



Celtic Cement Technology

The Production of High performance Low Carbon Cement (Technical)

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ABSTRACT: In the United Kingdom (UK) in recent years we have been experiencing substantial price increases and supply rationing in both the Portland cement and Slag Cement industries. Cenin Limited is in a position to partially fill the gap with an alternative cement substitute using by-products. The problems the industry has been facing is that in Europe no one appears to commit to the difference between by-products and waste, it as been quoted that a by-product must be a material that has been produced with a specific use and have a specific timescale for its use. In the UK there has been a significant breakthrough for the steel industry as by-product status as been confirmed for blast-furnace slag by the Environment Agency. Global warming is a hot topic in all industries especially the construction industry, all industries are now improving on their carbon footprint and is a major issue for most companies. Celtic Cement Technology have developed alternative prototype cements from wastes and by-products that are shown to be acceptable in terms of commonly used characterisation parameters quoted in the BS EN196 series. Cenin Limited has developed a centre of excellence to produce cement substitutes equivalent to slag cement using 100% renewable energy and 100% recycled materials, probably the first of its type in the world today. The company's carbon Footprint is probably one of the leading footprints in the cement related industries.

Keywords: Celtic Cement Technology (CCT), Industrial by-product, X-ray fluorescence (XRF), X-ray diffraction (XRD), Thermal treatment, Particle size distribution, Chemical engineering, Ground Granulated Blast-furnace Slag (GGBS) and Pulverised Fuel Ash (PFA).

M Popham is the Managing Director of Cenin Limited and has until recently ran his own ready mix, sand dredging and quarrying operations in S Wales who provides a wealth of knowledge from the ready mix industries.

G Hunt is the Technical Director of Celtic Cement Technology. He has over 20 years experience in the pre-cast sector of the construction industry, he has been researching alternative materials for the construction industry since 1992. From 2000 – 2006 he was a visiting honorary research fellow at Cardiff University. He now heads the research centre for Cenin Limited.

INTRODUCTION

In the United Kingdom for the first time to our knowledge the construction industry has been experiencing rationing on Portland cement and Slag cement, this we have found to be also the case in many of the states in the United States of America (USA). This has highlighted that there is an opportunity for alternative cement substitutes within the construction industry within the UK and the USA.

In the United Kingdom and many other countries landfill sites in general are becoming over crowded and expensive for waste producers, then wherever possible, material going to disposal should be minimised. If the production of the waste cannot be prevented, then it is attractive to create an alternative use in another process before considering disposal. The key question that is always raised is "what is waste" and "what is a by-product". A definition on this subject will be most welcome. There has been years of disagreement on this definition between industry and the Environment Agency, in particular the steel and power station industries.

For example there has been a long going debate between the Electric Supply (ESI) industry and the Environment Agency (EA), The UK Environment Agency consider coal fired power station ash products such that Pulverised Fuel Ash (PFA) and Furnace Bottom Ash (FBA) to be wastes. The Electricity Supply Industry has not accepted that they are classed as wastes when sold for use in construction applications.

In contrast the Environment Agency has recently acknowledged the debates of the steel industry that blast furnace slag (BFS) and granulated blast-furnace slag (GGBS) are by-products. The UK Environment Agency's regulatory position statement followed a lengthy and concentrated lobby from the British Quarry Products Association and the steel industry to ensure that some 3 million tonnes of BFS is maintained for the UK's national construction needs. The industry's position on BFS was also supported by the European Commissions recently published guidance using BFS as an example of a by-product.

Global warming and climate change is the biggest environmental issue facing society today with the power station, steel and cement industries all portrayed as heavy polluters. The slag cement companies are probably the most carbon friendly cement industries to date and claim to produce the worlds best Carbon Neutral Concrete (visit www.carbonneutralconcrete.ie) Cenin Limited has developed a centre of excellence to produce cement substitutes equivalent to slag cement using 100% renewable energy and 100% recycled materials, probably the first of its type in the world today.

Gary Hunt Technical Director of Celtic Cement Technology have been researching and evaluating the use of alternative materials for the last fifteen years. During this time over fifty industrial wastes and by-products have been tested with significant results. Included in this research a wide range of slag's from all sectors of the steel producing industries have been examined and an extensive database on these materials have been collected.

The purpose of this paper is to present data to show the results of this work and the depth of knowledge that have been gained over this time period.

MATERIALS

The cement substitutes presented in this paper have been composed of raw materials currently being put to landfill, stockpiled causing environmental damage and obscuring local landscapes or being used as a low cost by-product that is still a cost to the producer of these materials. The materials used are obtained from many industrial sectors outside the more common industries such as the Iron, Steel, Power Stations and Quarrying Industries.

The process has been developed from the knowledge we have obtained during our extensive research and involves a process using thermal treatment, particle size distribution and chemical engineering. CCT have developed a fifteen point material analytical system to ensure that when an end cement substitute is produced it will comply with all the requirements of EN196 standards. Cenin have adopted a full quality control (QA) system to

comply with the requirements set out in the EN: 197 standards. Cement and cement substitutes are referenced as 'C' these include PC, GGBS and PFA.

Table 1 A range of chemical elements that are found in Portland cement's, GGBS and PFA.

Cements

	C1	C2	C3	C4	C5	GGBS	PFA
Oxide	%	%	%	%	%	%	%
CaO	59.58	60.22	62.33	58.39	58.92	40.67	6.10
SiO ₂	20.89	20.28	22.95	21.42	21.47	34.73	43.30
Al ₂ O ₃	5.23	5.68	4.66	4.53	4.18	12.80	31.52
Fe ₂ O ₃	3.34	2.05	2.92	2.04	2.04	0.37	15.28
MgO	2.59	1.59	1.17	1.34	1.91	8.48	2.01
TiO ₂	0.31	0.35	0.43	0.24	0.23	0.63	1.99
Na ₂ O	0.42	0.18	0.18	1.16	0.13	0.00	0.95
K ₂ O	1.21	1.31	0.67	0.55	0.62	0.55	0.74
P ₂ O ₅	0.09	0.11	0.05	0.07	0.05	0.01	0.70
ZnO	0.00	0.00	0.00	0.00	0.00	0.02	0.27
V ₂ O ₅	0.02	0.02	0.01	0.03	0.00	0.01	0.11
MnO	0.06	0.05	0.04	0.07	0.10	0.56	0.17
Cr ₂ O ₃	0.00	0.02	0.03	0.09	0.01	0.00	0.04

In the table above I have highlighted the major elements that we require to optimise cement performance. The trace elements labelled in red are naturally occurring in Portland cement, GGBS and PFA. Although some of the trace elements have a role when chemical compounds form during hydration, it is the major elements that we are most concerned with.

Table 2 A range of chemical elements that are found in some industrial wastes and by-products.

Industrial Waste & By-products

	RM 3	RM 7	RM 8	RM 9	RM 12	RM 16	RM18
Oxide	%	%	%	%	%	%	%
CaO	42.52	32.72	21.22	36.78	40.78	55.36	59.65
SiO ₂	34.31	28.30	41.15	3.99	34.60	2.44	1.24
Al ₂ O ₃	11.79	12.97	16.21	0.47	12.87	0.66	0.23
Fe ₂ O ₃	0.80	0.37	3.51	32.51	0.51	0.42	0.17
MgO	8.26	0.60	11.61	0.16	8.27	0.54	2.49
TiO ₂	0.48	0.05	0.44	0.01	0.66	0.04	0.01
Na ₂ O	0.37	1.16	0.38	0.95	0.37	0.13	0.09
K ₂ O	0.95	1.38	0.18	0.90	0.46	0.00	0.00
P ₂ O ₅	0.00	22.19	0.00	0.00	0.13	0.11	0.00
ZnO	0.00	0.01	0.01	0.01	0.00	0.01	0.00
V ₂ O ₅	0.01	0.00	0.02	0.04	0.00	0.00	0.01
MnO	0.51	0.00	2.29	0.11	0.54	0.02	0.01
Cr ₂ O ₃	0.00	0.00	0.18	4.73	0.01	0.00	0.00

In this table it can be seen that many industrial wastes and by-products contain the same elements that are found in Portland cement, GGBS and PFA. However, with these materials the elemental range is far more wide spread.

It is accepted that we are all aware of the trace elements that are present in the above mentioned cements and raw materials and also the effect that they have during hydration in mortar and concrete. So for the purpose of this paper we shall just refer to the major elements

from this point forward. Also for the rest of this paper we are going to make direct comparisons between Portland cement GGBS and Cenin cement and discard PFA at this point.

RESEARCH PROCEDURES AND RESULTS

During the development of alternative cement substitutes or replacements we have split our evaluation into two sectors, chemical and physical characteristics. All the development work as been carried out in our own cement laboratories based in ECM² which is a Welsh Assembly Government research centre based in the Corus Steel works in Port Talbot, S Wales, UK.

Our work as also been verified by accredited independent laboratories in the UK, both commercial and university laboratories, the main research work was carried out at the School of Civil Engineering Cardiff University where Gary was an visiting honorary research fellow for six years.

Chemical Characteristics XRF

Using XRF analysis we were able to develop our table of desired elements and from these tables we were able to compare the ratios of major elements in particular the calcium/silica ratios that are found in Portland cement, GGBS and Cenin Cement.

Table 3 Ratio changes with PC/GGBS composite cement

Replacement Levels								
GGBS	PC		25%	30%	40%	50%	60%	70%
C7	C3	Oxide	%	%	%	%	%	%
40.67	62.33	CaO	56.92	55.83	53.67	51.50	49.34	47.17
34.73	22.95	SiO₂	25.89	26.48	27.66	28.84	30.02	31.19
12.80	4.66	Al₂O₃	6.69	7.10	7.91	8.73	9.54	10.36
0.37	2.92	Fe₂O₃	3.00	3.36	4.09	4.82	5.55	6.28
8.48	1.17	MgO	2.28	2.15	1.90	1.64	1.39	1.13
0.63	0.43	TiO₂	0.01	0.01	0.01	0.01	0.01	0.01

It can be seen from the table above that there is for example significant differences in the calcium/silica ratios between PC and GGBS, it can also be seen that when you increase the replacement levels of PC with GGBS these ratios become closer.

Table 4 Ratio changes with PC/Cenin 2 composite cement

Replacement Levels								
Cenin	PC		25%	30%	40%	50%	60%	70%
2	C3	Oxide	%	%	%	%	%	%
39.57	62.33	CaO	56.64	55.50	53.22	50.95	48.67	46.40
26.65	22.95	SiO₂	23.88	24.06	24.43	24.80	25.17	25.54
9.93	4.66	Al₂O₃	5.98	6.24	6.77	7.29	7.82	8.35
6.04	2.92	Fe₂O₃	2.28	2.50	2.94	3.39	3.83	4.27
5.61	1.17	MgO	3.70	3.86	4.17	4.48	4.79	5.10
0.51	0.43	TiO₂	0.10	0.12	0.16	0.20	0.24	0.28

GGBS is an excellent engineering and Carbon Neutral cement, so therefore we can also produce a similar product except we are able to maintain an improved calcium/silica ratio or alternatively match that of GGBS.

Table 5 Ratio changes with PC/Cenin 1 composite cement

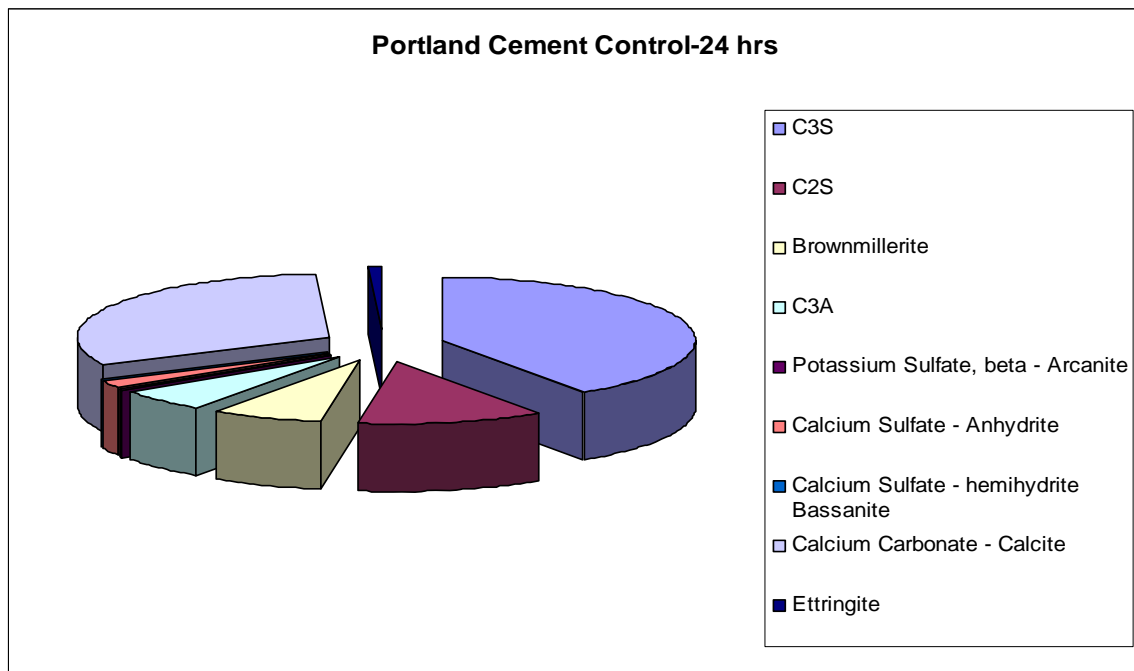
		Replacement Levels						
Cenin	PC		25%	30%	40%	50%	60%	70%
1	C3	Oxide	%	%	%	%	%	%
43.85	62.33	CaO	57.71	56.79	54.94	53.09	51.24	49.40
24.59	22.95	SiO ₂	23.36	23.44	23.61	23.77	23.93	24.10
9.31	4.66	Al ₂ O ₃	5.82	6.06	6.52	6.99	7.45	7.92
6.10	2.92	Fe ₂ O ₃	3.72	3.87	4.19	4.51	4.83	5.15
0.72	1.17	MgO	1.06	1.04	0.99	0.95	0.90	0.86
0.37	0.43	TiO ₂	0.41	0.41	0.40	0.40	0.39	0.39

With our technology we can further improve the calcium/silica ratios, closer to that found in PC.

Chemical Characteristics XRD

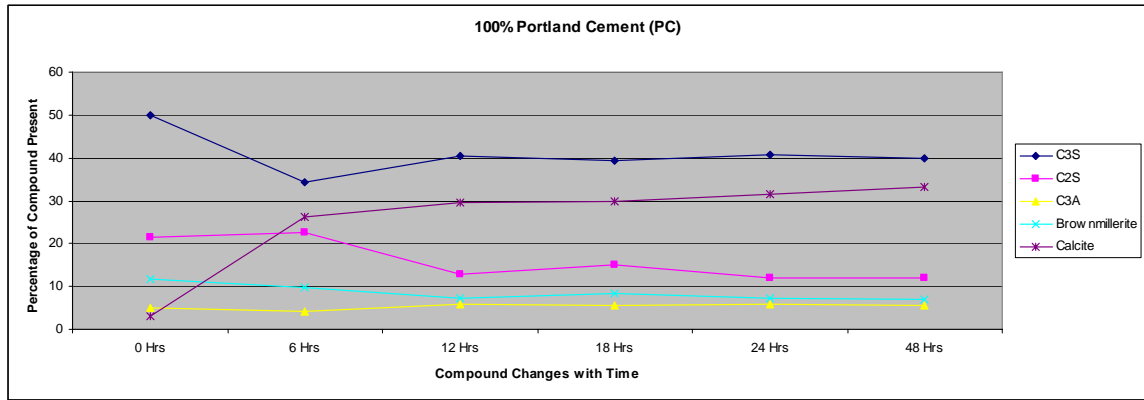
Using XRD analysis we can monitor the phase changes during the hydration of cement and compare the changes that take place between PC and GGBS, we can then chemically engineer our substitutes to match those changes, What is more important is the fact that we can tailor make the substitute for different applications and processes which is unique to Cenin Limited.

Figure 1 Chart showing compound phases present during hydration in Portland cement



In the figure above is an illustration of the compound phases that form during the hydration of cement. It is well known what these phases are; we also know what phases are present with composite cements such as a PC/GGBS composite. For the purpose of this paper we shall now only concentrate on the following chemical notation: Tricalcium Silicate (C3S), Dicalcium silicate (C2S). Tetracalcium aluminoferrite or Brownmillerite (C4AF) and Calcite.

Figure 2 Chart showing the major phase changes with time in Portland cement (PC



It can be seen in the chart above by 12 hours the C3S and Calcite stabilise

Figure 3 Chart showing major phase changes with a composite 75% PC/GGBS 25%

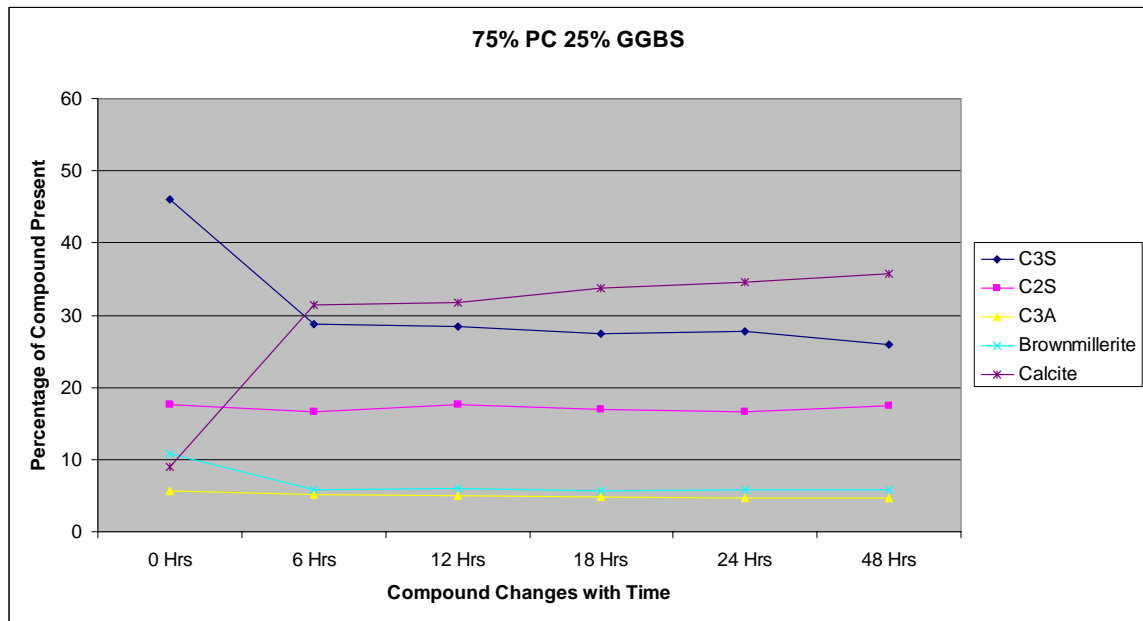
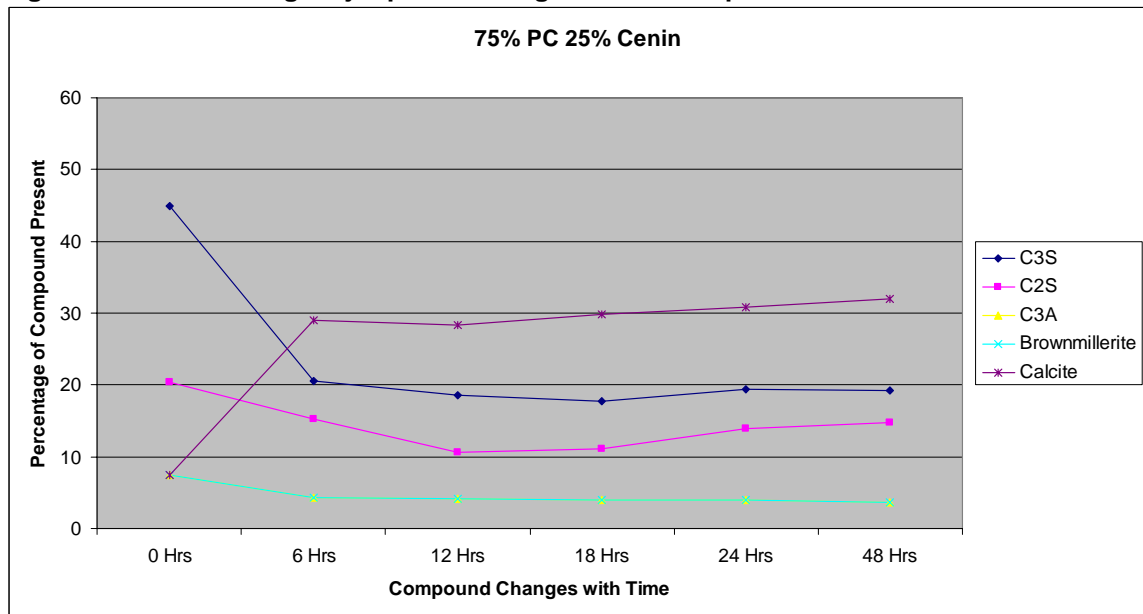


Figure 4 Chart showing major phase changes with a composite 75% PC/Cenin 25%



In the two charts above it can be seen that the calcite phase is stronger than the C3S phase in the composite cements with the percentage of C3S present being reduced to below 30% when combined with GGBS and below 20% with Cenin.

Figure 5 Chart showing major phase changes with a composite 50% PC/GGBS 50%

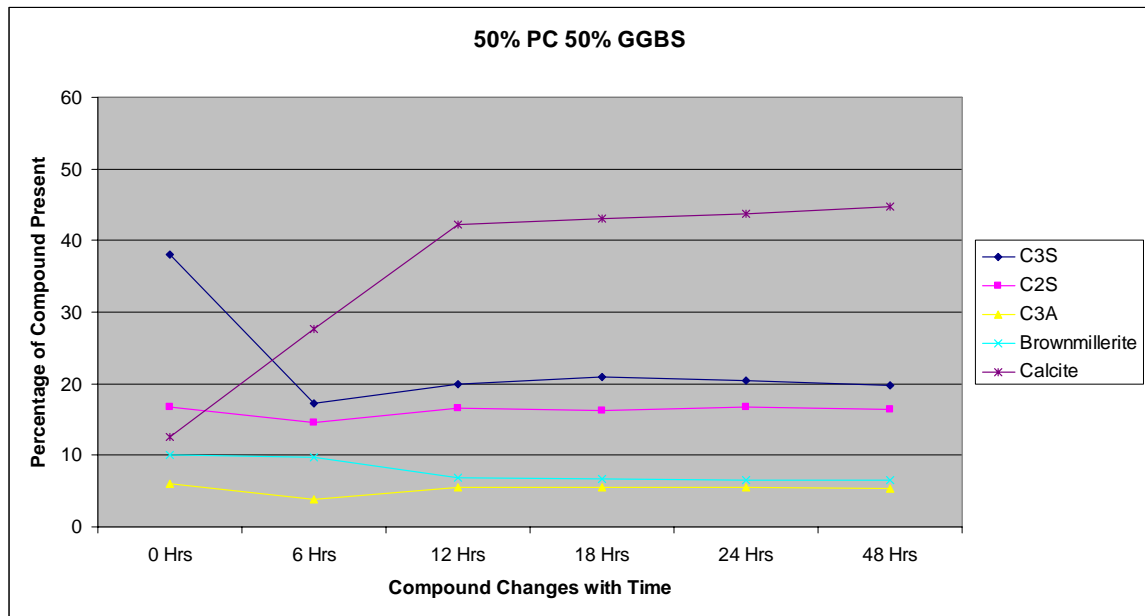
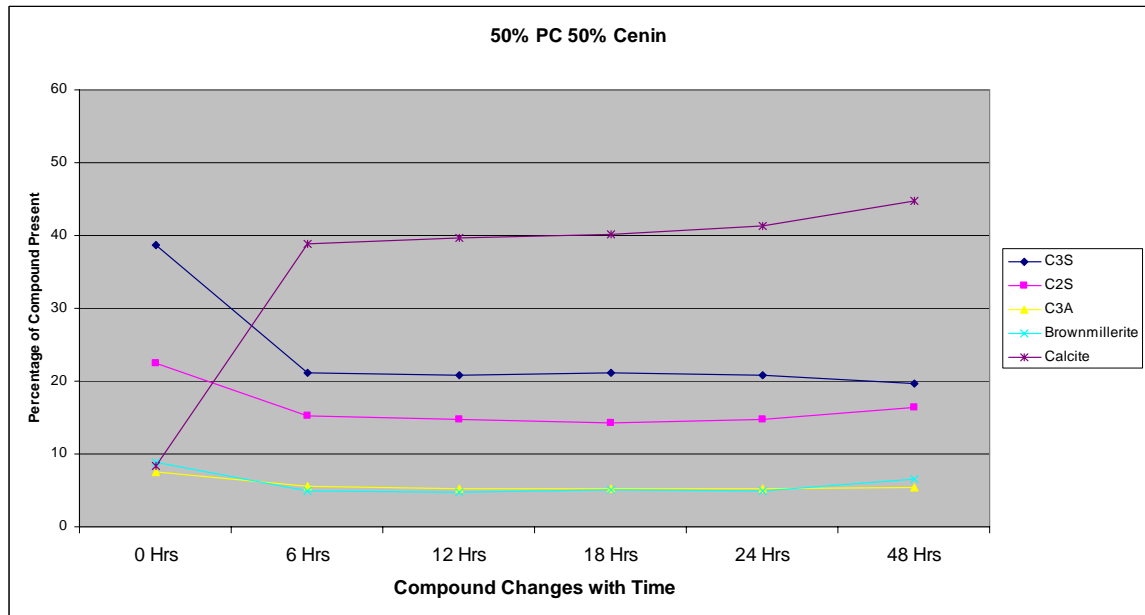


Figure 6 Chart showing major phase changes with a composite 50% PC/Cenin 50%



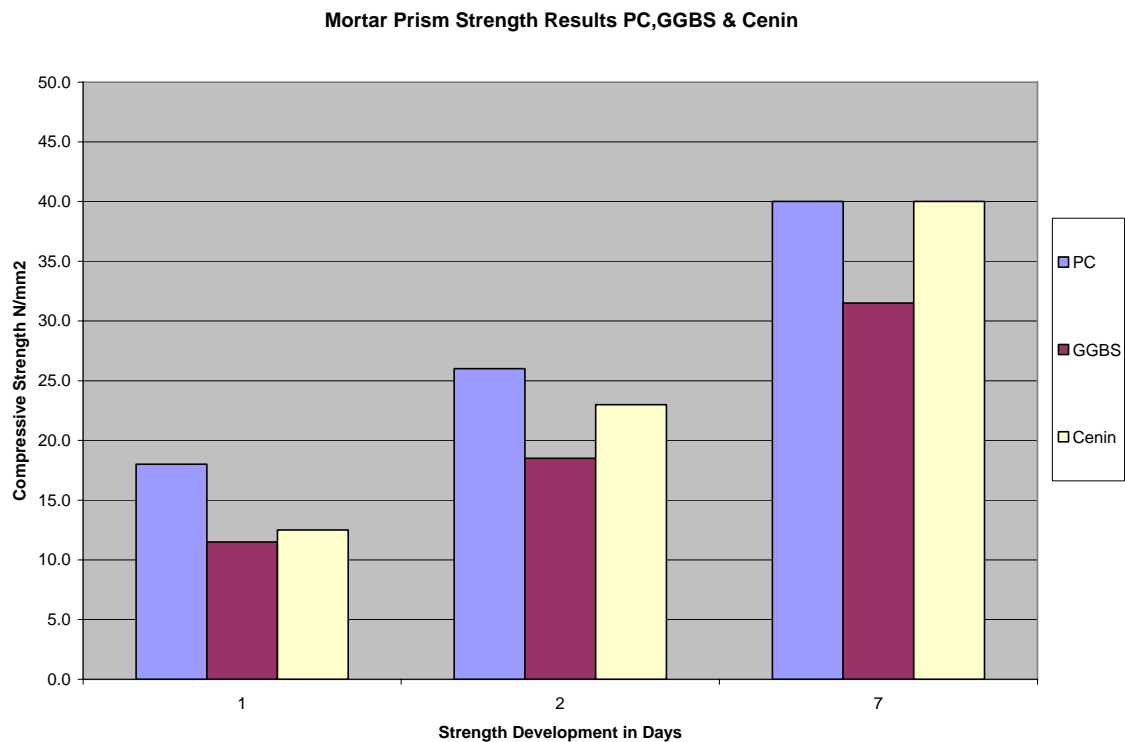
In figures 5&6 it can be seen that in both cases the percentage of Calcite present increases to above 40%. With GGBS the C3S phase reduces to around 20% the same as Cenin, but what is interesting to note is the fact that the C3S phase remains at around 20% with both 25% & 50 replacement levels when using the Cenin composite cement.

Using Celtic Cement Technology allows producers to chemically engineer the compounds that form when used as composite cement, thus allowing you to vary the rate of heat of hydration, setting times and strength development. This enables the producer to tailor make cement substitutes to the requirements of the end user effectively making bespoke cements. The raw materials are the same but the changes are made by a combination of thermal treatment, particle size distribution and chemical blending.

The problems that the industry face when using GGBS is you cannot achieve high early strength without increasing the total cement content, also the use of GGBS in cold conditions is restricted as at low temperatures concrete will take a long time to set or fail to set at all. In hot climatic conditions GGBS is beneficial as it reduces the heat of hydration and therefore minimises thermal cracking,

With Cenin cement you can vary these conditions by retarding the setting times and heat of hydration in hot climatic conditions and accelerating them in cold climatic conditions.

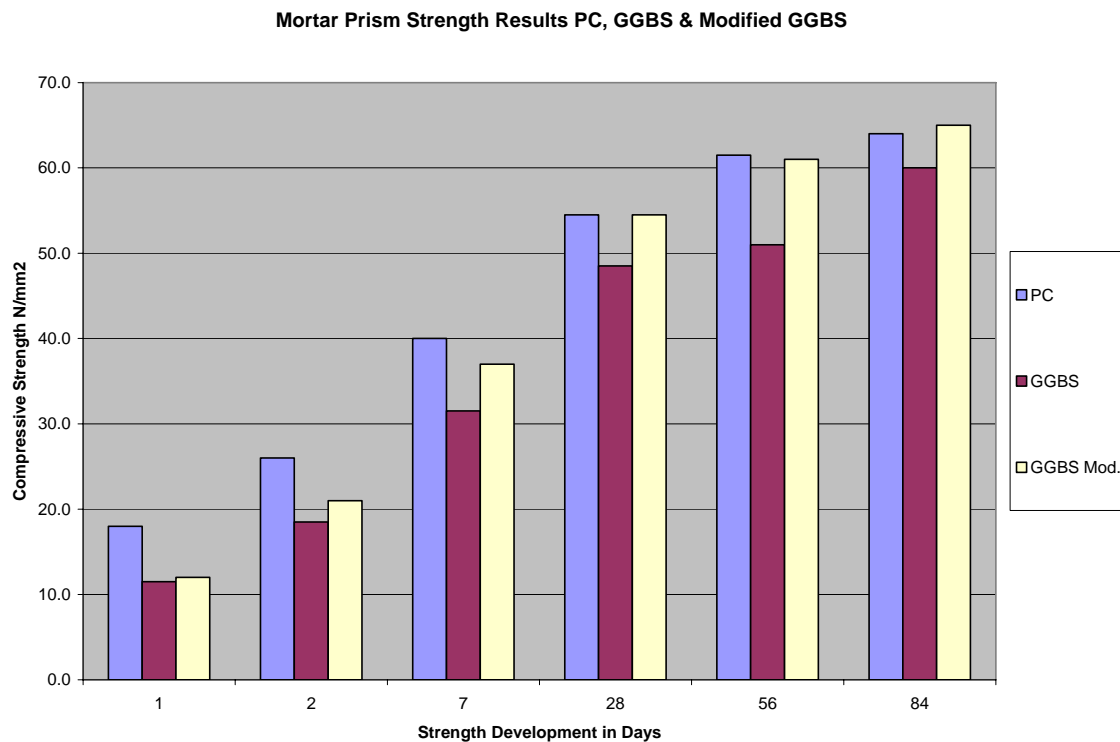
Figure 7 Chart showing effects of strength development by chemically engineering the compound phase changes with composite Cenin cement compared to GGBS.



It can be seen in the chart above that by chemically engineering the compound changes it is possible to achieve the same strength as Portland cement within 7 days using Cenin composite cement.

Celtic Cement Technology can also be applied to existing manufacturers of slag cement to improve their performance on setting times, strength development and cold climate concreting.

Figure 8 Chart showing strength developments of PC, GGBS and modified GGBS.



It can be seen in the chart above that it is possible to improve the strength development of GGBS and have an equal strength to Portland cement at 28 days.

Discussion and Conclusion

It has been demonstrated during this paper that it is possible to chemically engineer cement substitutes/replacements to alter and improve the properties of the cement. Cement substitutes can be produced from alternative materials to equal or improve on the performance of Portland cement and Ground Granulated Blast Furnace cement.

It is also possible to add value to existing GGBS cement to alter or improve the physical and chemical properties of GGBS by adopting Celtic Cement Technology.

These properties have been achieved by over fifteen years of research and development and by our depth of knowledge that we have gained during this period. The process is a unique combination of thermal treatment, particle size distribution and chemical engineering.

It is well documented and known that with the right replacement levels that a composite PC/GGBS cement becomes higher in strength than that of Portland cement on its own, also GGBS is probably the best civil engineering cement available to the construction industry. Cenin strongly believes that we are one of a few companies that can produce a cement substitute that is equal in strength to Portland cement within seven days, and is cost effective.

This is a truly sustainable technology that has been developed using 100% renewable energy and 100% recycled material, probably with one of the best carbon footprints in the industry today. We look forward to your comments and feedback on this paper.

The information provided during this paper has been the result of many years of research between Cenin and independent testing laboratories both from industry and academic facilities in the UK and Ireland.

Acknowledgments

We would like to acknowledge the support we have received during our research and development of this process from the following:

Welsh Assembly Government

Testing Solutions Wales (Corus Group)

National Oceanography Centre, University of Southampton

Materials & Surface Science Institute, University of Limerick Ireland.

Panalytical UK X-ray systems

Sympatec Particle size instruments

We would also like to acknowledge the support and supply of samples from the Portland cement and GGBS manufacturers in the UK.