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Cementitious properties of metallurgical slags

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TABLE IV.

LIQUIDUS TEMPERATURES, PRIMARY PHASES, QUENCHING RATES

Sample Number	Liquidus Temperature °C	Primary Phase	Quench Rate °C per second
A-1	1408 ± 2	α CS	29.2
A-2	1274 ± 1	Pyroxene	26.1
A-3	1305 ± 3	Pyroxene	30.8
A-4	1466 ± 6	M_2S	33.5
A-7	1332 ± 5	α CS	30.4
A-8	1309 ± 4	Melilite	27.1
A-9	1454 ± 4	M_2S	33.3
A-10	1571 ± 2	M_2S	32.8
A-12	1358 ± 4	Undetermined *	35.9
A-13	1368 ± 6	Melilite	32.4
A-14	1423 ± 5	M_2S	30.9
A-15	1573 ± 3	M_2S	50.6
A-19	1427 ± 3	C_3MS_2	77.7
A-20	1607 ± 4	M	>144.7 **

* Repeated attempts to obtain an X-ray diffraction film containing sufficient lines for identification failed. Crystals could be readily grown, but all films showed only faint diffraction lines which could not be identified.

** Some crystal growth could not be prevented at the maximum programmed quench rate used, although no crystal growth was observed at a rate of approximately 400 °C per second. A pseudo-liquidus temperature of 1233 °C was noted.

B-1	1343 ± 4	α CS	35.1
B-2	1268 ± 7	CAS_2	33.5
B-3	1294 ± 5	Pyroxene	33.2
B-4	1402 ± 4	M_2S	36.3
B-7	1285 ± 6	α CS	34.7

TABLE IV. (Continued)

Sample Number	Liquidus Temperature °C	Primary Phase	Quench Rate °C per second
B-8	1260 ± 4	Pyroxene	34.3
B-9	1416 ± 5	M_2S	34.6
B-10	1524 ± 5	M_2S	30.9
B-12	1346 ± 2	Melilite (C_2AS)	33.9
B-13	1343 ± 6	Melilite	32.6
B-14	1370 ± 3	M_2S	34.3
B-15	1520 ± 4	M_2S	31.0
B-18	1454 ± 6	Melilite	35.2
B-19	1446 ± 5	MA	33.5
B-20	1522 ± 5	MA	31.9
B-24	1452 ± 3	C_3MS_2	>146.3*

* Some crystal growth could not be prevented at the maximum programmed quench rate used, although no crystal growth was observed at a rate of approximately 400 °C per second.

C-1	1383 ± 6	CAS_2	33.2
C-2	1368 ± 4	CAS_2	33.0
C-3	1358 ± 3	CAS_2	32.8
C-4	1338 ± 4	M_2S	31.3
C-7	1341 ± 5	CAS_2	32.8
C-8	1351 ± 5	CAS_2	38.1
C-9	1380 ± 4	M_2S	32.8
C-10	1446 ± 5	M_2S	35.0
C-12	1345 ± 5	Melilite (C_2AS)	35.2
C-13	1315 ± 4	Melilite	33.8
C-14	1437 ± 3	MA	32.7
C-15	1497 ± 5	M_2S	32.2
C-18	1482 ± 3	Melilite	32.7
C-19	1472 ± 4	MA	34.6
C-20	1560 ± 3	MA	35.8

TABLE IV. (Continued)

Sample Number	Liquidus Temperature °C	Primary Phase	Quench Rate °C per second
C-23	1382 ± 3	Melilite-C_2S *	>139.6 **
C-24	1469 ± 3	Melilite	36.6
C-25	1385 ± 4	MA	31.0

* Regardless of the technique used to grow crystals, both phases precipitated simultaneously. This was confirmed visually and by X-ray diffraction analysis. The composition of this slag places it near a phase boundary.

** Some crystal growth could not be prevented at the maximum programmed quench rate used, although no crystal growth was observed at a rate of approximately 400 °C per second.

D-1	1462 ± 2	CAS_2	28.6
D-2	1336 ± 4	CAS_2	32.9
D-3	1378 ± 4	CAS_2	31.4
D-4	1352 ± 4	MA	27.6
D-7	1416 ± 2	CAS_2	30.7
D-8	1392 ± 4	CAS_2	31.3
D-9	1404 ± 6	MA	30.5
D-12	1346 ± 3	CAS_2	29.3
D-13	1325 ± 5	CAS_2	29.6
D-14	1485 ± 3	M_2S	37.8
D-15	1531 ± 3	MA	32.4
D-18	1421 ± 3	Melilite	32.4
D-19	1497 ± 4	MA	30.7
D-23	1578 ± 4	Melilite (C_2AS)	32.4
D-24	1500 ± 3	MA	29.3

TABLE IV. (Continued)

Sample Number	Liquidus Temperature °C	Primary Phase	Quench Rate °C per second
D-29	1541 ± 6	Melilite	>400 *
D-30	1576 ± 5	MA	56.2
D-35	1494 ± 3	M	100.0
E-1	1546 ± 4	CAS_2	34.5
E-2	1482 ± 4	CAS_2	30.2
E-3	1422 ± 4	CAS_2	30.3
E-7	1511 ± 3	CAS_2	30.2
E-8	1460 ± 4	CAS_2	32.4
E-9	1444 ± 2	MA	30.4
E-12	1488 ± 4	CAS_2	33.2
E-13	1429 ± 5	CAS_2	31.9
E-14	1487 ± 4	MA	29.1
E-15	1562 ± 2	MA	31.2
E-18	1370 ± 4	Melilite	30.5
E-19	1528 ± 7	MA	35.0
E-23	1560 ± 2	Melilite (C_2AS)	33.6
E-24	1514 ± 3	MA	30.4
E-29	1562 ± 4	Melilite	32.8
E-30	1635 ± 5	MA	32.0
E-34	1604 ± 7	Melilite-C_2S *	103.0
E-35	1587 ± 5	MA	80.0
E-36	1720 ± 20	MA	>400 **

* Some crystal growth could not be prevented at this rate.

* Both phases precipitated simultaneously.

** Some crystal growth could not be prevented at this rate.

TABLE IV. (Continued)

Sample Number	Liquidus Temperature °C	Primary Phase	Quench Rate °C per second
F-1	1509 ± 4	CAS_2	30.2
F-2	1502 ± 2	CAS_2	30.4
F-7	1528 ± 4	CAS_2	30.0
F-8	1470 ± 3	CAS_2	32.7
F-9	1481 ± 4	MA	30.4
F-12	1530 ± 2	CAS_2	30.7
F-13	1495 ± 7	CAS_2	30.0
F-14	1512 ± 3	MA	35.0
F-15	1584 ± 4	MA	30.8
F-18	1420 ± 3	CAS_2	28.6
F-19	1562 ± 3	MA	32.0
F-23	1501 ± 3	Melilite (C_2AS)	30.7
F-24	1550 ± 3	MA	32.4
F-29	1543 ± 3	Melilite	55.8
F-34	1608 ± 3	Melilite (C_2AS)	48.0
F-35	1582 ± 2	MA	46.9

TABLE V.

COMPARISON OF LIQUIDUS TEMPERATURES OF STANDARD SAMPLES

As Obtained By Different Workers

Sample	Dr. Steyn*	Dr. Sehlke**	Dr. Jochens+	Author++
A	1392	-	1385	1395
B	1478	1480	1473	1476
C	1484	1481	1483	1486

* High temperature microscope using the technique of Cavalier (27) which employs a platinum alloy sample holder cum furnace. Temperature measurement is made by means of a micro-thermocouple inserted into the melt.

** Classical quench method.

\+ High temperature microscope based on the technique developed by Welch.

++ High temperature microscope function of the microdifferential thermal analyzer described in the text.

results and on the close agreement between the results obtained for each sample, it is felt that the liquidus temperatures reported in Table IV. are correct to within the precision shown, although the accuracy of the thermocouple (± 4°C at 1400°C) has not been taken into account.

It was desired to quench all bulk slag samples from a temperature 30 - 80°C above their liquidus temperature for the reasons discussed in Section 2.3. Thus, when the liquidus temperatures had been determined, those samples quenched from a temperature out of this range were remelted and quenched from 5[illegible] above their determined liquidus temperature.

2.6 Determination of Quenching Behaviour

It was discussed in Section 1.3 that a slag destined for cement manufacture should contain as small an amount of crystalline material as possible. To determine if the samples within the selected compositional limits were capable of being successfully granulated, a test was made to determine that quenching rate at which crystallization would not occur. This test was made on the μDTA using a thermocouple and slag sample as prepared in Section 2.5.

2.6.1 Homogeneous Nucleation-Crystallization

Both homogeneous and heterogeneous nucleation with subsequent crystal growth were expected. In homogeneous nucleation, areas having a higher degree of order than other areas will become nucleation sites. This order is achieved through a grouping together of ions. Because a lower amount of free energy exists in a system that is ordered, the natural tendency is for ions to congregate in such a way that their collective free energy is at a minimum. Hence as the temperature of a molten slag is lowered, ions will migrate to areas where the free energy is the lowest, those being the areas where the greatest degree of ordering exists.

Homogeneous nucleation depends upon a seed crystal being formed

on which subsequent precipitant can reside. It has been shown that a maximum ordering of the liquid state exists at the liquidus temperature, or lower if the system is capable of being supercooled. At this temperature, the quasi-crystallinity discussed by Solacolu [22] is at a maximum. That is to say that although ordering at random in the form of bonded silica tetrahedra exists, this order is the maximum possible in the liquid state. As areas of order are being increased and decreased randomly throughout the melt, the same degree of order overall is maintained. The thermal agitation is sufficient to prevent a sufficient number of ionic "building blocks" from joining together to form a nucleus. These groups of "building blocks" or embryos must become larger in order to become seed crystals. This can be accomplished by a slight reduction in temperature which will induce more order in the system.

The transformation of embryos to seed crystals occurs at a temperature below the liquidus temperature. Theoretically crystals should grow at a temperature just below the liquidus temperature, but, depending upon the system, the seed crystals are redissolving in the melt as rapidly as they are formed. A further reduction in temperature permits the seed crystals to grow to such a size that they cannot rapidly redissolve. These then become the nuclei of the crystalline phase.

Crystallization potential exists immediately below the liquidus temperature and increases as the system cools. As the viscosity increases due to this decrease in temperature, the mobility of the ions is restricted until the crystallization potential again decreases. Nucleation cannot occur until a certain amount of supercooling exists and hence starts at a temperature somewhat below liquidus. The zone between the liquidus temperature and the start of nucleation is referred to as the metastable zone [28].

In the case of slags whose structure is based on silica, the mobility of ions through the melt is very restricted making nucleation and

crystallization time dependent. This restriction is due to the relatively large size of the $(SiO_4)^{-4}$ ions in question. Hence highly siliceous slags can be quenched to a glass without the formation of crystals. Slags with only small amounts of silica, however, are relatively fluid and permit rapid association of the required ions into nuclei and crystals.

2.6.2 Heterogeneous Nucleation-Crystallization

Heterogeneous nucleation occurs when the melt precipitates on nuclei of some composition other than that of the crystallizing material. Blast furnace slags will normally contain varying amounts of material which do not fall into the SiO_2-Al_2O_3-MgO-CaO system. This material may be part of the melt or may exist as solidified particles or crystals.

If the impurities are present as crystals, areas in the melt which contain the impurities are areas of higher free energy, i. e., unsatisfied bonds exist. As the temperature of the melt is lowered, and thermal agitation is no longer sufficient to prevent a linking up of various ionic and molecular groups, the unsatisfied bonds of the impurities are the first to be satisfied resulting in an embryo of the melt composition forming on the foreign material which might exist as small undissolved particles or as ions. From this point on, crystallization occurs by the same mechanism as in homogeneous nucleation-crystallization.

2.6.3 Non-equilibrium Crystallization

The above discussions deal with essentially equilibrium conditions: temperature changes are rather slow allowing the maximum nucleation and crystallization to occur. Consider now the changes which occur in a slag rapidly quenched from the liquidus temperature, at a rate of several hundred degrees per second.

Highly siliceous melts will remain in the glassy state because of the immobility of crystal building ions. This immobility is brought about by the rapidly increasing viscosity of the system. Slags having

a low silica content which under equilibrium conditions would crystallize may not crystallize at all and if they do, will only do so to a limited extent. Further, if the primary phase consists of large bulky ions, there may be insufficient time for these to migrate together before the viscosity of the melt impedes their mobility. Thus a less complex secondary phase may crystallize in the absence of the primary phase.

2.6.4 Rate of Crystallization

Crystallization of silicate glasses will generally proceed at a rate given by the equation [29]:

$$R = k(T_{liq.} - T)(1/\eta)^2$$

where R = Rate of crystal growth

k = Constant

$T_{liq.}$ = Liquidus temperature of the system

T = Temperature at which rate of growth is measured

η = Viscosity.

From this equation, it can be seen that if the viscosity of the system is high or the initial cooling rate is high, the tendency of the system to crystallize is lower. Silicate slags containing relatively large amounts of silica will have a high viscosity hence their rate of crystallization will be low. Slags containing relatively smaller amounts of silica, which is present as short chains or isolated tetrahedra, will be more fluid and consequently will crystallize more readily.

2.6.5 Quenching Procedure

The μDTA used in this work provided a feature whereby the sample could be heated or cooled at programmed rates from 20°C per second to 150°C per second. These rates were found to be practically linear from 1650°C to 900°C. The method used to achieve these programmed rates was that described by Jochens [24] except that a multi-vibrator circuit capable of a wider range of preselected rates was used. In addition to

these programmed rates, a rate of approximately 400°C per second could be achieved by switching off the input current to the thermocouple.

Samples were initially quenched from a temperature 50°C above their determined liquidus temperature at a nominal rate of 35°C per second. The actual rate of quenching varied from sample to sample because of size differences in the sample and slight differences in thermocouple configuration.

Both the reference and sample thermocouples could be subjected to the same rate of cooling. The sample temperature was recorded by one pen of a two-pen recorder while the differential temperature was recorded by the second pen. The small amount of heat liberated during crystallization manifested itself as a peak on the differential temperature trace. The formation of crystals during quenching could also be monitored visually through the microscope.

The majority of the samples thus quenched showed no signs of crystallizing at this rate (35°C per second) either by visual observation or monitoring on the μDTA. Those samples which were observed to crystallize were quenched at successively higher and higher rates until crystallization was prevented. Two samples exhibited crystallization peaks on the μDTA. These peaks were accompanied by an almost explosive growth of crystals. By supercooling the melt, the crystallization potential is increased. Thus when nucleation occurs, spontaneous crystallization of the melt occurs.

The quenching rates determined are shown in Table IV. The nominal 35°C per second rate is shown for those slags which exhibited no crystallization, and that rate just sufficient to prevent crystallization is shown for those which had crystallized at lower rates. The quenching behaviour of those slags which crystallized at the maximum programmed rate (150°C per second) was observed when they were quenched at approximately 400°C. Jochens, et al. [14] have shown that the rate of quenching (about

500°C per second) on an industrial granulation plant could be simulated on the μDTA by a rate of 30 - 50°C per second because of the smaller quantity of slag used on the thermocouple. Hence the results of these tests indicate that industrial slags of similar composition could be successfully granulated without the formation of harmful quantities of crystalline materials.

2.7 Primary Phase Determination

As a molten slag is cooled from a temperature greatly in excess of its liquidus temperature, certain ions begin to link up as the thermal agitation required to keep them separate is diminished. Depending upon the composition of the melt, i. e., the molar ratios of the constituents, certain molecules will preferentially arrange themselves together. As the temperature approaches the liquidus temperature, a certain degree of order has been established. More important is the pattern of this order. This pattern or quasi-crystallinity, determines the primary phase that will eventually precipitate out of the melt when actual crystallization occurs.

The degree and patterning will differ for each slag, but slags can generally be grouped according to the primary phase that will form. Thus the determination of the primary phase is necessary.

The final operation performed on the μDTA was the preparation of partially crystallized samples for X-ray determination of the primary phase. Samples were slowly cooled from a temperature about 20°C above the liquidus temperature until a crystal was seen to grow. At this point the sample was allowed to soak until sufficient crystalline material formed to permit identification. The samples were observed during this time to detect the formation of secondary phases. These could be identified by the presence of crystals different from those formed by the primary phase.

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