It is therefore quite possible that some slags within the compositional limits chosen, but excluded by virtue of the estimated liquidus temperature might well have liquidus temperatures somewhat below 1600°C.

2.2 Slag Preparation

Thirty grams of the selected slags were prepared by mixing the weighed amounts of the pure oxides. The resultant mixture was compressed into cylindrical pellets, 25×10^{-3} m in diameter and approximately 25×10^{-3} m high. It was found that the subsequent melting step was facilitated by pelletizing and that material loss due to "blow out" was prevented.

The oxides used in preparing the individual slags were of the analytical reagent grade supplied commercially. In order to ensure that the premolten slags were of the desired composition, random slags were submitted for chemical analysis. The results of these analyses are shown in Table III. In some cases these analyses differed from that expected by as much as two per cent for an individual component. For the most part, however, the analyses indicated that the compositions of the slags were within the limits imposed by subsequent experimental accuracy. Hence all further work is based on the slag compositions proposed in Section 2.1.

2.3 Slag Melting

Those slags having an estimated liquidus temperature of less than 1500°C were melted in a both-end-open vertical tube furnace capable of 1550°C. This furnace consisted of nine silicon carbide resistance elements placed equidistantly on the circumference of a 125×10^{-3} m diameter circle. Six of the resistance elements were powered by a 220V/34A - 10 to 60V/125A step transformer and three through a variable output transformer. The former elements were used for rough temperature control and the latter for fine control. The temperature was regulated by an on-off controller connected to the three elements on the auto-

TABLE III.

RESULTS OF CHEMICAL ANALYSES OF SELECTED SLAGS

Sample Number	Weight Per Cent			
	SiO_2	Al_2O_3	MgO	CaO
A-7	45.49	11.14	4.59	39.79
A-12	40.95	11.07	<0.01	49.01
A-15	39.5	9.8	29.7	20.1
A-19	34.8	10.6	16.3	37.4
B-2	49.62	15.41	7.18	27.74
B-8	44.90	15.37	11.81	27.72
B-9	44.60	15.42	20.11	19.62
B-20	35.84	15.63	24.82	25.49
B-24	31.25	14.47	11.24	44.09
C-15	40.97	19,58	24.08	16.48
C-23	29.5	19.3	<0.01	48.9
C-25	30.94	20.15	20.11	29.84
D-3	50.03	25.70	9.45	15.22
D-15	40.55	24.17	21.22	13.96
E-1	50.55	29.58	<0.01	20.32
E-13	39.70	31.13	6.16	23.51
E-29	25.9	29.4	5.3	39.8
E-35	20.5	30.3	10.5	39.2
F-14	40.24	35.32	10.39	15.69
F-18	36.2	35.1	3.0	26.1
F-35	19.9	34.4	8.9	35.6
Commercial Slagment	37.39	10.00	16.16	33.55

transformer circuit. This controller was actuated by the emf output of an EL - 18 (6%Rh/Pt - 30%Rh/Pt) thermocouple. Additionally, the sample temperature was monitored on a potentiometer with an EL - 18 thermocouple inserted in the furnace next to the sample.

Samples having an estimated liquidus temperature of greater than 1500°C were melted in a molybdenum-wound resistance furnace also of the both-end-open vertical tube type, which was powered by a double ganged auto-transformer. The molybdenum resistance element was protected from oxidation by passing anhydrous ammonia gas through the furnace shell. Temperature control was achieved by a controller which activated or deactivated the resistance element. Temperature monitoring was accomplished with an EL - 18 thermocouple and a potentiometer. Both furnaces incorporated a device for sealing the lower end of the furnace tube during heating to eliminate the "chimney effect".

The pelletized oxide mixtures were placed in a platinum - 5% gold crucible and suspended in the furnace tube next to the temperature monitoring thermocouple by means of a platinum wire. The 5% gold alloy crucible was chosen as the molten slag does not wet it as easily as it does pure platinum, so facilitating solidified slag removal. Samples were held in this position at a temperature of 50°C above the estimated liquidus temperature.

If a melt of pure silica at a temperature well above its liquidus temperature is considered, the thermal agitation of the system is sufficient to disrupt any long-range order of the $(SiO_4)^{-4}$ tetrahedra. Some of the corners are shared, but a significant number are not, resulting in a distorted structure. The structure of molten SiO_2 becomes more and more disordered the higher the temperature above the liquidus temperature, but as the temperature is lowered, a certain degree of order is restored as the tetrahedra again link up. The maximum possible order in the fully liquid system exists at the liquidus temperature.

Slightly above the liquidus temperature, a molten silica-based slag will also have a certain amount of structural order, but this is not as complete as it would be if it were actually at the liquidus temperature. Now if the melt is suddenly quenched to well below the liquidus temperature, the resulting glass (assuming that crystallization does not occur) contains a certain amount of order "frozen in", and this is the same (or nearly the same) amount that existed before quenching. The degree of order that exists in a melt above its liquidus temperature has been referred to as "quasi-crystallinity" (22). Although the melt is not crystallized, the impending crystal structure is forming as the temperature is lowered. The degree of order in the liquid state is inversely related to the temperature above the liquidus temperature.

For this reason, each slag was kept at 50°C above the estimated liquidus temperature so that the same relative degree of ordering in the liquid state could be achieved. The liquidus temperature was later determined to ensure that each sample had been quenched from 50°C above the true liquidus temperature.

After a minimum period of four hours, the molten sample was visually inspected to ensure that the slag was completely molten. The crucible suspension wire was then released allowing the sample to fall out of the furnace tube into water which was maintained at about 20°C. The height of drop from the melting zone of the furnace to the quenching bath was about one metre. Microscopic examination of selected quenched slags (particularly those high in alúmina and/or magnesia and low in silica) indicated that the quenching rate thus achieved was sufficient to prevent crystallization of the slag, i. e., the quenching procedure produced glass slags.

2.4 Grinding of Slags

The quenched slags were dried under heating lamps and removed from the crucible. Following this, they were placed in a mechanical grinding mill having agate containers; the grinding media were tungsten-carbide balls. Each slag was ground for a period of two hours and then screened through a 325 mesh Tyler screen. The very small proportion of oversize was discarded.

Although each sample now consisted of the same size fraction after screening (-325 mesh Tyler) the amount of oversize material resulting from the screening operation was visually different for different samples. This indicated that the relative ease of grinding is different for different samples and hence the size distribution of the undersize is probably different. The hydraulic properties of the resulting cement may be influenced by this probable variation in particle size distribution.

The bulk of the ground slag was allocated for the manufacture of cement cylinders as described in Section 3.3. The remainder was used for various determinations as discussed below.

2.5 Liquidus Temperature Measurement

A small quantity of each sample was examined on the micro-differential thermal analyzer described by Sommer, Jochens and Howat (23). This apparatus provides a double function: (1) a standard hot-stage microscope and (2) a differential thermal analyzer. Various slag characteristics including liquidus temperature, quenching behaviour and primary phase could be determined using this apparatus.

2.5.1 Micro-differential Thermal Analyzer

The micro-differential thermal analyzer (μDTA) used for this work was first described by Jochens (24) and later modified to include more sophisticated circuitry (25). The hot-stage microscope principle, the more basic function of the μDTA, has been known for a number of years (26). The hot-stage microscope employs a triple-function thermocouple which (1) acts as a specimen holder, (2) acts as a microfurnace for heating the specimen and (3) provides an emf output for specimen temperature measurement. This thermocouple and the contained sample can be viewed through a standard stereoscopic microscope.

An electrical circuit is incorporated in the μDTA which permits the alternate heating and temperature measurement of a sample mounted on the thermocouple. Heating of the sample is done by supplying the thermocouple with pulses of positive half-cycle current. Power is provided through a variable output transformer and a silicon-controlled rectifier. The silicon-controlled rectifier can be biased to vary the length of the heating pulse. Negative half-cycles of the input alternating current are suppressed by means of a half-wave circuit (23). During the time of negative half-wave suppression, the emf output of the thermocouple can be monitored.

The differential thermal analyzer function of the apparatus is made possible by including a second thermocouple and associated heating and temperature monitoring circuitry. It has been found (24) that a reference sample is not necessary. Rather, a standard thermocouple as used for liquidus temperature determinations was made such that the hot junction was about 1½ times the diameter of the arms (see Section 2.5.2). By using this bead of platinum alloy as the reference sample, errors which could be introduced due to reference sample size, sample volatization or other factors were eliminated. Both the reference and the sample thermocouples may be thermally balanced by a variable transformer which controls the input to the reference thermocouple.

2.5.2 Thermocouple Fabrication

The thermocouples used for liquidus temperature determinations were fabricated from EL - 18 wire. A typical thermocouple containing a bead of slag is shown as Figure 2. Referring to Figure 2, the legs (A) were fabricated from 0.5×10^{-3} m diameter wire while the "arms" (B) were made from 0.35×10^{-3} m diameter wire. The positive and negative arms of the thermocouple were welded to their respective legs at point C. The hot junction of the thermocouple was made by butt-welding the positive and negative arms together. This was accomplished by holding the two arms end-to-end and playing a propane-oxygen flame on the positive (30%Rh/Pt) arm which has the higher melting point. As the positive arm melted, it flowed onto the negative arm fusing the two together. The completed junction should not exceed the diameter of the original wires, i. e., 0.35×10^{-3} m.

Thermocouples were formed by bending the arms over a 0.35×10^{-3} m thick former at the hot junction. Care must be exercised to ensure that the junction is at the centre of the inverted "U". The distance of 0.35×10^{-3} m (the diameter of the arms) must be maintained in order to provide a uniform heating and heat loss configuration. After forming, the thermocouples were placed in a water-cooled holder. The water cooling provided a constant temperature cold junction alleviating the need for correcting for cold junction error. The arms of the thermocouples were preferentially heated by virtue of their greater resistance than the legs.

2.5.3 Sample Bead Preparation

A small quantity of powdered slag was placed in the "U" of the hot thermocouple junction and melted by increasing the power input to the thermocouple. After the sample melted, it was positioned so that it could be observed through the microscope.

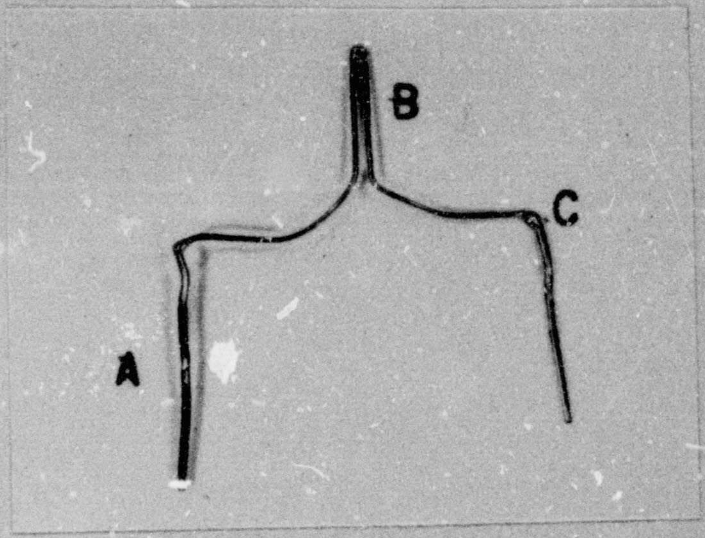

Figure 2. Typical thermocouple used for determining liquidus temperature and quenching characteristics

Observations were normally made at 50X or 100X with Polarized light, ordinary transmitted light or, occasionally no light at all other than that provided by the heated thermocouple. The type of light used depended upon the liquidus temperature of the sample, the type of crystals formed and other considerations.

The melted sample often contained minute bubbles of air which had to be consolidated and removed. Consolidation occurred more or less rapidly depending upon slag viscosity by allowing the sample to soak at a temperature about 100°C above the estimated liquidus temperature. If the consolidated bubble did not "pop" on its own accord, it could be removed by piercing it with a pointed platinum wire.

To ensure that no thermal gradient existed in the melted sample, its size was limited so that the sample bead was not longer than it was broad, i. e., 0.35×10^{-3} m. Capillary action and surface tension held the molten bead at the hot junction of the thermocouple. Additionally, surface tension allowed the bead to bulge out and assume a quasi-spherical shape. The sample size could be increased by adding more slag powder or decreased by pricking it with a platinum wire. During the pricking, a certain amount of slag would freeze out on the wire and could be removed.

2.5.4 Liquidus Temperature Determination

The technique for determining the liquidus temperature has been documented by various authors (13,20,24). The initial step is to grow crystals of the primary phase in the melt. This was done in one of two ways:

1. Slowly lower the specimen temperature until nucleation and crystallization occur spontaneously.

2. Seed the melt with slag sample dust.

The technique used depended upon the relative ease with which the former method worked.

For a slag system to crystallize, ions which will compose the primary phase must migrate together. In the case of silica-based phases the $(SiO_4)^{-4}$ tetrahedra must link up. If the viscosity of the system is sufficiently high, movement of the ions through the melt is restricted, and crystallization will occur slowly. If the temperature is decreased rapidly, solidification of the melt, which further increases the viscosity of the system, occurs, preventing crystallization.

The viscosity of a slag is dependent on the chemical composition of the melt and the temperature. Slags which contain a relatively large amount of network forming ions become rather viscous near their liquidus temperatures, thus the mobility of crystal-building ions is impaired. If, in order to achieve crystallization, ions must come together, it is clear that crystallization cannot result if the movement of ions in the melt is restricted. Although a certain amount of quasi-crystallinity must exist, the growth of crystals will not occur in highly siliceous slags unless they are cooled at very slow rates.

All samples were heated to a temperature in excess of 100°C above their estimated liquidus temperature. After observing that the sample was completely molten, the temperature was lowered at a rate of about 30°C per minute until crystals were observed to grow or until a temperature of about 50°C below the estimated liquidus temperature was reached. Those samples which crystallized were handled as discussed below while those that did not were subjected to the same procedure again except that the rate of cooling was reduced to about 10°C per minute.

Samples which still did not crystallize were cooled to room temperature and lightly dusted with powdered sample. They were then slowly heated until crystals were nucleated and began to form.

In the case of low-silica slags in which the silica is present as short chains or isolated tetrahedra the viscosity is relatively low, hence the ions in the melt have a greater degree of mobility. For a melt such as this to crystallize, the ions must present themselves in the proper order and in the proper proportions to form a particular crystal structure. Further, nucleation sites must exist for the ions to combine to form crystals.

Two types of nucleation are possible: (1) homogeneous nucleation and (2) heterogeneous nucleation. In the former, the nucleus is of the same composition as the crystal, while in heterogeneous nucleation, the nucleus differs from the crystalline phase. In pure synthetic slags, homogeneous nucleation occurs, while industrial slags contain impurities which may act as heterogeneous nucleation sites, although a certain amount of homogeneous nucleation may also occur.

Nucleation also occurs in pure synthetic slags which is caused by areas of increased free energy. Particles of foreign material in the melt will have a certain proportion of ruptured bonds at their surfaces. When material which can satisfy these bonds (ions from the melt) comes into contact with the solid, crystal growth will begin at the surface of the impurity. This type of crystallization was apparent on the arms of the thermocouples used. New, smooth thermocouples are not as conducive to nucleation-crystallization as old thermocouples which have scratches, pits, and other imperfections. Because of the broken bonds that exist at these sites, the molten slag may preferentially crystallize at these sites rather than elsewhere.

When crystallization had been induced, crystal-containing samples were slowly heated from 50 - 75°C below the estimated liquidus temperature until only small, isolated crystals remained. The procedure was then reversed, lowering the temperature to about 30°C below that point where crystals almost disappeared. The liquidus temperature was determined by raising the temperature by 3°C steps and allowing the sample to equilibrate for at least two minutes between steps. A point was eventually reached when very small crystals were in evidence prior to a 3°C increase in temperature but not afterwards. The liquidus temperature was taken as the mean of these two temperatures.

After determining the liquidus temperature in this manner, the sample was removed from the thermocouple and the thermocouple reformed. A second determination was made using the reformed thermocouple. In all, four determinations were made, two on new thermocouples, two on used, reformed thermocouples. The averages of these values and their precision are shown in Table IV.

2.5.5 Results of Liquidus Temperature Determinations

In many cases the value obtained for the liquidus temperature and that estimated from the literature differed. There are perhaps several reasons for this, the most important probably being differences in the composition of the slag as analytically determined and that assumed from the preparation procedure. Table III shows differences as great as two per cent between the amount of a constituent assumed to be in a sample and the actual amount determined analytically. Such a difference could account for a 10 - 15°C difference in liquidus temperature. Detailed analyses of the slags measured by the authors of the various references were not always reported, and their compositions may have differed slightly from those published. The analysis of the slags in this investigation is only accurate to ± 1.5 per cent based on a total of 100 per cent. Other reasons for differences in the liquidus temperatures include difficulty in interpolating between iso-thermal lines on the referenced phase diagrams, and inaccuracies in these diagrams.

To determine the accuracy of the technique, several samples of slags of known liquidus temperature were investigated by the author and compared with the results obtained by other workers using different techniques (24). These data are presented in Table V. Based on these

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