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# Cementitious properties of metallurgical slags

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## 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 (1) | | 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 $5 \times 10^{-3}$ 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

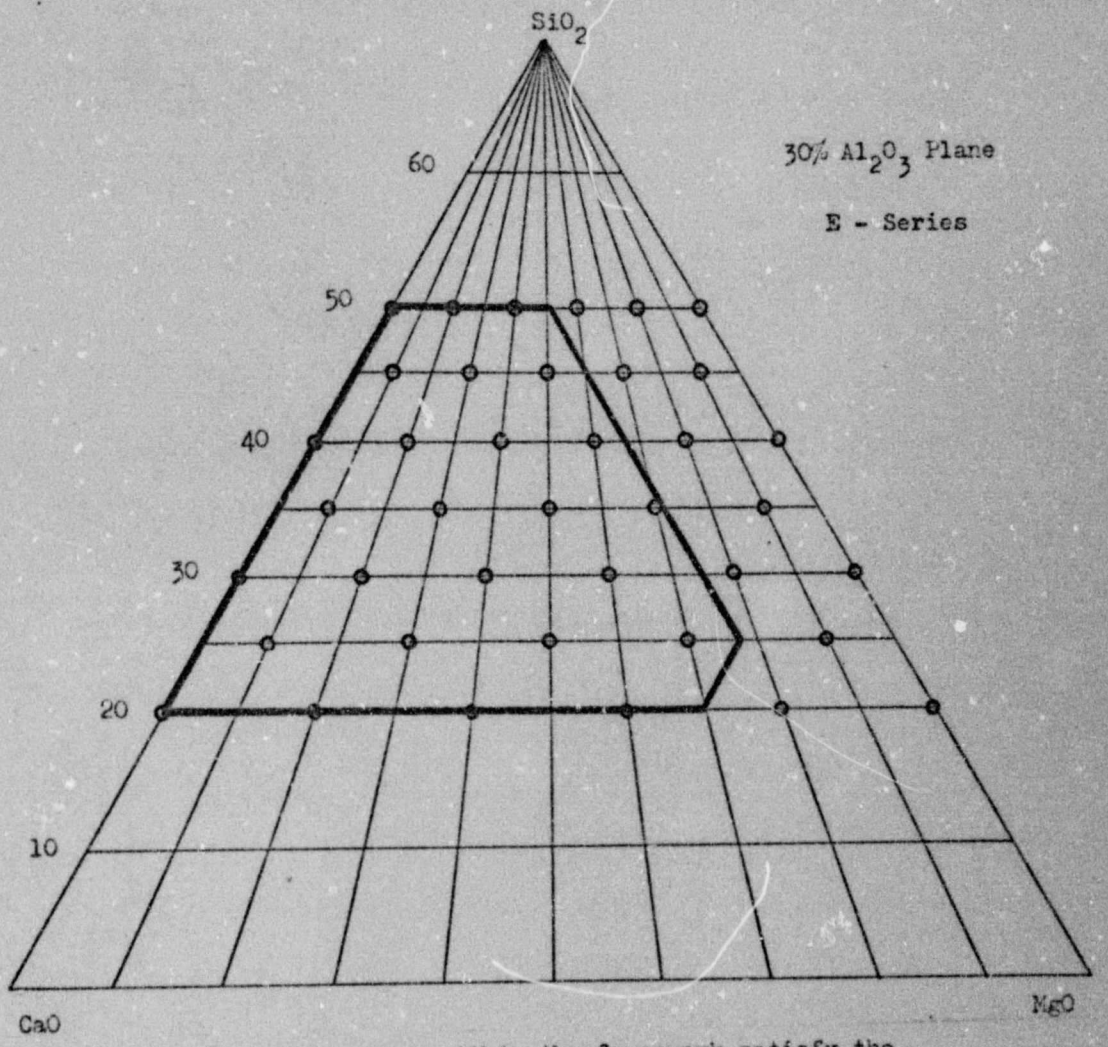
MgO : 0 - 35 per cent

CaO : 10 - 50 per cent.

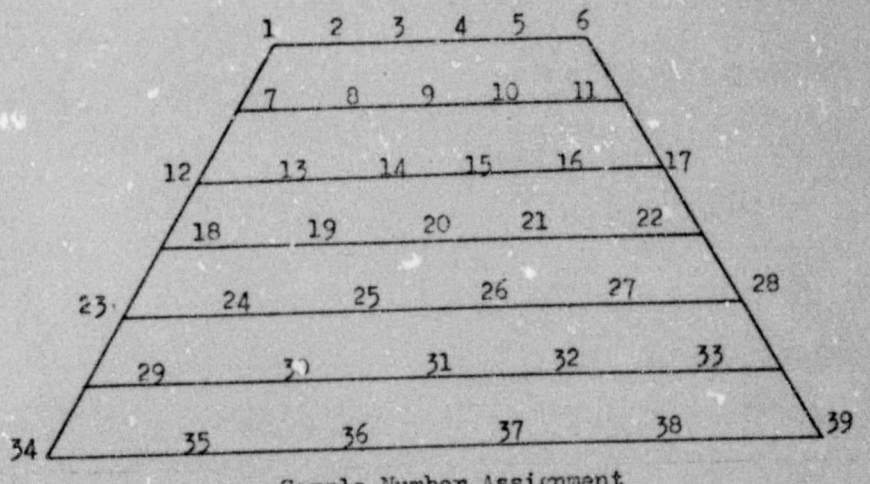
These compositional limits best reflect the entire range of slags available for cement manufacture. Additionally, those slags which fall into the above compositional criteria but which have a liquidus temperature of 1600°C or higher were not investigated.

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 | $\alpha$CS | 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 | $\alpha$ 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 | $\alpha$ 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 | $\alpha$ 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 | [illegible] | 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 |

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