TABLE I.

TYPICAL SLAG COMPOSITIONS

Slag Source		Weight Per Cent SiO_2	Al_2O_3	MgO	CaO
Basic Blast Furnace (1)	(min)	30.1	7.9	1.2	16.6
	(max)	38.0	21.9	6.0	53.4
Basic Blast Furnace (2)	(min)	30.8	12.3	3.3	35.7
	(max)	33.8	18.5	12.6	43.8
Foundry Blast Furnace (2)	(min)	26.1	12.3	2.4	40.0
	(max)	44.7	26.3	5.5	48.4
Blast Furnace (3) *		33.2	18.2	18.5	28.2
Blast Furnace (4)		35.9	11.9	20.5	26.6
Blast Furnace (8)	(min)	28.2	6.7	3.5	27.0
	(max)	39.0	19.5	22.6	47.0
Blast Furnace (10)	(min)	29.3	7.6	1.8	37.9
	(max)	38.0	21.9	6.0	53.4
Blast Furnace (12)	(min)	13.0	12.2	0.6	30.4
	(max)	36.7	37.8	20.4	46.7
Blast Furnace (13)	(min)	31.0	9.0	2.5	27.0
	(max)	38.0	14.0	22.0	42.0
Krupp-Renn ([illegible])		57.4	14.8	4.0	8.9
Ferro-manganese (2)	(min)	27.2	13.1	1.5	39.6
	(max)	28.3	14.3	6.2	42.1
Ferro-chromium (14)		27.4	16.2	11.2	42.3
Ferro-manganese (15)		24.0	8.0	0.9	19.3
Basic Oxygen Furnace (16)		29.7	0.0	6.6	43.2
Table I.	(min)	13.0	0.0	0.6	8.9
	(max)	57.4	37.8	22.6	53.4
Table I.		32.9	14.9	8.4	36.2

* Values not indicated as (min) or (max) are average values

1.4.1 Iron Blast Furnace Slags

Blast furnace slags are formed during the reduction of iron ores, primarily haematite and limonite. Slags consist of material derived from minerals associated with the ore and certain fluxing additions intentionally added to aid in the melting and refining of pig iron. The composition of blast furnace slag varies from plant to plant, but will normally have the following constituents in the proportions indicated:

SiO_2	:	28 - 41 per cent
Al_2O_3	:	6 - 30 per cent
MgO	:	2 - 20 per cent
CaO	:	27 - 45 per cent
CaO/SiO_2 ratio	:	1 - 1.5.

Much of the material which composes blast furnace slag is charged with the iron ore as gangue, notably SiO_2 and Al_2O_3. A certain amount of CaO and/or MgO may be present in the naturally occurring ore, but lime or dolomite is usually added separately. Ores which contain the proper proportion of acidic and basic components are said to be self-fluxing but additions of lime or silica are usually required to produce a slag with proper refining characteristics, suitable viscosity, reasonable liquidus temperature, and other qualities. Each of the four oxides and the interaction of these provide these functions which are optimized at specific slag compositions.

1.4.2 Steelmaking Slags

The constituents of steelmaking slags, like iron blast furnace slags, fall into the four-oxide system SiO_2-Al_2O_3-MgO-CaO. There are a number of different processes practised in steelmaking, viz., acid and basic open hearth, Bessemer, electric arc, basic oxygen, Kaldo and others, e. g., tandem and rotor. In spite of the wide variation in composition of steelmaking slags, many of them have a suitable composition which warrants their use as cement.

Unlike blast furnace slags, steelmaking slags often contain considerable amounts (5 - 10 per cent) of metallic iron as well as other impurities. Thus steelmaking slags are sometimes reprocessed to recover valuable constituents. After iron removal, steelmaking slags are occasionally used as fluxing additions to blast furnaces. This is possible because of the high CaO/SiO_2 ratios present in basic steelmaking slags. For this same reason, these slags may develop good hydraulic properties from the hydration of di- and tricalcium silicate.

Other than metallic iron, a significant amount of material representing impurities is also present in steelmaking slags. Oxides (FeO, P_2O_5, MnO, etc.) may affect the hydraulic capabilities of steelmaking slags, hence careful evaluation of these effects must be made prior to making slag cement from these slags. A considerable amount of steelmaking slags is used as raw material in the manufacture of portland cement clinker.

1.4.3 Ferro-alloy Slags

Considerable tonnages of slags are produced during the manufacture of ferro-alloys, notably ferro-chromium and ferro-manganese. Again, the major constituents of these slags are the four oxides, SiO_2 Al_2O_3, MgO, and CaO, but often considerable amounts of other oxides are present, mainly Cr_2O_3 (ferro-chromium), MnO (ferro-manganese), Fe_2O_3 and others. Jochens, Wolhuter and Howat (14) have shown that certain slags from ferro-alloy production would make satisfactory cement provided that certain compositional adjustments are made. These adjustments, in fact, yield a slag with a composition similar to that of blast furnace slags and subsequently permit treatment of the ferro-alloy slags as blast furnace slags in the manufacture of cement.

1.5 Granulation of Slags

Slags which are destined for cement manufacture must be treated in such a way that minimum crystallization occurs during cooling. The temperature at which nucleation ceases in blast furnace slags is about 840°C [17] so the problem that arises is to cool the slag rapidly from the tapping temperature to below 840°C at such a rate that crystallization cannot occur.

The commercial granulation processes provide a double function: (1) quenching of the slag from the liquid state to the solid state at such a rate as to preclude crystallization and (2) rendering the quenched product more easily handled by virtue of transforming it into small grains normally less than 5×10^{-3} m. This process is usually accomplished by directing a stream of molten slag into a high pressure jet of water, steam, or air. The rapid cooling thus achieved is sufficient to prevent crystallization. These rates depend upon the granulation method employed but it is believed that they are in excess of 500°C per second.

During commercial granulation processes, some crystals are often formed but it is believed that this is due to precooling of the slag to below its liquidus temperature prior to granulating. This usually occurs when the slag must be transported away from the furnace for granulation [13].

II. EXPERIMENTAL PROCEDURE - SLAGS

2.1 Selection of Slag Compositions

For this investigation, samples of synthetic slag were chosen within the following range of composition:

SiO_2 : 20 - 50 per cent

Al_2O_3 : 10 - 35 per cent

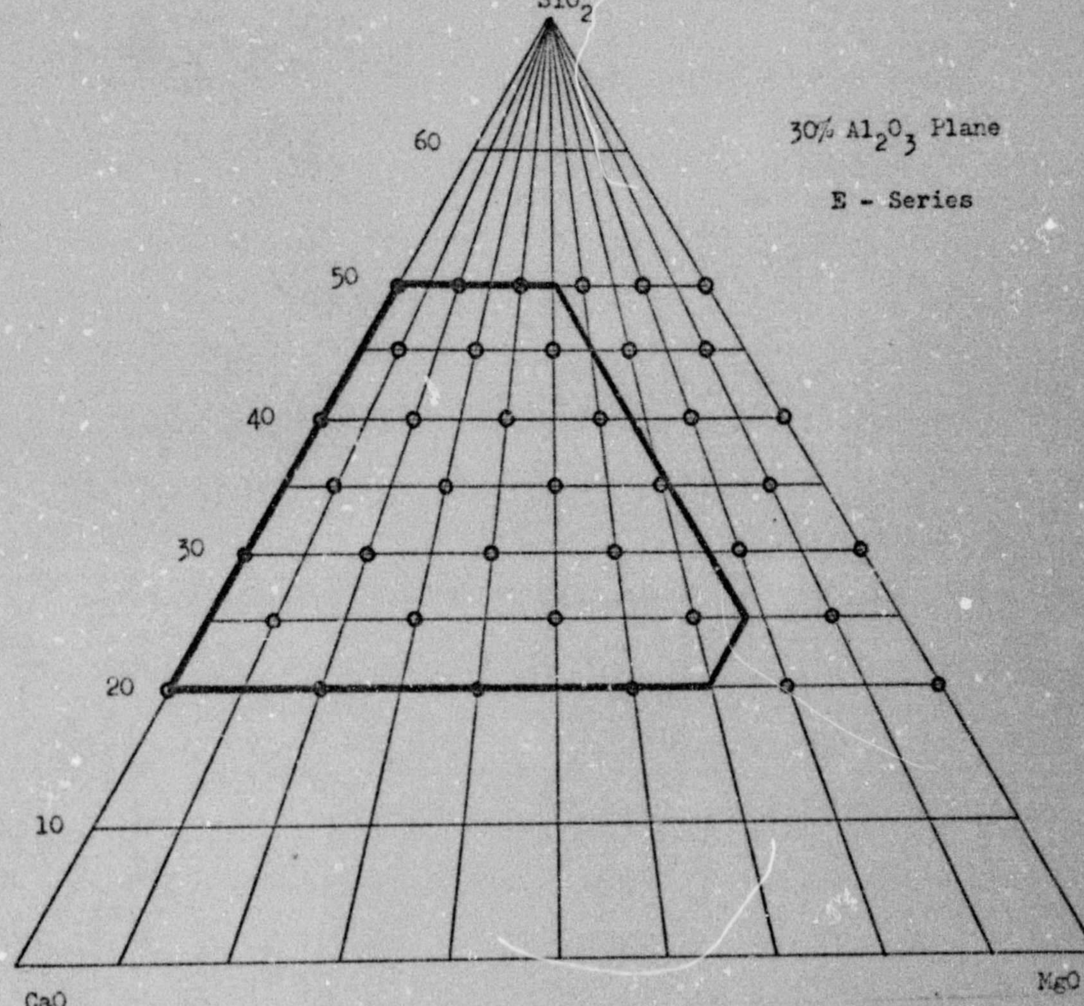
MgO : 0 - 35 per cent

CaO : 10 - 50 per cent.

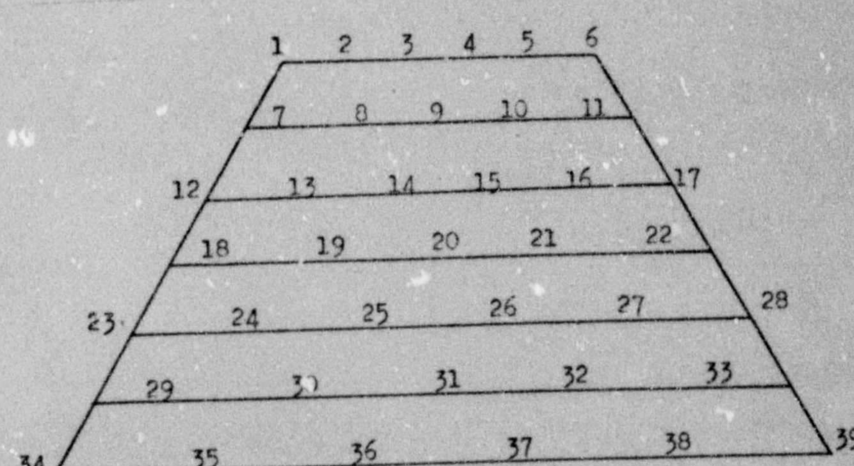
These compositional limits best reflect the entire range of slags available for cement manufacture. Additionally, those slags which fall into the above compositional criteria but which have a liquidus temperature of 1600°C or higher were not investigated.

The slag compositions chosen were based on the SiO_2-Al_2O_3-MgO-CaO diagrams prepared by Osborn, DeVries, et al (18), which consist of SiO_2-MgO-CaO pseudo-ternary diagrams plotted at constant Al_2O_3 levels. The CaO to MgO ratio is maintained constant at the various Al_2O_3 levels by the technique of plotting them on lines drawn from the SiO_2 apex to 10 per cent intervals on the MgO-CaO axis of the three-component (SiO_2-CaO-MgO) phase diagram. By plotting points on these lines at alternating intersections with the five per cent SiO_2 levels, the entire area in question was covered and closely-spaced points were avoided. A sample diagram indicating the technique of point selection is shown in Figure 1. The approximate liquidus temperatures and the primary phases present were taken from various sources (12,13,18,19,20,21).

One-hundred-one points satisfied the above requirements of both liquidus temperature and composition, based on the available data in the literature. These points were grouped into series based on the alumina content. These series are shown alphamerically with the sample composition, approximate liquidus temperatures, and assumed primary phase



All points on or within the framework satisfy the imposed composition requirements.



Sample Number Assignment

Figure 1. Method of Point Selection

in Table II.

Table II incorporates the shorthand notation for oxides as follows:

S = SiO_2

A = Al_2O_3

M = MgO

C = CaO.

Other oxides represented in this thesis are:

H = H_2O

F = Fe_2O_3.

Using this shorthand system, various compounds and solid solutions may thus be written:

Ackermanite	C_2MS_2
Anorthite	CAS_2
Dicalcium silicate	C_2S
Forsterite	M_2S
Gehlenite	C_2AS
Melilite	C_2MS_2 - C_2AS (solid solution)
Merwinite	C_3MS_2
Mullite	A_3S_2
Periclase	M
Pyroxene	CMS_2 - MS (solid solution)
Rankinite	C_3S_2
Spinel	MA
Tricalcium aluminate	C_3A
Tricalcium silicate	C_3S.

It should be noted that several slags had liquidus temperatures close to but greater than 1600°C as determined from the literature. These were excluded from study. It was later found that the liquidus temperature of some of the slags included for study exceeded 1600°C.

TABLE II.

SAMPLE NUMBER ASSIGNMENT, COMPOSITION, ESTIMATED LIQUIDUS TEMPERATURE, AND ASSUMED PRIMARY PHASE

Sample Number	Weight Per Cent Al_2O_3	SiO_2	MgO	CaO	Assumed Primary Phase	Estimated Liquidus Temperature
A-1	10	50	0.0	40.0	αCS	1435°C
A-2	10	50	8.0	32.0	Pyroxene	1280
A-3	10	50	16.0	24.0	Pyroxene	1340
A-4	10	50	24.0	16.0	M_2S	1450
A-7	10	45	4.5	40.5	α CS	1340
A-8	10	45	13.5	31.5	Melilite	1330
A-9	10	45	22.5	22.5	M_2S	1440
A-10	10	45	31.5	13.5	M_2S	1555
A-12	10	40	0.0	50.0	C_3S_2	1370
A-13	10	40	10.0	40.0	Melilite	1375
A-14	10	40	20.0	30.0	M_2S	1400
A-15	10	40	30.0	20.0	M_2S	1560
A-19	10	35	16.5	38.5	C_3MS_2	1465
A-20	10	35	27.5	27.5	M	1560
B-1	15	50	0.0	35.0	α CS	1330
B-2	15	50	7.0	28.0	CAS_2	1270
B-3	15	50	14.0	21.0	Pyroxene	1300
B-4	15	50	21.0	14.0	M_2S	1420
B-7	15	45	4.0	36.0	α CS	1270
B-8	15	45	12.0	28.0	Pyroxene	1280
B-9	15	45	20.0	20.0	M_2S	1410
B-10	15	45	28.0	12.0	M_2S	1550

TABLE II. (Continued)

Sample Number	Weight Per Cent Al_2O_3	SiO_2	MgO	CaO	Assumed Primary Phase	Estimated Liquidus Temperature
B-12	15	40	0.0	45.0	Melilite	1360°C
B-13	15	40	9.0	36.0	Melilite	1355
B-14	15	40	18.0	27.0	M_2S	1400
B-15	15	40	27.0	18.0	M_2S	1525
B-18	15	35	5.0	45.0	Melilite	1445
B-19	15	35	15.0	35.0	MA	1420
B-20	15	35	25.0	25.0	MA	1520
B-24	15	30	11.0	44.0	C_2S	1485
C-1	20	50	0.0	30.0	CAS_2	1370
C-2	20	50	6.0	24.0	CAS_2	1370
C-3	20	50	12.0	18.0	CAS_2	1320
C-4	20	50	18.0	12.0	M_2S	1320
C-7	20	45	3.5	31.5	CAS_2	1325
C-8	20	45	10.5	24.5	CAS_2	1315
C-9	20	45	17.5	17.5	M_2S	1345
C-10	20	45	24.5	10.5	M_2S	1450
C-12	20	40	0.0	40.0	Melilite	1360
C-13	20	40	8.0	32.0	Melilite	1305
C-14	20	40	16.0	24.0	MA	1420
C-15	20	40	24.0	16.0	MA	1530
C-18	20	35	4.5	40.5	Melilite	1460
C-19	20	35	13.5	31.5	MA	1460
C-20	20	35	22.5	22.5	MA	1595

TABLE II. (Continued)

Sample Number	Weight Per Cent Al_2O_3	SiO_2	MgO	CaO	Assumed Primary Phase	Estimated Liquidus Temperature
C-23	20	30	0.0	50.0	C_2S	1560°C
C-24	20	30	10.0	40.0	Melilite	1450
C-25	20	30	20.0	30.0	MA	1570
D-1	25	50	0.0	25.0	CAS_2	1450
D-2	25	50	5.0	20.0	CAS_2	1425
D-3	25	50	10.0	15.0	CAS_2	1380
D-4	25	50	15.0	10.0	MA	1360
D-7	25	45	3.0	27.0	CAS_2	1410
D-8	25	45	9.0	21.0	CAS_2	1400
D-9	25	45	15.0	15.0	MA	1405
D-12	25	40	0.0	35.0	CAS_2	1340
D-13	25	40	7.0	28.0	CAS_2	1340
D-14	25	40	14.0	21.0	MA	1495
D-15	25	40	21.0	14.0	MA	1560
D-18	25	35	4.0	36.0	Melilite	1420
D-19	25	35	12.0	28.0	MA	1510
D-23	25	30	0.0	45.0	Melilite	1560
D-24	25	30	9.0	36.0	MA	1480
D-29	25	25	5.0	45.0	Melilite	1500
D-30	25	25	15.0	35.0	MA	1550
D-35	25	20	11.0	44.0	M	1500
E-1	30	50	0.0	20.0	CAS_2	1540
E-2	30	50	4.0	16.0	CAS_2	1475

TABLE II. (Continued)

Sample Number	Weight Per Cent Al_2O_3	SiO_2	MgO	CaO	Assumed Primary Phase	Estimated Liquidus Temperature
E-3	30	50	8.0	12.0	Melilite	1425°C
E-7	30	45	2.5	22.5	CAS_2	1490
E-8	30	45	7.5	17.5	CAS_2	1460
E-9	30	45	12.5	12.5	MA	1470
E-12	30	40	0.0	30.0	CAS_2	1490
E-13	30	40	6.0	24.0	CAS_2	1400
E-14	30	40	12.0	18.0	MA	1520
E-15	30	40	18.0	12.0	MA	1550
E-18	30	35	3.5	31.5	Melilite	1380
E-19	30	35	10.5	24.5	MA	1520
E-23	30	30	0.0	40.0	Melilite	1525
E-24	30	30	8.0	32.0	MA	1510
E-29	30	25	4.5	40.5	Melilite	1540
E-30	30	25	13.5	31.5	MA	1595
E-34	30	20	0.0	50.0	MA	1590
E-35	30	20	10.0	40.0	MA	1550
E-36	30	20	20.0	30.0	MA	1580
F-1	35	50	0.0	15.0	A_3S_2	1520
F-2	35	50	3.0	12.0	A_3S_2	1530
F-7	35	45	2.0	18.0	CAS_2	1515
F-8	35	45	6.0	14.0	MA	1475
F-9	35	45	10.0	10.0	MA	1490
F-12	35	40	0.0	25.0	CAS_2	1500

TABLE II. (Continued)

Sample Number	Weight Per Cent Al_2O_3	SiO_2	MgO	CaO	Assumed Primary Phase	Estimated Liquidus Temperature
F-13	35	40	5.0	20.0	CAS_2	1440°C
F-14	35	40	10.0	15.0	MA	1525
F-15	35	40	15.0	10.0	MA	1590
F-18	35	35	3.0	27.0	CAS_2	1450
F-19	35	35	9.0	21.0	MA	1565
F-23	35	30	0.0	35.0	Melilite	1475
F-24	35	30	7.0	28.0	MA	1540
F-29	35	25	4.0	36.0	Melilite	1525
F-34	35	20	0.0	45.0	Melilite	1590
F-35	35	20	9.0	36.0	MA	1550