Studies of the system CaO-SiO₂-AI₂O₃-MgO **in relation to the stability of blastfurnace slag**

W. GUTT, A.D. RUSSELL *Building Research Station, Garston, Watford, UK*

Phase equilibria in the 5% magnesia plane of the quaternary system CaO-SiO₂-AI₂ O₃-MgO and in the high lime region of one of the bounding ternary systems, namely CaO- $Al_2O_3-SiO_2$, have been investigated by high temperature microscopy and X-ray analysis and substantial new data is presented. This study is one of a series designed to determine the extent of dicalcium silicate formation in the system $CaO-SiO₂-Al₂O₃ -MgO$ which accounts for over 95% of the composition of blastfurnace slag. Phase diagrams are presented based on an examination of approximately 150 synthetic compositions. The results are relevant to the stability of blastfurnace slag. The mineralogical information assembled will be of use also however in the wider application of industrial by-products **some** of which contain compounds occurring in the system lime-silica-aluminamagnesia. The results are also relevant to cement chemistry and to the study of igneous rocks.

1. Introduetion

The system $CaO-SiO₂-Al₂O₃-MgO$ is of considerable importance in the technology of a large number of industrial processes. In particular, high temperature phase equilibria in this system are of practical importance in the selection of blastfurnace slags for use as concrete aggregate or roadstone; 95% of the composition and compounds found in blastfurnace slag are accounted for by the component oxides CaO, $SiO₂$, $Al₂O₃$ and MgO.

Dicalcium silicate, one of the compounds which occurs in some blastfurnace slags, can undergo a polymorphic inversion (metastable β to stable γ) which involves an approximately 10% volume increase and may cause disruption of the slag. Blastfurnace slags containing dicalcium silicate may therefore be potentially unstable and are at present excluded from use by criteria derived from high temperature phase equilibrium studies, embodied in BS1047:1952 'Air Cooled Blastfurnace Slag Coarse Aggregate for Concrete'. Although long term stabilization of the beta form is well known, the work described in this paper had the objective of improving the stability equations by which slags containing dicalcium silicate are excluded from use. It was hoped that it might be possible to widen the range of slag compositions passing the acceptance clauses particularly at the high magnesia levels. To improve the criteria, new knowledge has been sought and obtained on the occurrence of dicalcium silicate in the relevant systems.

Dicalcium silicate has a large primary crystallization volume in the quaternary system CaO- $Al_2O_3-SiO_2-MgO$, and the extent of this has been under investigation. Earlier results of these studies $[1-3]$ have permitted delineation of the dicalcium silicate primary crystallization field in the partial systems $C_2 S-M_2 S-Al_2 O_3$, $C_3 MS_2 MA-C_2AS$ and $C_2MS_2-C_2AS-C_3MS_2$.^{*} In the present study, the liquidus surface of the 5% magnesia plane of the quaternary system CaO- $Al_2O_3-SiO_2-MgO$ has been delineated. As part of this investigation the tricalcium silicate field in

^{*}A shorthand nomenclature for the chemical formulae of complex silicates is used C = CaO, S = SiO₂, A = Al₂O₃, $P = P_2O_5$, $M = MgO$, but this notation is not used for individual oxides where they occur. *9 1977 Chapman and Hall Ltd. Printed in Great Britain.* 1869

Figure 1 Liquidus surface of the 5% magnesia plane in the quaternary system CaO-A1₂O₃-SiO₂-MgO. The 5% MgO plane represents a section through the tetrahedron, representing the system CaO-SiO, $-AI$, O₃ $-M$, O constructing lines parallel to the sides of the equilateral triangle, through any point within the triangle, the composition percentages in weight at this point in terms of the oxides constructing lines parallel to the sides of the equilateral triangle, through any point within the triangle, the composition percentages in weight at this point in terms of the oxides Figure 1 Liquidus surface of the 5% magnesia plane in the quaternary system $CaO - Al_2O_3 - SiO_2 - MgO$. The 5% MgO plane represents a section through the tetrahedron, representing the system CaO-SiO₂ - M₃O₃ - MgO. Compositions are represented by triangular co-ordinates: Each side of the equilateral triangle is divided into 95 parts, and by can be read off where the constructed lines intersect the sides of the triangle. This method of presentation is normal for condensed ternary systems. can be read off where the constructed lines intersect the sides of the triangle. This method of presentation is normal for condensed ternary systems.

the 5% magnesia plane and in the bounding plane $CaO-SiO₂-Al₂O₃$ has also been delineated.

2. High temperature phase equilibrium studies

2.1. Experimental

Compositions studied were prepared from crushed quartz (99.95% pure), $CaCO₃$ (99.9% pure) MgO (99.9% pure) and Al_2O_3 (99.9% pure) and heat treated as described earlier [1].

The technique of high temperature microscopy [4,5] enabled liquidus temperatures up to 2150° C to be determined. Where possible, both the primary phase and the secondary phases crystallizing were identified by their characteristic crystal growth in the melt. Quenching of selected compositions either on the microscope hot-stage, or by heat treatment simulated in a quench furnace, provided confirmation of the identity of the phases observed on the microscope hot-stage. Quenches were examined optically and by X-ray analysis using a de Wolff type quadruple focussing camera of 114.6 mm diameter with copper K_{α} radiation.

2.2. Results

Translations of certain boundary points from phase diagrams of the partial systems $C_2 S-M_2 S \text{Al}_2\text{O}_3$, $\text{C}_3\text{MS}_2-\text{MA}-\text{C}_2\text{AS}$ and $\text{C}_2\text{MS}_2-\text{C}_2\text{AS} C_3MS_2$ [1-3] and from the phase equilibria in the 0, 5, 10, 15, 20, 25, 30 and 35% alumina planes in the quaternary system published by Osborne *et al.* [6] provided guidance in selecting compositions for study in the 5% magnesia plane. At the liquidus, seventeen solid phases were found in this plane, each clearly identifiable by its mode of growth, behaviour in the melt and optical properties. Fig. 1 shows the complete liquidus surface of the 5% magnesia plane.

At the liquidus, dicalcium silicate crystals were of low birefringence; on cooling, the marked inincrease of birefringence associated with the α to α' inversion, first observed in the system $C_2 S - C_3 P$ [7] was readily visible. Over a small compositional region, (shaded in Fig. 1) high refractive index crystals showing strong birefringence and twinning were found as the primary phase. These crystals which grew as 'hour glass' structures illustrated in Fig. 2 were positively identified by quenching and X-ray analysis as the calcium magnesiosilicate $C_{1.7}M_{0.3}S$ characterised by Gutt [8]. The crystallographic identity of $C_{1.7}M_{0.3}S$ also known as 'T phase' is a complex subject which will not be discussed in detail in the present paper. It should be noted however that phase equilibrium studies by Gutt [8] and by Schlaudt and Roy [9] have indicated, in agreement with Gutt's original work, that $C_{1.7}M_{0.3}S$ is a compound. Comparison of this outlook with the crysto-chemical appraisal of the identity of $C_{1.7}M_{0.3}S$ based on studies of the polymorphism of dicalcium silicate have already been considered [10].

In the region where $C_{1.7}M_{0.3}S$ has been found, the temperature contours are steep, and a much more extensive analysis of compositions in this region would be needed to delineate the exact field of this phase.

Melilite crystals grew in perfect rectangular plates which, however, did not always exhibit the strong polarization colours associated with this phase. Anorthite which grew as hexagonal crystals in the melt was easily distinguished from the melilite plates. Isotropic spinel octahedra and hexagonal plates of low birefringence corundum crystals were readily grown from compositions where they were the primary crystallization phases. Mullite crystals exhibited the acicular (needlelike) growth associated with this phase, and were easily distinguished from the arrow-headed type crystals of quartz. Some difficulty was experienced in

Figure 2 Crystals of 'T' phase growing in melt at 1310° C \times 75.

crystallizing compositions after melting in the high silica regions where pseudo-wollastonite, quartz and pyroxene occurred as the primary phases. Slow melting, due to high viscosity of the melt, tended to give elevated false liquidus temperatures for these compositions. The primary crystallization fields of the calcium aluminates in the 5% MgO plane are essentially those by Parker [11] based on his own work and that of McMurdie and Insley [12]. It appears probable that in a completely dry atmosphere a eutectic is formed between C_3 A and CA in the system $CaO-A1₂O₃$, but at normal humidities a compound intermediate between $Ca_{12}Al_{14}O_{33}$ and $Ca_{12}Al_{14}O_{32}$ (OH)₂ intervenes [13]. Therefore under the practical conditions of the present study, where moisture was not rigorously excluded, the formation of a "C₁₂ A₇" phase in appropriate circumstances can be assumed. The composition of the quaternary compound reported by Parker [11] C_6A_4MS has not been confirmed, although it has been suggested that this phase may be two separate compounds [14].

Liquidus temperatures in the region of tricalcium silicate primary phase field in both the 5% magnesia plane and in the bounding plane CaO- $\text{Al}_2\text{O}_3-\text{SiO}_2$ (Fig. 3) reach values up to 2000°C. Angular tricalcium silicate crystals were visible in melts at these temperatures. Prolonged heating of compositions in this region tended to alter the primary phase indicating some loss of lime. Direct high temperature microscopy has confirmed yet again the finding of Welch and Gutt [15-17] that tricalcium silicate does not decompose in the solid state at 1900° C into $2CaO.SiO₂$ and lime, but that it melts incongruently and can therefore be found in contact with liquid.

Where possible, the second phase crystallizing as well as the primary phase have been identified directly by high temperature microscopy and a summary of compositions studied and individual observations made is given in Tables I and II. These are offered in addition to the phase diagrams, since such individual results provide data for direct translation into related phase systems.

Figure 3 The tricalcium silicate primary field in the system CaO-A1₂O₃ -SiO₂ (compositions in wt %). **1872**

Mix No.		Composition (Wt %)			Liquidus	Second and third phases	Method of	
	CaO	AI ₂ O ₃		MgO	temperature $(^{\circ}C)$	where identified and their dissolution tempera- ture $(^{\circ}C)$	Identification	
		Primary phase dicalcium silicate $(C_2 S)$						
7	46.5	10	38.5	5	1379	Melilite T Phase $C_{1,7}M_{0,3}S$	a,b,c	
14	50.5		44.5	5	1376	Rankinite $(C_3 S_2)$	a	
15	51		44	5	1450		a	
18	50	2.5	42.5	5	1444		\mathbf{a}	
19	51	2.5	41.5	5	1585		\mathbf{a}	
20 23	49.5	2.5	43	5 5	1407	Rankinite (C_3S_2)	a,b,c	
32	48 47	7 27	40 21	5	1428	Melilite	a	
33	47	15	33	5	1510 1494		a	
39	54	29	12	5	1507		\mathbf{a}	
	50	10	35	5	1607		a a	
48	52	10	33	5	1707		a	
49	54	10	31	5	1780		a	
50	47	25	23	5	1515		a	
51	47	23	25	5	1532		a	
52	48	5	42	5	1371	T Phase, Melilite	a,b,c	
53	50	4	41	5	1530		a	
54	50	5	40	5	1559		a	
55	49	4	42	5	1422		a	
57	49	6	40	5	1474		a	
58	50	$\pmb{7}$	38	$\sqrt{5}$	1587		а	
59	55	5	35	5	1855		a	
74	47	8	40	5	1365	T Phase	\mathbf{a}	
81	62	10	23	5	1807	Tricalcium Silicate	a	
103	52	35	8	$\sqrt{5}$	1400	Tricalcium Aluminate	a	
119	48	$\boldsymbol{6}$	41	5			a	
		Primary phase Melitite (Solid solution of C_2 AS and C_2MS_2)						
5	44.5	12	38.5	5	1357		a	
$\boldsymbol{6}$	44	12	39	5	1360		a	
8	46	10	39	5	1376	Merwinite	a	
12	45	10	40	5	1347		a,b	
13	45	15	35	5	1456		\mathbf{a}	
22	46	$\pmb{7}$	42	5	1332	T Phase	a,b,c	
27	34	32	29	$\sqrt{5}$	1479		\mathbf{a}	
31	45	28	22	5	1477	Dicalcium Silicate	\mathbf{a}	
36	40	12	43	5	1299		a	
38	33	21	41	5	1288		a,b	
42	46	5	44	$\mathfrak s$	1336	T Phase, Rankinite	a,b	
60	45	17	33	5	1438	Dicalcium Silicate	a,b	
64	32	28	35	5	1401	Anorthite	a	
75	46	9	40	5	1340		$\mathbf a$	
76	46	8	41	5	1316	T Phase	a	
79	32	26	37	5	1400		a	
106 110	44 41	40 44	11 $10\,$	5 5	1378 1416		a a	
29		Primary phase anorthite $(CAS2)$ 30	40		1398			
30	25 25	32	38	$\mathfrak s$ 5	1409	Spinel	\bf{a}	
37	31	21	43	5	1308		a a,b	
68	$30\,$	14	51	$\mathfrak s$	1213		\bf{a}	
69	12	28	55	5	1394		a	
${\bf 78}$	30	26	39	5	1319		a	
							Table I continued	

TABLE I Liquidus and other data for individual compositions studied in the 5% MgO plane of the system

TABLE I continued

Mix No.		Composition (Wt %)			Liquidus	Second and third phases	Method of		
	CaO	AI ₂ O ₃	SiO ₂	MgO	temperature $(^{\circ}C)$	where identified and their dissolution tempera- ture $(^{\circ}C)$	Identification		
		Primary phase Pseudo Wollastonite (CS)							
35	40	10	45	5	1319		\bf{a}		
61	47	2.5	45.5	5	1412		\mathbf{a}		
67	32	12	51	5	1283		$\mathbf a$		
73	47	$\overline{4}$	44	5	1365	T phase	a		
80	48	$\mathbf{1}$	46	5	1425	Rankinite	\mathbf{a}		
120	32	5	58	5	1337		a		
126	28	$\overline{7}$	60	5			\mathbf{a}		
Primary phase Calcium Aluminate (CA)									
45	41	52	2	5	1419		a,b		
		Primary phase Magnesian Pleochroite							
26	45	42	8	5	1363		a		
104	46	40	9	5	1357		\mathbf{a}		
105	45	40	10	5	1359		a		
		Primary phase Tricalcium Aluminate C ₂ A							
101	54	35	6	5	1412		a		
43	52	40	3	5	1410		\mathbf{a}		
107	50	40	5	5	1364		a		
Primary phase Pyroxene									
92	25	10	60	$\mathfrak s$	1250		a,b		
113	23	10	62	5	1253		a		
114	28	10	57	5	1247		\mathbf{a}		
122	25	13	57	5	1223		a		
127	30	10	55	5			a		
Primary phase $C_{12}A_{71}$									
109	48	42	5	5	1344		a		

TABLE I continued

a: Recognition by behaviour in melt.

b: Recognition by optical examiniation of quenched charge.

c: Recogntion by X-ray examination of quenched charge.

In general, paths of experimentally determined phase Boundaries in the 5% magnesia plane are essentially in agreement with those predicted from the translations from other intersecting planes, although the primary phase field for merwinite $3CaO.MgO.2SiO₂$ predicted by Cavalier [18] was not found. By contrast, the finding of the primary phase field of $C_{1,7}M_{0,3}S$ located in this plane was not predicted from previous work at all but it correlates with the presence of $C_{1.7}M_{0.3}S$ in some blastfurnace slags examined at Building Research Station and recently reported in some Russian blastfurnace slags [19].

Biggar [20] has suggested that the $C_{1.7}M_{0.3}S$ of Gutt is identical with Bredigite and is not related to the calcium orthosilicates. Midgley [10], on the basis of unit cells and space group, considers that bredigite and $C_{1.7}M_{0.3}S$ are substituted polymorphs of the α'_{L} form of calcium orthosilicate. The polymorphism of the calcium orthosilicates is complex however, and while the position of $C_{1,7}M_{0,3}S$ within the system $CaO-SiO_2-Al_2O_3-$ MgO and its stability is still under examination, it is probably best to keep in mind the alternative views of $C_{1.7}M_{0.3}S$ as either a compound or a polymorph of dicalcium silicate. It should be noted that Sabine [21] has detected the mineral that corresponds to $C_{1.7}M_{0.3}S$ as described by Gutt [8] in larnite-magnetite rock of Carneal. Confirmatory work on this discovery is in progress [211.

3. Discussion

3.1. Phase equilibria

The new results of high temperature phase equilibrium studies of the 5% magnesia plane have indi-

a: Recognition by behaviour in the melt

b: Recognition by optical examination of quenched charge

cated the extent of the dicalcium silicate primary crystallization volume towards the silica-rich side of the plane. Compositions in the plane behave as quaternary mixtures and the crystallization paths will be complex especially where solid solution occurs as in the melilite series. Crystallization paths in this plane can be expressed in terms of liquid and crystalline phases lying above and below the plane.

In this plane no quaternary invariant points were located, and these points must therefore lie above or below this plane. Since there are none on the 10% plane [22], those relevant to blastfurnace slag chemistry must lie between the 5 and 10% magnesia planes. Several piercing points (intersections of three adjacent volumes) have been located in the plane. At these points three solid phases and one liquid are in contact giving a condition of univariant equilibrium. It is difficult to determine experimentally the actual temperatures of the piercing points, since unlike those of eutectic or reaction points they cannot be obtained accurately by comparison of liquidus temperatures of adjacent compositions. Only by preparing mixtures falling exactly at the composition of the piercing point can the actual temperature be determined. In the present paper, temperatures are given for all the compositions studied and not the piercing points.

At complete equilibrium the relative amounts of crystalline phases in a composition are determined by the compatability sub-systems. Since there are a large number of compounds occuring in the system, a large number of compatability tetrahedra are possible. The results of the present study and those of the partial systems $C_2 S - M_2 S - Al_2 O_3$, $C_3MS_2-MA-C_2AS$ and $C_2MS_2-C_2AS-C_3MS_2$ in the system $CaO-SiO_2-Al_2O_3-MgO$ will help to establish the Alkemade joins and this will allow the system to be completely subdivided into the requisite quaternary sub-systems comprising the various equilibrium phase assemblages which could occur.

	Composition (wt $\%$)					Application of equations in BS 1047:1952		Soundness test	
	CaO	AI, O,	SiO ₂	MgO	Sulphide s	AŤ	B^{\dagger}	By calcu- lation [‡]	By observation
Synthetic slags	45.7	15.9	35.6	2.65		$47.8 \le 49.1$	$45.7 \le 41.6$	Sound	Unsound X-ray shows $\gamma + \beta$ C, S
	47.0	16.4	36.6			$47.0 \le 50.6$	$47.0 \le 42.8$	Sound	Potentially Unsound X-ray shows βC , S
Actual* slags	42.72	16.01	33.95	2.52	0.94	$44.7 \le 48.5$	$42.7 \le 41.8$	Sound	Potentially Unsound X-ray shows $10-20%$ $\beta C_2 S$
	41.05	15.59	33.88	3.79	0.91	$44.1 \le 48.6$	$41.0 \le 41.6$	Sound	Potentially Unsound X-ray shows substan- tial quantities
	38.26	16.95	31.51	8.53	0.76	$45.1 \le 45.9$	$38.3 \le 39.9$	Sound	of βC , S Potentially Unsound βC , S present

TABLE III Compositions producing dicalcium silicate on crystallization

* minor component not given

† Equation (1) CaO + 0.8 MgO ≤ 1.2 SiO₂ + 0.4 Al₂O₃ + 1.75 S (wt %)

 (2) CaO ≤ 0.9 SiO₂ + 0.6 Al₂O₃ + 1.75 S (wt %)

 $\ddot{\text{F}}$ Compliance with either Equation 1 or 2 is sufficient to establish freedom from potential lime unsoundness according 'to BS 1047:1952

3.2. Blastfurnace slag technology

An analysis of the high temperature phase equilibria from the present and previous studies $[1-3]$ would be needed to establish the Alkemade joins in the slag quaternary system. This would allow the quaternary sub-systems relevant to slag chemistry to be determined. Such analysis would be complex and has not so far been carried out. From the crystallisation paths on the appropriate bounding planes common to the sub-systems which contain $C_2 S$ and those that do not it should be possible to delineate additional space volumes within the main quaternary system in which it can be shown that $C_2 S$ will not occur. The incongruent melting behaviour of C_3MS_2 resulting in the formation of $C_2 S$ under transient conditions and the nature of 'T' phase, whether it is a compound or polymorph of $C_2 S$, produce complications in slag mineralogy.

When the present criteria in BS 1047 were formulated, it was thought that the equations erred on the safe side at low MgO levels, and to a very much larger extent at higher MgO levels. This last

point was of little consequence in that MgO levels were generally much lower in practice than they are today.

On the basis of the more extensive phase equilibrium data, $[1-3]$ now assembled, and examination of synthetic and actual slag compositions, the use of Equation 1 for low magnesia compositions does not now seem justified (see Table III). The newly delineated phase boundaries of the dicalcium silicate primary phase volume extend further towards the silica apex of the CaO- $Al_2O_3-SiO-MgO$ tetrahedron than envisaged by Parker and Ryder. Consequently some phase assemblages which were assumed by Parker and Ryder to be free of dicalcium silicate on crystallisation are likely to produce the phase. It is pertinent to point out that Parker and Ryder's equation for low magnesia compositions (Equation 1) represented a compromise between the ideal of absolute safety and obtaining a practically useful equation. Parker and Ryder were clearly aware that crystallization of $C_2 S$ could occur on the safe side of Equation 1. This is evident from Fig. 5 of

their paper, where they show what quantities of the phases, including $C_2 S$, would be precipitated during the course of crystallization.

On the basis of the present knowledge, Equation 2 would appear to be a much more satifactory condition for separating those compositions which are undoubtedly safe from those which may not be so. Parker and Ryder [23] felt that Equation 2 was somewhat too safe at low magnesia levels and that in these circumstances the use of Equation 1 was justified. It is clear from the present research that Equation 2 is in fact not excessively safe at low magnesia levels although at higher magnesia levels, for instance 10%, it undoubtedly becomes so.

Two complicating factors in establishing simple criteria for slag stability are 'arrested equilibrium' and the effect of minor components on the phase assemblages that can occur. Until these factors can be fully taken into account, and this will be very difficult to achieve, it will not be possible to improve on Equation 2 as the criterion for slag stability. Another aspect of slag stability is the question of the polymorphism of $C_2 S$ and its stability. It is not possible as yet to predict reliably and reproducibly whether a particular dicalcium silicate present in a slag is stable or only present in sufficiently small quantities to have no deleterious effect if it does disintegrate. This position could be advanced by either finding a quantitative tolerance limit below which conversion would be physically harmless or obtaining enough knowledge to distinguish between thermodynamically permanent stabilization, where the inversion temperature has been lowered to below ambient temperature, and temporary stabilization, which can be long term, but leaves the β form metastable. Inevitably the best safeguard for the present is to exclude from use slag which contains $C_2 S$ using Equation 2 and the microscope test as prescribed in BS 1047. The results reported here will be discussed with the slag processors to consider the best way of using the new data. It is important to continue to make the best possible use of current arisings of slag and to avoid any unnecessary restrictions. It should also be noted that very little slag is currently used as aggregate for concrete, the bulk of the slag being used as road material.

Acknowledgements

The work described has been carried out as part of the research programme of the Building Research Establishment of the Department of the Environment and this paper is published by permission of the Director. The work received financial support from the Slag Section of the British Quarrying and Slag Federation. Paper published by permission of Controller, H.M.S.O., holder of Crown copyright.

References

- 1. W. GUTT, J. *Iron and Steel lnst.* 201 (1963) 532.
- *2. Idem, ibid* 202 (1964) 770.
- *3. Idem, ibid* 206 (1968) 840.
- 4. J.H. WELCH, J. *ScLInstrum.* 31 (1954) 458. *Ibid* 38 (1961) 402. British Patent No 961,019/64.
- 5. W. GUTT, J. *Sei. Instrum.* 41 (1964) 393.
- 6. E. F. OSBORNE, R. C. DEVRIES, K. H. GEE and H. M. KRANER, *J. Metals* (1954) 3.
- 7. R.W. NURSE, J.H. WELCH and W. GUTT, *J. Chem. Soc.* 220 (1959) 1077.
- 8. W. GUTT, *Nature* 190 4773 (1961) 339. 207 4993 (1965) 184.
- 9. C.M. SCHAULDT and D. M. ROY, J. *Amer. Ceram. Soe.* 49 (1966) 430.
- 10. H. G. MIDGLEY, Paper presented at the VI International Congress on the Chemistry of Cement, Moscow, September 1974.
- 11. T. W. PARKER, Proceedings of 3rd International Symposium on the Chemistry of Cement (C and CA, London, 1952).
- 12. H. F. MeMURDIE and H. INSLEY, *J. Res Nat. Bur. Stand.* 16 (1936) 467.
- 13. R.W. NURSE, J.H. WELCH and A. J. MAJUMDAR, *Trans. Brit. Ceram. Soc.* 64(6) (1965) 323.
- 14. F. P. GLASSER and J. MARR, *Trans. Brit. Ceram. Soc.* 74 (1975) 113.
- 15. J. H. WELCH and W. GUTT, J. Amer. Ceram. Soc. 42 (1959) 11.
- 16. W. GUTT, PhD Thesis, London 1966.
- 17. *Idem,* Proceedings of the Fifth International Symposium on the Chemistry of Cement, Tokyo, 1968 (Cement Assoc. Japan, Tokyo, 1969).
- 18. G: CAVALIER and M. SANDREA-DEUDON. *Revue de Metallurgie* 57 (1960) 1143.
- 19. E. VED, I. ZAZHARSKII, I. KOVEL and V. BRYN-ZIV, *Budivel'niMater Konstr.* (1971) 627.
- 20. G.M. BIGGAR, *Cement and Concrete* 1 (1971) 493.
- 21. P. A. SABINE (with X-ray analysis by B. R. Young) Philo. Trans. Roy. Soc. Lond. 280A (1294) (1975) 225.
- 22. A.T. PRINCE, J. *Amer. Ceram. Soc.* 37 (1954) 402.
- 23. T.W. PARKER and J. F. RYDER, J. *Iron and Steel lnst.* 2 (1942).

Received 11 October and accepted 6 December 1976.