Clinker Mineralization using Refined By-products from the Aluminium Industry

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Abstract

Refined by-products from the aluminium industry's spent pot lining (SPL) waste are a valuable source of fluoride, alkali, alumina and carbon for clinker manufacturing. Fluoride acts as a cost effective mineralizer resulting in an easier clinker burnability that reduces thermal energy consumption and/or promotes higher clinker alite levels. Alkalis allow an increase of the alkali level in clinker which can improve the alkali-sulfur balance and increase the content of soluble alkalis in cement. Alumina can substitute partially other alumina correctives in raw meal or can be employed to increase the portion of aluminate in mineralized clinker. Finally, the carbon fraction of refined by-products from the aluminium industry substitutes fossil fuels in the clinkering process.
To better understand the impact of the refined by-products on the clinker manufacturing process and their mineralizing properties in particular, a series of laboratory burnability investigations was performed and industrial clinker produced using refined by-products from the aluminium industry was characterized.

This work has established that the beneficial effect of fluoride on clinker burnability does not depend on the type of fluoride mineral used, be it cryolite (Na_3AlF6), villiaumite (NaF), fluorite (CaF_2), or sodium silicofluoride (Na_2SiF_6). The different pure fluoride salts including those present in refined by-products from the aluminium industry such as HiCAl 40 were used to dope industrial rawmeals and undergo laboratory burnability testing. These doped rawmeals exhibited similar burning behaviour at the same fluoride content.

It has also established that HiCAl 40, a refined by-product derived from spent potlining, has similar burnability improvement characteristics to fluorite tested in rawmixes at 94 Lime Saturation (LS). At this LS, to achieve a free lime of 1.5%, a temperature reduction of the order of 100 ^{O}C is indicated - with commensurate potential energy and other savings in industrial clinker burning. HiCAl 40 exhibited similar characteristics when incorporated into rawmixes at 97 and 101 LS.

A clinker sample produced with refined by-product from the aluminium industry resulting in enhanced cement strength development was characterized. It confirms the transfer and incorporation of fluoride and sodium from the by-product into clinker.

Originality
Pure fluoride minerals potentially occurring in the by-products from the aluminium industry such as cryolite (Na_3AlF_6), villiaumite (NaF), fluorite (CaF_2), and sodium silicofluoride (Na_2SiF_6) were tested as mineralizers by doping industrial raw meals.

Clinker burnability studies using industrial raw materials were conducted for different levels of clinker lime saturation, mineralizer dosage and burning temperature. Thereby the impact of refined by-product from the aluminium industry was benchmarked against the use of calcium fluoride and hence other fluoride carriers.
Finally, the studies were complemented with results from industrial clinker mineralized with refined by-product from the aluminium industry.

Keywords: Clinker Mineralization, Burnability, Fluoride Minerals, Spent Pot Lining

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1. Introduction

Refined by-products from the aluminium industry's spent pot lining (SPL) waste can be a valuable source of fluoride, alkali, alumina and carbon for cement clinker manufacture. The optimum value of these components can be realized only when the refinement process produces a material that is safe and chemically consistent, the most suitable clinkering process can be identified and the efficacy of the product relative to alternatives can be proven.

Cooper, B.J., (2014) has described the application of industrial ecology to address environmental issues associated with SPL generated by the aluminium smelting industry and has identified the processes necessary to successfully introduce refined SPL into the cement industry. An important aspect of these processes is the calcination and treatment to remove cyanides, oxidize residual sodium and aluminium metal and safely burn the resultant explosive hydrogen and organic gases which would otherwise prevent refined SPL materials from being classified as a safe and valuable by-product.

The optimum cement/clinker plant scenario for the utilization of the fluoride and other components in refined SPL has been described by Zimmermann,Y.C.,(2015) who demonstrates the case where maximum value that can be obtained from all the ingredients in refined SPL when applied to the appropriate cement plant.

The mineralization properties of fluoride in cement manufacture is well known and is extensively documented (Christensen, N.V., *et al* (1993), Glasser, F.P., (2004), Gosh, S.P., (1997), Hertford, D., (2003, 2010), Johansen, V., *et al* (1979, 2011), Klemm, W.A., *et al* (1993), Moir, G.K., *et al* (1992), Taylor, H.F.W., (1997)). It is common to use calcium fluoride (fluorite), often commercially also known as fluorspar, as a fluoride source and cement plants with reliable supplies of fluoride are known to produce a mineralized clinker which has superior strength making characteristics compared to conventionally produced clinker. The higher quality of such clinkers may be used to improve cement quality and/or increase the yield of cement per unit of clinker.

This work makes a contribution to the understanding of the efficacy of 'HiCAl 40', a refined product derived from SPL, relative to other fluoride carriers and provides examples from its' industrial application.

2. Experimental

2.1. Raw Materials

Industrially produced cement rawmeals were sourced from a cement plant utilizing natural gas as major fuel in the clinkering process. Smaller quantities of flyash, finely ground silica sand and high grade limestone used as corrective materials were also supplied by this manufacturer. In all cases the rawmaterial combinations necessary to achieve the desired clinker compositions were materials used and produced commercially.

The fineness of rawmeal was typical of industrial roller mill product at 85% < 90 microns.
High grade limestone was ground to a similar size. Silica sand corrective was specifically ground to < 32 microns to minimize the effect of this material on burnability.

SPL derived HiCAl 40 was a sample of a commercial export shipment.

2.2.1 Characterization of Rawmixes

Various physical - chemical models developed in the industry indicate that the burnability of cement clinker rawmix is predominantly related to the content of coarse (> 32 microns) Quartz, coarse (> 90 microns) Calcite, Lime Saturation (LS) and Silica Ratio (SR).

For the initial study using analytical grade fluoride carriers adjustment of the rawmix composition was not considered necessary.

In the case of evaluating the effect of Fluoride level, Lime Saturation and Temperature, rawmixes were prepared with the intention to keep constant, to the greatest extent possible, all variables other than those being investigated. Particle size was 'controlled' by maximizing the content of the industrially produced rawmeal. Only the mixes containing relatively larger proportions of HiCAl 40 required correction with high grade limestone which was ground to a fineness similar to rawmeal. The very small quantities of fine silica sand and /or flyash corrective are not considered to be of any consequence.

The simple equations traditionally used in the cement manufacturing industry (Bogue R.H. (1955)) were used to calculate rawmaterial proportions, rawmix composition (to achieve hypothetical clinkers) and the product hypothetical clinker composition.

2.2.2 Characterization of HiCAl 40

The SPL derived HiCAl 40 used in this study was sourced from samples retained from commercial export sales or deliveries.

The major characteristics are shown below in table 1. Note that the chemical analysis total exceeds 100 as SPL derived HiCAl 40 is a product of a reduction furnace and the inorganic analysis results here are expressed as the highest oxidation state as practised in the cement industry.

Table 1a Chemical composition of HiCAl 40

Property	Unit	Value
Moisture	%	14.8
Ash	%	54.6
SiO_2	%	9.1
Al_2O_3	%	17.5
Fe_2O_3	%	4.9
CaO	%	1.7
SO_3	%	1.5
K_2O	%	0.27
Na_2O	%	13.2
F	%	10.1
C	%	43.3
Heat Value	MJ/kg	13.6

Table 1b Mineralogical Composition of HiCAl 40

Mineral	Formula	Unit	Value
Graphite-2H	C	%	35.5
Villiaumite	NaF	%	11.2
Corundum	Al_2O_3	%	15.0
Gibbsite	$Al(OH)_3$	%	2.7
Cryolite	Na_3AlF_6	%	14.9
Fluorite	CaF_2	%	3.4
Diaoyudaoite	$NaAl_{11}O_{17}$	%	4.3
Other crystalline	Unidentified, possibly $NaAlSiO_4$	%	Est 8.7
Other crystalline		%	Est 4.3

2.3. Methodology

2.3.1 Sample / Nodule Preparation

Samples of known composition of the required cement rawmeal, fine flyash, finely ground silica sand and fluoride carrier (or HiCAl 40) was accurately proportioned to the required chemical composition. Two levels of fluoride were selected as variables for sodium fluoride (NaF), calcium fluoride (CaF_2), cryolite (Na_3AlF_6) and sodium fluorosilicate (Na_2SiF_6) as the fluoride sources. Three levels of added 'Target Fluoride' were used for the study involving HiCAl 40 and calcium fluoride (CaF_2).

The materials were selected and proportioned to keep constant other factors known to influence rawmix burnability.

8-10 nodules of each of the mixtures were prepared by mixing with water to form a stiff paste, rolling by (gloved) hand to a diameter of 8-10mm and then kept in a drying oven at 105 °C for several days prior to burning.

Selected samples from each test series were then analyzed by XRF to ensure that the desired hypothetical clinker characteristics had been achieved. This provided evidence that the original analyses and rawmaterials were correctly proportioned.

2.3.2 Rawmix Burning

The laboratory furnace was programmed so that the starting temperature for burning samples was 200°C below the target burning temperatures of 1400°C in the case of the pure fluoride carriers. For the work conducted at 97 and 101 Lime Saturation (LS) the target burning temperatures were 1350°C, 1400°C and 1450°C respectively.

Following introduction of the sample the furnace was programmed to increase temperature by 8°C per minute for 25 minutes to the target temperature. (For the work at 94 LS conducted earlier (also at target burning temperatures of 1350°C, 1400°C and 1450°C) the rate of temperature rise was 10°C per minute requiring 20 minutes to reach the target temperature).

Given the relatively large energy input to the furnace the very small and variable contribution from the carbon content of the HiCAl was not considered to be of significance.

The samples were then 'soaked' at the target temperature for 20 minutes prior to being removed and rapidly cooled. This process produced a furnace produced 'clinker'.

2.3.3 Chemical Analysis of Furnace produced Clinkers

Clinker samples were analyzed for uncombined residual free lime (CaO_f) by the traditional glycerol/alcohol method (ASTM C114) as the burnability indicator. Selected clinker samples were also analyzed by XRF to confirm that the *potential* characteristics (LSF, SR, AR) did not change during the burning process.

3. Results and Discussion

3.1. Burning Results for Analytical Grade Fluoride Carriers

Rawmixes containing sodium fluoride (NaF), calcium fluoride (CaF_2), cryolite (Na_3AlF_6) and sodium fluorosilicate (Na_2SiF_6) were prepared, nodulized and burnt at 1400^oC. This range of fluoride carriers contains also those minerals present in SPL, as determined by X-Ray Diffraction analyses of HiCAl 40 during the past decade. Villiaumite (NaF) and cryolite (Na_3AlF_6), the major fluoride contributors in HiCAl 40, were also included as a 50/50 blend, i.e. each contributing half of the added fluoride.

Table 2 below shows the hypothetical clinker characteristics calculated from the compositions of the rawmixes prepared for this study, conducted with a LS target of 100 - indicating only marginal differences in variables known to affect burnability.

Table 2 - Hypothetical Clinker Characteristics - Analytical Grade Fluoride Carriers

	Unit		NaF		CaF_2		Na_3AlF_6		Na_2SiF_6		NaF + Na_3AlF_6	
Added Fluoride	%	NIL	0.20	0.40	0.20	0.40	0.20	0.40	0.20	0.40	0.20	0.40
LS	-	100	100	100	101	101	100	100	100	100	100	100
SR	-	2.50	2.50	2.50	2.50	2.50	2.47	2.44	2.51	2.52	2.48	2.47
AR	-	1.64	1.64	1.64	1.64	1.64	1.66	1.69	1.64	1.64	1.65	1.66
Na_2O eq.	%	0.51	0.84	1.17	0.51	0.51	0.68	0.84	0.62	0.73	0.76	1.01
Alkali/Sulfur	-	2.40	3.95	5.52	2.40	2.40	3.16	3.93	2.90	3.42	3.56	4.74
C_3S	%	74	74	74	75	76	73	73	73	72	74	73
C_3S (corrected for 1% free lime)	%	70	70	70	71	72	69	68	69	68	70	69
C_2S	%	3.9	3.8	3.8	2.9	2.0	4.3	4.7	4.8	5.6	4.1	4.3
C_2S (corrected for 1% free lime)	%	6.9	6.9	6.9	6.0	5.1	7.4	7.8	7.8	8.7	7.1	7.3
C_3A	%	8.4	8.4	8.3	8.4	8.3	8.6	8.8	8.4	8.3	8.5	8.6
C_4AF	%	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6
Liquid phase (1338 °C)	%	22.1	22.3	22.6	22.0	21.9	22.2	22.3	22.1	22.2	22.3	22.4
Liquid phase (1400 °C)	%	25.0	25.2	25.4	24.9	24.8	25.3	25.7	25.0	25.0	25.3	25.6
Liquid phase (1450 °C)	%	25.4	25.6	25.9	25.3	25.2	25.7	26.1	25.4	25.5	25.7	26.0

Table 3 shows the residual free lime content (as burnability indicator) of the clinkers produced from the rawmixes containing fluoride derived from analytical grade carriers.

Table 3 - Free Lime content of clinker burned at 1400°C

Added Fluoride	NaF	CaF$_2$	Na$_3$AlF$_6$	Na$_2$SiF$_6$	NaF/Na$_3$AlF$_6$
%			Free Lime (%)		
NIL			3.4		
0.2	2.7	2.7	2.4	2.6	2.3
0.4	2.6	2.8	2.3	2.2	2.5

The results suggest there is little difference attributable to the fluoride carrier type. By addition of 0.20 % of F to rawmixes, the free lime level could be reduced from 3.4 % to around 2.5 % in this laboratory test. The results also indicate that there is little improvement in burnability when increasing the added F content to 0.40%.

3.2. HiCAl 40 as Fluoride Carrier

Rawmixes were prepared at LS 94, 97, and 101 respectively, nodulized and burnt at temperatures of 1350°C, 1400°C and 1450°C as previously described. The LS 94 series was done in conjunction with a series of burns containing fluorite as fluoride source for comparison.

3.2.1 Burning Results for HiCAl 40 and CaF2 (fluorite) at 94 LS

Table 4 summarizes the hypothetical clinker characteristics of rawmixes for the LS target of 94 and shows that only added F level and in the case of HiCAl 40, the associated Na$_2$O are significant variables. Selected XRF analyses of rawmixes provided evidence that the hypothetical targets were achieved.

Table 4 - Hypothetical Clinker Characteristics at LS 94 - HiCAl 40 and CaF$_2$ as fluoride source

Fluoride Source		LS Target 94				LS Target 94			
		HiCAl 40				CaF2			
Added Fluoride	%	0.00	0.07	0.20	0.33	0.00	0.07	0.20	0.33
LS	-	94.0	93.9	93.8	93.8	94.0	94.0	94.0	94.1
SR	-	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
AR	-	1.69	1.68	1.65	1.61	1.69	1.71	1.73	1.75
Na$_2$O	%	0.41	0.48	0.61	0.75	0.41	0.41	0.41	0.42
C$_3$S	%	60.1	60.0	59.8	59.6	60.1	60.0	60.0	59.9
C$_3$S (corrected for 1% free lime)	%	56.1	56.0	55.8	55.6	56.1	56.0	56.0	55.9
C$_2$S	%	18.2	18.2	18.2	18.3	18.2	18.1	18.1	18.0
C$_2$S (corrected for 1% free lime)	%	21.2	21.2	21.2	21.3	21.2	21.1	21.1	21.0
C$_3$A	%	9.2	9.1	8.9	8.7	9.2	9.3	9.4	9.5
C$_4$AF	%	10.0	10.1	10.2	10.3	10.0	10.0	9.9	9.8

The results of free lime tests on the actual clinkers produced from the rawmixes above are shown in Figure 1 below.

As expected the free lime content (as burnability indicator) reduces as the temperature increases. The free lime content also reduces as the added fluoride content is increased to 0.33%. Comparison of

the two sets of data suggests that the HiCAl 40 fluoride carrier has a very similar affect on burnability to that of fluorite.
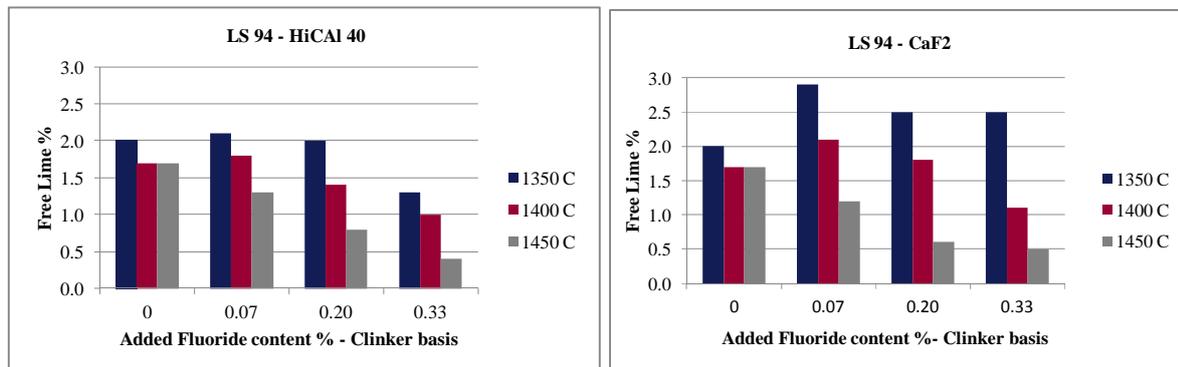
Figure 1 - Effect of Added Fluoride on Free Lime - HiCAl 40 and Fluorite at various temperatures - LS 94

In figure 2 below the same results are shown differently and can be used to infer that to achieve a free lime content of 1.5% a reduction in burning temperature of the order of $100^{O}C$ is indicated. A similar reduction is apparent for fluorite sourced fluoride at 94 LS whereby the conclusion is not as well defined at the lower temperatures.
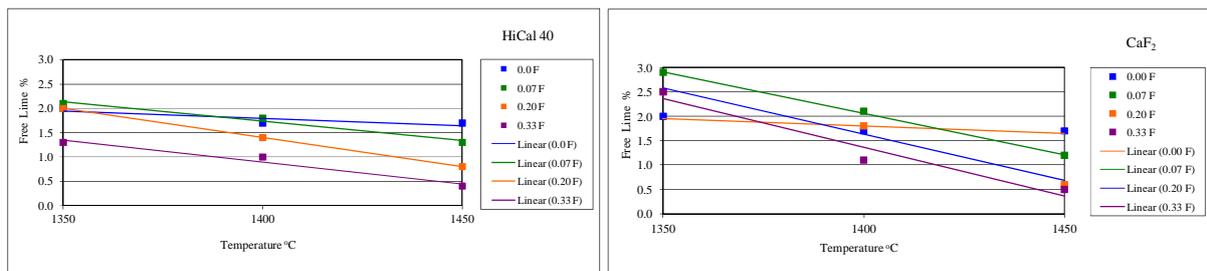
Figure 2 - Relationship between Free Lime and Temperature for levels of HiCAl 40 and CaF$_2$ sourced fluoride

3.2.2 Burning Results for HiCAl 40 at 97 LS and 101 LS

Table 5 summarizes the hypothetical clinker characteristics of rawmixes for the LS target of 97 and 101 and again shows that only the added fluoride level and perhaps the associated Na$_2$O are significant variables. The purpose of the highest lime saturation rawmix was essentially to see whether any degree of mineralization could be observed in a static furnace environment under these conditions.

Selected XRF analyses of rawmixes again provided evidence that chemical composition was not changed during burning and that the hypothetical clinker targets were achieved.

Table 5 Hypothetical Clinker Composition HiCAl 40 at LS 97 and LS 101

Fluoride Source		LS Target 97				LS Target 101			
		HiCAl 40				HiCAl 40			
Added Fluoride	%	NIL	0.07	0.20	0.33	NIL	0.07	0.20	0.33
LS	-	97.0	97.0	97.0	97.0	101.0	101.0	101.0	101.0
SR	-	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
AR	-	1.79	1.77	1.85	1.94	1.71	1.75	1.84	1.93
Na_2O	%	0.48	0.56	0.71	0.87	0.46	0.55	0.71	0.86
C_3S	%	66.6	66.6	66.2	65.7	76.0	75.8	75.3	74.7
C_3S (corrected for 1% free lime)	%	62.6	62.6	62.2	61.7	72.0	71.8	71.3	70.7
C_2S	%	11.5	11.5	11.6	11.8	2.8	2.9	3.1	3.3
C_2S (corrected for 1% free lime)	%	14.5	14.5	14.6	14.8	5.8	5.9	6.1	6.3
C_3A	%	9.4	9.3	9.7	10.0	8.8	9.0	9.4	9.7
C_4AF	%	9.4	9.5	9.2	8.9	9.4	9.3	8.9	8.6

Figure 3 below shows the free lime results for the clinkers produced from rawmixes at LS 97. Results are very similar to those at LS 94 except that as expected, the level of residual free lime is higher. The effect of the added fluoride and temperature are again clearly demonstrated. The effect on burning temperature for equivalent free lime is again of the order of 100°C.
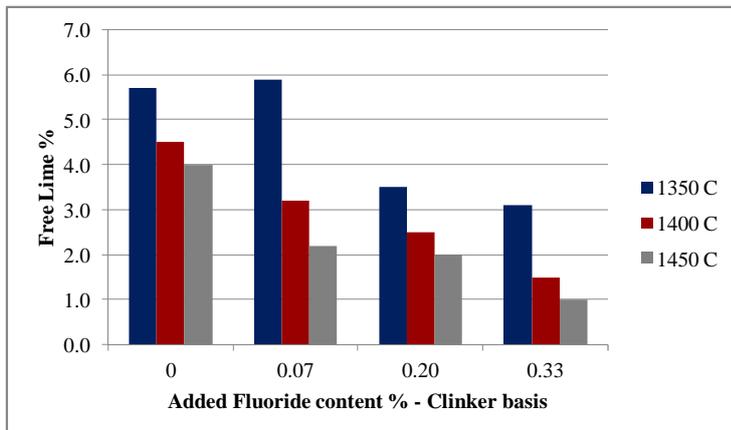
Figure 3 Effect of Added Fluoride on Free Lime - HiCAl 40 - LS 97

Figure 4 shows the residual free lime content for the clinkers produced from rawmixes at 101 LS. Whilst it is apparent that both temperature and fluoride level improve burnability it is also apparent that free lime levels below 2% were not attained even at 1450°C and the highest fluoride addition rate. This implies that whilst the burnability is improved reduction of free lime below 1% has not been achieved in the static furnace at the high LS.
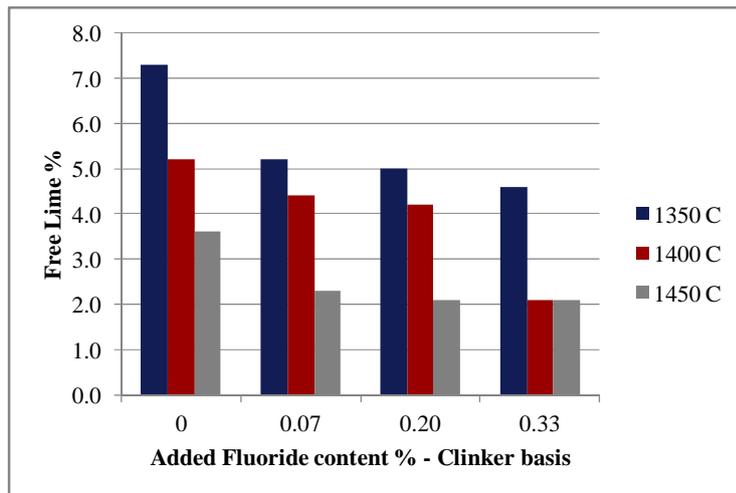
Figure 4 Effect of Added Fluoride on Free Lime - HiCAl 40 - LS 101

4. Industrial Application

HiCAl 40 is used in several plants to exploit the potential of alkali and fluorides from this source for cement manufacturing. Table 6 shows the chemical and mineralogical composition of a clinker produced using HiCAl 40 with a F level of 0.19% and a Na_2O content of 0.41%. It confirms the successful incorporation of the minor elements from the refined by-products into clinker.

The mineralogical composition with 66% of alite and 10% of aluminate indicate a good clinker reactivity.

Table 6a - Chemical composition of industrial clinker with HiCAl 40

Property	Unit	Value
LOI	%	1.40
SiO_2	%	20.59
Al_2O_3	%	5.83
Fe_2O_3	%	2.97
CaO	%	66.61
MgO	%	0.93
SO_3	%	0.30
K_2O	%	0.23
Na_2O	%	0.41
TiO_2	%	0.26
Cl	%	0.01
F	%	0.19

Table 6b - Mineralogical composition of industrial clinker with HiCAl 40

Mineral	Unit	Value
Alite (XRD)	%	65.70
Belite (XRD)	%	16.18
Aluminate (XRD)	%	9.95
Ferrite (XRD)	%	7.27

Figure 5 shows a comparison of industrial cement mortar strength measured for cements produced from clinker with and without HiCAl 40. The results confirm the better clinker reactivity as expected for clinker with elevated fluoride and alkali contents whereby the relative impact is most pronounced for the 3 and 7 days strength results.
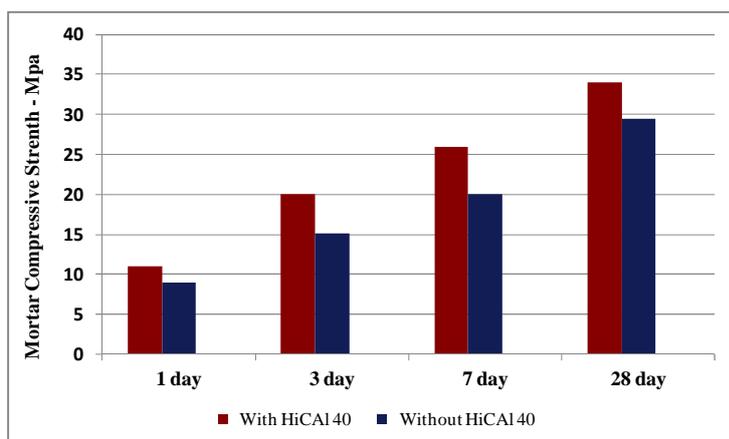
Figure 5 Effect of HiCAl 40 on Cement Mortar Strength

5. Conclusions

This work has established that the beneficial effect of fluoride on clinker burnability does not depend on the type of fluoride mineral used, be it cryolite (Na_3AlF_6), villiaumite (NaF), fluorite (CaF_2), or sodium silicofluoride (Na_2SiF_6). The different pure fluoride salts including those present in refined by-products from the aluminium industry such as HiCAl 40 were used to dope industrial rawmeals and undergo laboratory burnability testing. These doped rawmeals exhibited similar burning behaviour at the same fluoride content.

It has also established that HiCAl 40, a refined by-product derived from spent potlining, has similar burnability improvement characteristics to fluorite tested in rawmixes at 94 LS. At this LS, to achieve a free lime of 1.5%, a temperature reduction of the order of 100 ^{o}C is indicated - with commensurate potential energy and other savings in industrial clinker burning. HiCAl 40 exhibited similar characteristics when incorporated into rawmixes at 97 and 101 LS.

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6. Acknowledgements

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