S-H
- Mc grows into voids formed from fully hydrated cement grains
- Large amount of BFS not reacted and no voids formed.



# ICC of $\text{BaCO}_3$ in OPC



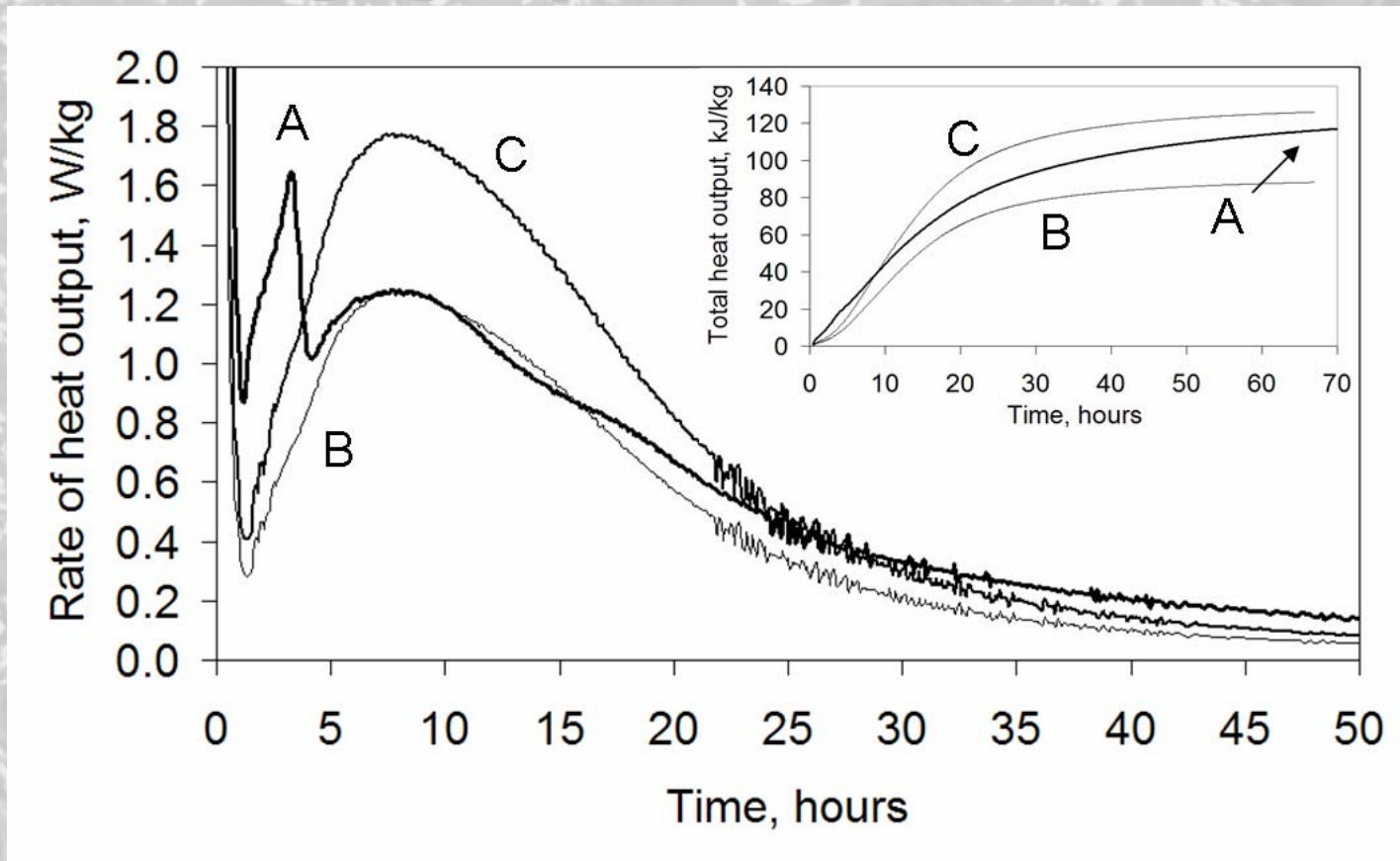
Rate and total heat output for OPC with 30%  $\text{BaCO}_3$  cured at 40°C

A- neat OPC, B – OPC with 30%  $\text{BaCO}_3$ , C- normalised OPC with 30%  $\text{BaCO}_3$

# OPC with 30% BaCO<sub>3</sub> cured at 40°C

- Initial reduction in  $Q_{\max}$  as insoluble BaSO<sub>4</sub> coats OPC particles
- Conversion of ettringite to BaSO<sub>4</sub> allows later hydration of C<sub>3</sub>A
- C<sub>3</sub>S hydration rate increased as fine BaCO<sub>3</sub> particles provide nuclei on which C-S-H can grow.
- Ultimate total heat output increased.

# BaCO<sub>3</sub> addition to 9:1 BFS:OPC



Rate and total heat output for BaCO<sub>3</sub> in 9:1 BFS:OPC at 40°C

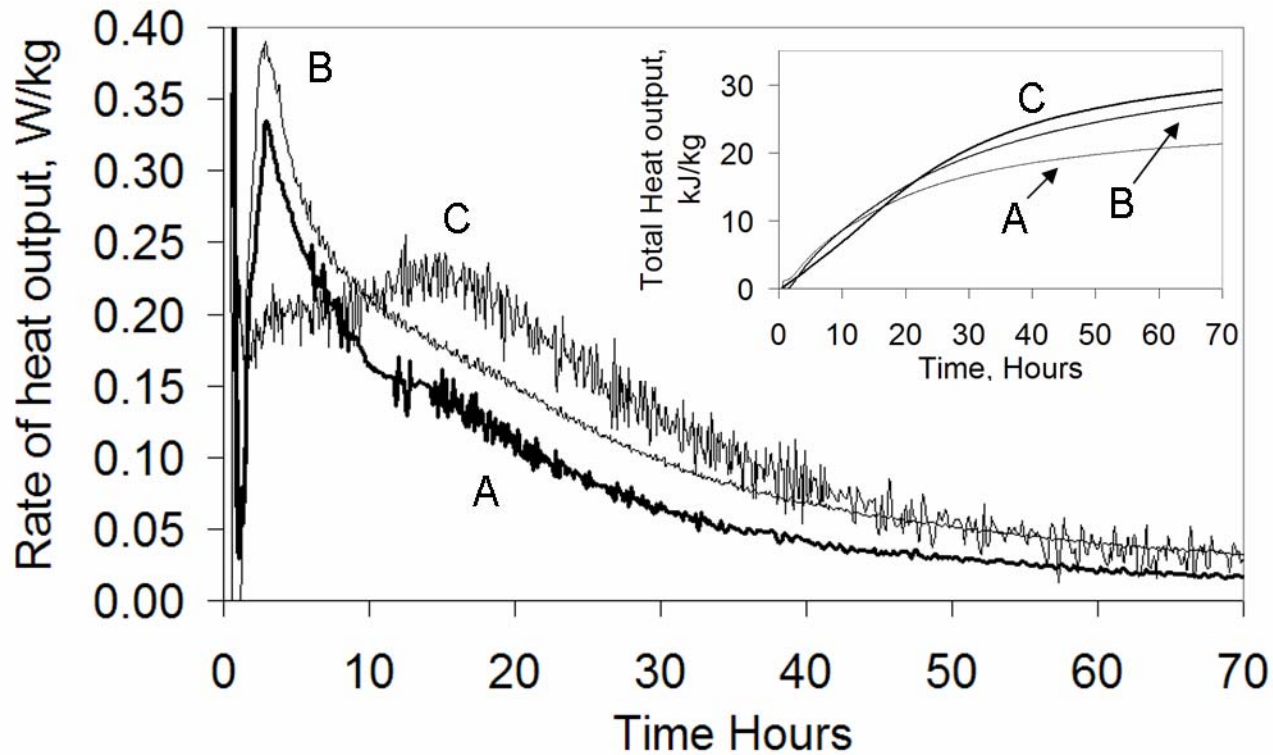
A- neat 9:1 BFS:OPC, B – 9:1 BFS:OPC with 30wt% BaCO<sub>3</sub>,

C- normalised 9:1 BFS:OPC with 30wt% BaCO<sub>3</sub>



# BaCO<sub>3</sub> addition to 9:1 BFS:OPC

- Much lower heat output
- Spike due to OPC hydration not present when BaCO<sub>3</sub> added.
- Heat output delayed initially but overall heat increased



Heat output for BFS with and without  $\text{BaCO}_3$  cured at  $40^\circ\text{C}$ .  
A – BFS w/s 0.35, B – BFS w/s 0.5, C – BFS + 30wt%  
 $\text{BaCO}_3$  w/s 0.35

# BFS interaction with $\text{BaCO}_3$

- Very low heat output influenced by w/s ratio
- Initial wetting peak reduced
- Addition of  $\text{BaCO}_3$  increases amount of heat evolved.



- With OPC  $Q_{\max}$  is reduced but  $t_{\max}$  remains the same
- Normalised total heat evolved is greater with  $\text{BaCO}_3$
- Similar effect with 9:1 BFS:OPC
- $\text{BaCO}_3$  enhances hydration of slag

# Conclusions

- Despite very low solubility,  $\text{BaCO}_3$  is not inert
- All  $\text{SO}_4^{2-}$  converted into  $\text{BaSO}_4$
- Initially,  $\text{BaCO}_3$  retards hydration of OPC but at later times provides increased hydration both of OPC and BFS
- $\text{CO}_3^{2-}$  released into solution forms monocarbonate which grows into voids
- With very high pH and elevated temperature, Mc is not stable and breaks down to form hydrogarnet.
- No  $\text{CO}_3^{2-}$  containing phase distinguished with OPC
- In 9:1 BFS:OPC composite, more hydration, Mc stable at  $60^\circ\text{C}$  and along with hydrotalcite 'fix'  $\text{CO}_3^{2-}$  so  $^{14}\text{C}$  unlikely to be released

# Acknowledgements

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