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Dedicated to Dr. Robert Mackenzie on the occasion of his 75th birthday

THERMAL CHARACTERISTICS OF AGED GRANULATED BLAST FURNACE SLAGS

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Abstract

A series of aged granulated blast furnace slags were investigated by DTA. Devitrification characteristics were found to change as a function of age, and regular trends could be established. XRD showed the devitrification process to result predominantly in melilite formation and minor amounts of merwinite, depending on slag age.

Hydration of fresh slags resulted in the gradual formation of hydrated species and calcite. DTA indicated that the devitrification profile also changed with the extent of hydration.

Keywords: blast furnace slags, devitrification

Introduction

Blast furnace slag is a by-product of the iron-making process, resulting from the fusion of coke ash, aluminous and siliceous gangue from iron ore, with oxides from the breakdown of limestone and dolomite. When poured the molten stream of slag is quenched with a stream of water to yield the glassy granulated material.

Granulated slag is produced in large quantities throughout the world. Once dried and finely ground, it has considerable hydraulic properties when mixed with cement. These properties were first used in Germany in 1865, and by 1892 the Portland blast furnace type of cement was in production [1]. In Australia the first investigation into processing slag occurred in 1963 by Australian Iron and Steel and Portland Cement [1, 2].

Because the slag is stockpiled it ages with time, slowly undergoing changes to its properties that can affect performance and marketability. Therefore, an indication of aging within a slag would be a useful indicator of its worth in cement manufacture.

Experimental

Slags are essentially glasses belonging to the quaternary system, $CaO-MgO-Al_2O_3-SiO_2$. While their composition can vary significantly usually CaO occurs in the range 35–45%, SiO_2 30–35%, Al_2O_3 9–15% and MgO 4–12% [3]. The slags in this study had the typical composition shown in Table 1.

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Table 1 Chemical analysis of blast furnace slag

Slag	SiO$_2$/	FeO/	Al$_2$O$_3$/	TiO$_2$/	MnO/	CaO/	MgO/	Na$_2$O/	K$_2$O/	S/
					%					
N'cle	34.5	1.4	13.9	0.54	0.42	42.3	6.6	0.23	0.35	0.45

Granulated slags from BHP Newcastle Steelworks were sampled from various aged stock-piles, air-dried and investigated 'as received'. The age of the slags ranged over a stockpiling period of about up to 6 months.

Samples were investigated in granulated form, which meant that grains could be as large as 0.5 mm, and also as powders (<40 μm).

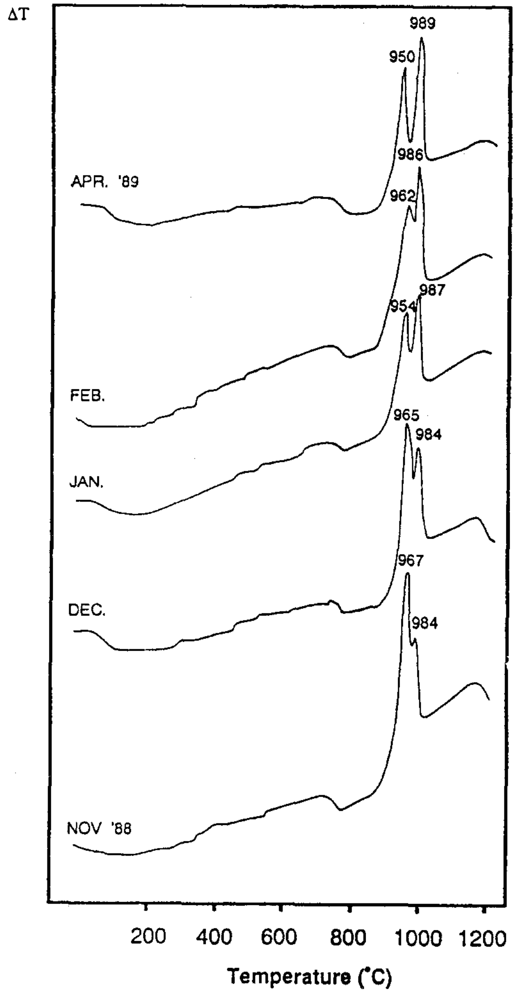

Fig. 1 DTA of Newcastle granulated slag (in N$_2$)

Devitrification studies were carried out using a Rigaku Denki Thermoflex 1500 instrument. Slag samples (50–70 mg) were heated in platinum cups to 1200°C in both nitrogen and oxygen atmospheres. The heating rate was typically 20°C, but a series of tests was done with rates between 10–50°C.

Powder diffraction patterns of slags were recorded on a Siemens D500 diffractometer using CuK_α radiation. Data were evaluated using DIFFRAC 11 software.

Hydration of fresh slags was carried out by mixing ground slag and water in a 1:1 ratio by weight and allowed to stand. At fixed intervals ranging from 1 day to 12 weeks, a portion of the mixture was removed, the slag dried and examined by XRD and DTA.

Results and discussion

DTA of granulated slags

The DTA curve obtained for each granulated Newcastle slag (Apr.89–Nov.88) taken from an individual stockpile, in nitrogen, is shown in Fig. 1. Each curve revealed essentially two devitrification peaks between 900–1000°C, preceded by a glass transition (T_g) just before 800°C. It is apparent however, that the curves underwent systematic changes, the peaks coalescing with slag age. At the same time the intensity of the first peak grew with respect to the second.

Also, the DTA curves recorded in O_2 were very similar to those obtained in N_2. This indicated that the slags were not influenced by atmosphere during devitrification, a result that is not surprising for grains of such large size. The atmosphere ef-

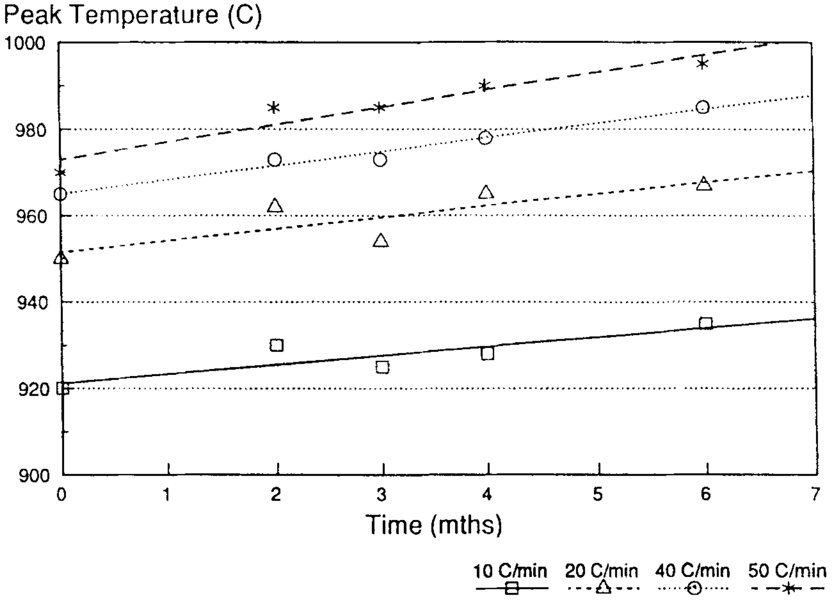

Fig. 2 Devitrification peak temperature *vs.* time for aged Newcastle slag heated at various rates

fected only the surface of the grain but had little influence upon the large bulk of it undergoing thermal crystallisation.

Each of the aged Newcastle slags was heated at variable rates, 10–50°C min^{-1}. From the corresponding DTA curves were obtained the devitrification peak temperatures, temperature differences between peaks and the ratio of their heights.

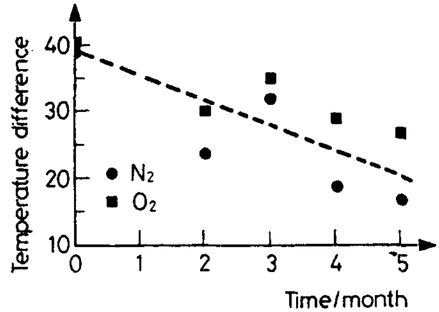

Fig. 3 Temperature difference between devitrification peaks vs. age of Newcastle slag (in N_2 and O_2)

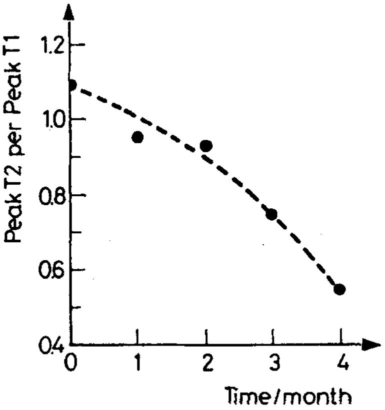

Fig. 4 Ratio of peak height temperatures *vs.* age of Newcastle slag

Figure 2 illustrates the increase in peak temperature for the first devitrification step at all heating rates, as the slag aged. As a result of coalescence, a decrease in peak temperature difference occurred with slag age (Fig. 3). And finally, the peak height ratio also decreased with slag age (Fig. 4). These trends were similar in both atmospheres.

Because heating slags of such large size at fixed rates caused grains to 'jump' unpredictably from the heating pans, the DTA curves were variable and peak heights did not necessarily bear a direct relationship to sample mass. To test the reproducibility of measured peak ratios a pair of slags were run repeatedly. The results in Table 2 show that while the peak heights for individual runs could vary widely, the ratio was effectively constant.

Table 2 Reproducibility of DTA results for aged Newcastle slag

Sample	Mass/mg	Pk Ht T_1/mm	Pk Ht T_2 /mm	T_2/T_1
Slag (Apr. 89)	37.88	13	14	1.08
"	43.56	45	45	1.00
"	39.08	30	35	1.17
"	32.77	30	32	1.07
"	33.84	16	18	1.18
"				1.09 (mean)
Slag (Dec. 88)	48.20	68	56	0.82
"	37.88	42	31	0.75
"	38.34	28	21	0.75
"	34.2	38	28	0.74
"	32.71	36	25	0.69
"				0.75 (mean)

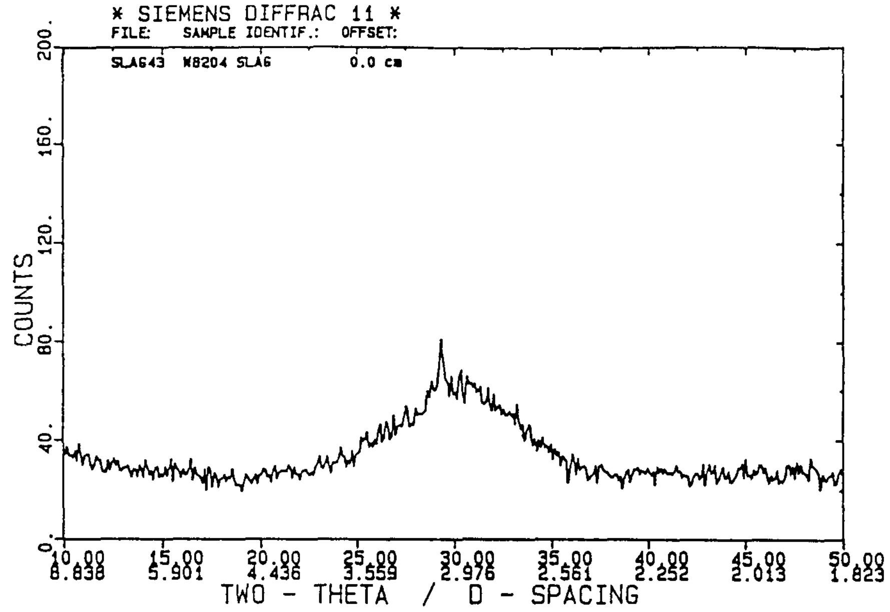

Fig. 5 XRD of Newcastle slag

Empirically, it would appear that the peak ratio and peak temperature of devitrification are the more reliable parameters to measure, and suggest a means of assessing the 'age' of a slag in a given strand without altering the sample by grinding or crushing.

It should be noted that, due to their unavailability, slags that had been stockpiled for longer than 6 months were not tested. Obviously the trends seen would reach a point of no further change with progressive age, and additional older slags would be necessary to establish that time period.

XRD of slags

Because of the glassy nature of the slags their XRD patterns revealed only broad humps centred at 2.95 Å (Fig. 5). Superimposed upon these were a few weak peaks due to small amounts of crystalline material. Nevertheless a consistent increase in area of the diffraction humps was observed throughout the series (Table 3). This undoubtedly related to changes in glass properties as the slag aged.

Table 3 XRD of aged Newcastle slags

Slag	Peak area/mm^2	Melilite	Merwinite	α-$CaSiO_3$	$Ca(OH)_2$
Ncl (Apr.89)	4330	M	L	–	T
Ncl (Feb.89)	4320	M	–	T	T
Ncl (Jan.89)	4360	M	–	–	–
Ncl (Dec.88)	4660	M	VL–L	VL	T
Ncl (Nov.88)	4475	M	–	VL–L	T

M=major, L=little, VL=very little, T=traces

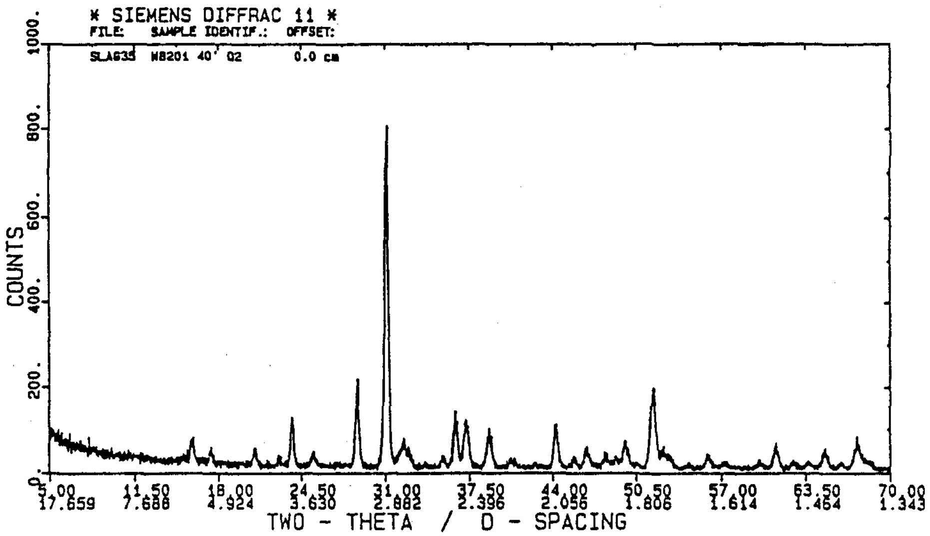

Fig. 6 XRD of devitrified Newcastle slag

Once devitrified however, Newcastle slags produced a characteristic crystalline pattern (Fig. 6). Each slag resulted in formation of melilite [4, 5], corresponding to the åkermanite-gehlenite ($2CaO{\cdot}MgO{\cdot}SiO_2$ – $2CaO{\cdot}Al_2O_3{\cdot}SiO_2$) solid solution. This was the identified final product for each slag sample.

The first devitrification step was not identified by XRD due to its close proximity in temperature of the second step. However, Negro and Murat [6] have verified that for slags with high Mg content the first crystallization step results in formation of merwinite ($Ca_3Mg(SiO_4)_2$). This subsequently reacts with alumina producing melilite. As Newcastle slag contained about 6.5% MgO the initial formation of merwinite was considered very likely.

In the diffraction patterns of crystallized slags the peak at 2.69 Å was consistent with the presence of merwinite. It was found in the freshest slag and in the older Jan.89 sample (Table 3). It was absent in the oldest slag where low levels of wollastonite (α–$CaSiO_3$) were seen. Traces of Portlandite ($Ca(OH)_2$) were present.

An earlier study [5] of different slags reported that the phase formed in the first devitrification step was affected by the mole fraction of alumina in slag. The fraction of alumina x, was expressed as:

$$x = \%(Al_2O_3)/\%(Al_2O_3+MgO)$$

For $x<0.4$ the first phase formed was merwinite which transformed to melilite during the course of crystallization. However, for $x>0.4$ direct conversion to melilite took place. Newcastle slags possessed values of about 0.7 suggesting that direct conversion to melilite should occur. Results of Table 3 indicate that this was not quite the case. Moreover, merwinite has been reported [4] in slags with $x>0.6$.

In conclusion, both DTA and XRD revealed that aging affects the devitrification process. It may be that aging influences the extent and course of surface and/or bulk crystallization and thereby, in the case of these slags, the merwinite-melilite conversion reaction.

Hydration of blast furnace slags

Slag undergoes reaction when added to water although it does not set unless an activator (lime, or cement and $CaSO_4$) is added.

In this brief study the hydration behaviour of fresh Newcastle ground slag was investigated over a period of 1 day to 12 weeks.

Figure 7 shows the DTA curves obtained over this period. DTA detected the changes the slags underwent in a few days, and proved sensitive to the ensuing hydrolysis reactions. The appearance of a broad endotherm at 100–130°C, becoming progressively more pronounced with length of the hydration period, resulted from the formation of hydrated species.

Simultaneously the character of the devitrification peaks changed and an endotherm gradually emerged at about 800°C. The latter was due to gradual carbonation and formation of calcite, as confirmed by XRD. Figure 8 shows the rapid development of $CaCO_3$ during the first 4 weeks of hydration and which was almost complete after this time.

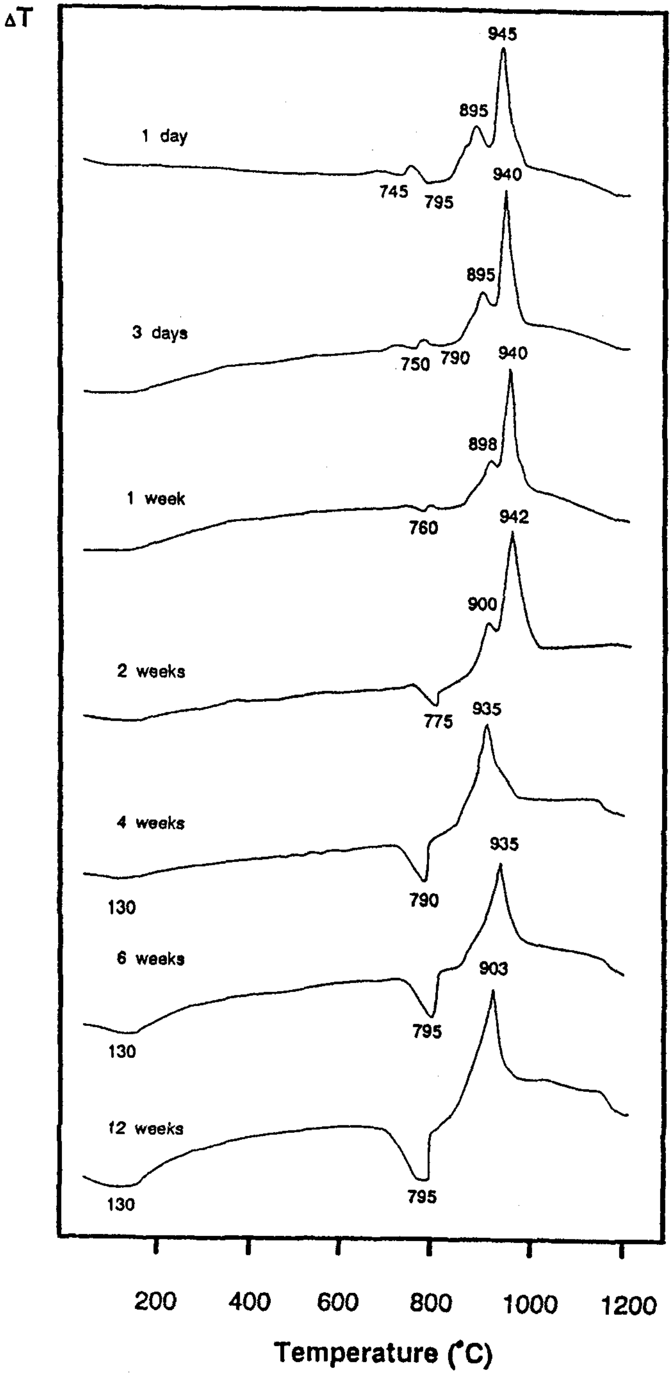

Fig. 7 DTA of hydrated Newcastle slag

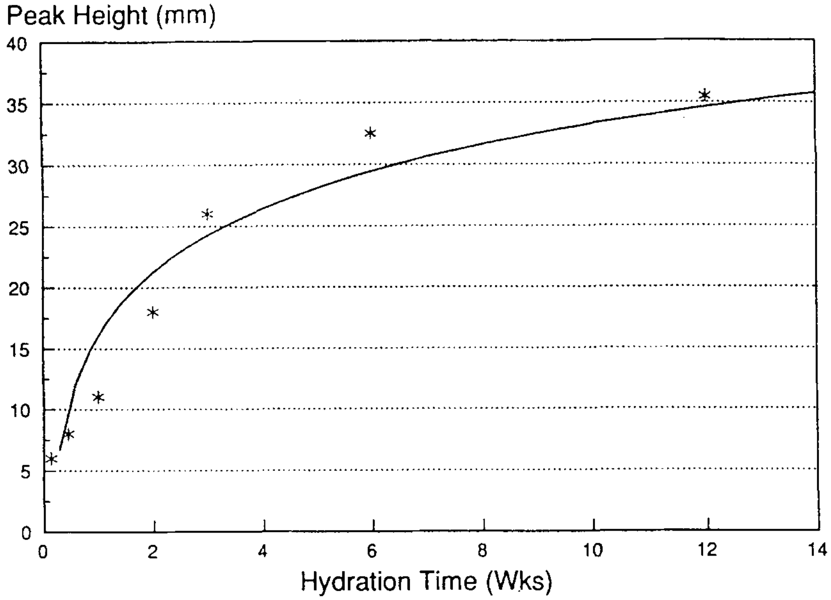

Fig. 8 Calcite peak height *vs*. hydration time for Newcastle slags

Earlier work [7] on the agglomeration of slags reported the formation of 10 μm particles of the hydrated species, ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$), and intergrowths of calcite.

The devitrification exotherms in both slags underwent temperature shifts and shape changes that may relate to processes that occur during slag aging.

Conclusions

1) The DTA results indicated that granulated slags, 'as received', can be analysed directly, revealing aging trends independent of the surrounding atmosphere.

2) Under suitable standardized conditions it seems feasible to monitor aging characteristics of granulated slags from a given production strand by DTA.

3) Hydration of fresh samples of slag resulted in changes to the glass component of the slag as well as gradual formation of calcite and complex hydrated species.

* * *

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