

Viscosities, electrical resistivities, and liquidus temperatures of slags in the system CaO–MgO–Al₂O₃–TiO₂–SiO₂ under neutral conditions

by J. VAN DER COLF*, B.Sc. (Cape), B.Sc. Eng. Met. (Rand), Ph.D. (Rand) (Member) and D. D. HOWAT†, B.Sc. (Glas.), Ph.D., F.I.M. (Fellow)

SYNOPSIS

This paper is the first in a series of three dealing with this subject and also with the rate of oxygen removal from the slags in the presence of solid carbon and with the physicochemical properties of the reduced slags. For selected members of the system, the melting temperatures and primary crystallization products were determined, as were the viscosity and the electrical resistivity of the corresponding melts. All the experiments were conducted in a neutral atmosphere.

Where determined, the primary phase was found to be either perovskite or magnesium aluminium titanate. The composition variable exerting the most pronounced influence on viscosity or resistivity was found to be the basicity expressed as the mass ratio (CaO + MgO)/SiO₂. The ratio CaO/MgO became important only at low basicity values. Although generally there is a direct proportionality between log (viscosity) and log (resistivity), slags having either a very high silica content or a very high titania content have anomalously low electrical resistance.

SAMEVATTING

Hierdie artikel is die eerste van drie wat handel oor hierdie onderwerp en verder ook handel oor die tempo van suurstofverlies deur die slakke in die teenwoordigheid van koolstof en die fisikochemiese eienskappe van sulke gereduseerde slakke. Die vloeibaarheid, elektriese geleidingsvermoë, smeltpunt en primêre kristallisatiefase is bepaal vir uitgesoekte slaksamestellings in 'n neutrale atmosfeer. Magnesium aluminium titaanaat en perovskiet is die enigste primêre fases wat waargeneem is. Die samestellingsveranderlike wat die grootste invloed uitoefen op vloeibaarheid en geleidingsvermoë is die basisiteit of die massaverhouding (CaO + MgO)/SiO₂. Die verhouding CaO/MgO is net belangrik by lae basisiteit. Alhoewel daar in die algemeen 'n direkte eweredigheid bestaan tussen log (viskositeit) en log (soortlike weerstand), het slakke met 'n hoë SiO₂ inhoud of 'n hoë TiO₂ inhoud 'n buitengewoon lae elektriese weerstand.

Introduction

If both metal and slag are produced during a pyrometallurgical process, smooth operation is possible only when the physical properties of the slag have the desired values. In particular, the work described here was undertaken as a result of the operational difficulties frequently experienced when a titaniferous magnetite ore is smelted in a submerged-arc electric furnace to produce vanadium-bearing pig iron and a slag rich in titanium oxide.

The melting temperature of the slag is important mainly owing to the requirement of satisfactory metal superheat. Completely molten slag that drains away from the reaction zone at the liquidus temperature of the alloy cannot provide the underlying metal bath with the required degree of superheat.

A high slag viscosity may retard the reaction steps such as the dissolution of solid oxides in the liquid slag and the reduction of metal oxides from the slag phase either by carbon dissolved in the metal or by solid reductant. The rate at which metal droplets, produced in the reaction zone, settle through a slag layer is also a function of slag viscosity. Finally, the time consumed by tapping, which is 'dead time' from a production point of view, is increased by an increase in slag viscosity.

The resistance of the burden as a whole influences the position of the electrodes in a submerged-arc furnace, but, while slag resistivity is becoming more prominent in recent approaches to the subject of power dissipation,

its relative contribution to furnace resistance is ill-defined. However, the existence of such a contribution cannot be discounted, and the measurements that formed part of this work were undertaken to gain some understanding of the influence of slag composition on its electrical resistance.

Numerous studies have been conducted into the liquidus temperatures and viscosities of titaniferous slags with blast-furnace operation in mind. Consequently, the most prominent system in these studies was CaO–SiO₂–Al₂O₃–TiO₂. The approach was frequently, also when MgO was included, the stepwise addition of titanium oxide to blast-furnace type master slags. The need for studies of the system that also contains MgO arises from the fact that this oxide is normally present in the large deposits of titaniferous magnetites. It is important as a variable when limestone is partially or completely replaced by dolomite as a flux. In this case the CaO/MgO ratio may further be varied by the addition of either limestone or serpentine.

Liquidus temperatures of the five-component system were determined by Holmes, Banning, and Brown¹, Zhilo *et al.*², Handfield *et al.*³, and Jochens, Sommer, and Howat⁴. The slags in the last-mentioned study, although relating to the same plant practice as the present investigation (that at Highveld Steel and Vanadium Corporation, Witbank, South Africa), were based on the analyses of slags from the pilot plant, which tended to be slightly higher in titanium oxide than are the slags that are now commonly tapped.

The viscosities of slags belonging to the five-component system were measured by Behrendt and Kootz⁵, Shavrin

*Anglo American Research Laboratories, Johannesburg.

†Formerly University of Witwatersrand, Johannesburg; now National Institute for Metallurgy, Randburg, Transvaal.

and Sakharov⁶, Zhilo *et al.*^{2, 7}, Freidenzon *et al.*⁸, and McRae⁹. McRae's measurements relate to the same period of development as those of Jochens⁴.

No reference could be found in the literature to the determination of the electrical conductivity of slags of intermediate titania contents (20 to 40 per cent TiO₂).

Experimental

Compositions and Preparation of Slag Samples

The primary aim of the project was to determine the effect of reducing conditions (as they exist during smelting) on the properties of titaniferous slags. The results of these investigations will be reported elsewhere. The number of initial (unreduced) slag compositions intended for the work described here thus had to be kept to a minimum and were determined largely by plant requirements. The analytical figures provided by the plant were 20,0 to 22,5 per cent SiO₂, 27,0 to 31,0 per cent TiO₂, 13,0 to 14,0 per cent Al₂O₃, 16,0 to 17,0 per cent CaO, 14,5 to 16,0 per cent MgO, 1,5 to 5,0 per cent FeO, and 0,5 to 2,0 per cent V₂O₅.

The slag compositions selected for study are given in Table I. Those marked with an asterisk represent the group chosen for detailed investigation (core group). Only the liquidus temperatures and viscosities of the others were determined. The following observations refer to the core group.

- All the slags have the mass ratio TiO₂/Al₂O₃ equal to 2,2. This is dictated by the compositions of the unfluxed ore and the coal, and the ratio could be kept constant.
- The composition of B14 closely approximates that of the plant slag.
- The series B11–B14–B17 represents a variation in the basicity of the slag, while the CaO/MgO ratio and the (TiO₂+Al₂O₃) content are constant.
- The series A5–B14–C23 represents a variation in the (TiO₂+Al₂O₃) content with basicity and CaO/MgO

ratio constant. This variable is influenced by the degree of dilution through flux addition.

- The series B14–B15–B16 have different CaO/MgO ratios, whereas (TiO₂+Al₂O₃) and basicity are constant. While the continued use of dolomite as a flux is preferred in plant operation to the use of the more costly limestone, variation in CaO/MgO is possible.

Owing to the complexity of the system CaO–MgO–Al₂O₃–TiO₂–SiO₂, the oxides of iron and vanadium are not included in the slags given in Table I. However, some experiments were performed on a composite plant slag as well as on synthetic slags containing these oxides¹⁰.

The chemically pure oxides were heated in vitreous-silica dishes at 1100°C for 1 hour and then cooled in a desiccator. Premelts were made in molybdenum crucibles in an argon atmosphere. The temperature was maintained at 1600°C for 1 hour.

The Furnace Assembly Used

The furnace was powered by an 18 kV.A output Intertherm induction generator operating at a frequency of 500 kHz (Fig. 1). The entire assembly was supported on a fixed steel table, which also carried four steel supporting columns bolted to a steel plate above the glove box that housed the viscometer or the electrical extensions. The two chains carrying the glove box on one side and a lead counterweight at the back of the furnace passed through slots in the top supporting plate over two pairs of gears bolted to the plate. Full details of the equipment are given elsewhere¹⁰.

A Pt–6%Rh/Pt–30%Rh thermocouple was used for all the temperature measurements. The thermocouple could be inserted into the hot zone either from above or from below, as shown in Fig. 1. A 500 kHz filter was included in the thermocouple circuit.

The protective atmosphere consisted of spectrographically pure argon.

TABLE I
COMPOSITIONS OF SYNTHETIC SLAGS SELECTED FOR STUDY
TiO₂/Al₂O₃=2,2

Slag group	Slag no.	TiO ₂ +Al ₂ O ₃ %	(CaO+MgO)/SiO ₂	CaO/MgO	TiO ₂ %	Al ₂ O ₃ %	SiO ₂ %	CaO %	MgO %	
A	2	36,000	1,710	1,000	24,800	11,200	23,620	20,190	20,190	
	5*	36,000	1,401	1,000	24,800	11,200	23,650	18,675	18,675	
	8	36,000	0,800	1,000	24,800	11,200	35,550	14,225	14,225	
B	10	44,000	1,699	2,000	30,200	13,800	20,750	23,500	11,750	
	11*	44,000	1,699	1,000	30,200	13,800	20,750	17,625	17,625	
	34	44,000	1,650	1,000	30,200	13,800	21,130	17,435	17,435	
	33	44,000	1,600	1,000	30,200	13,800	21,540	17,230	17,230	
	32	44,000	1,549	1,000	30,200	13,800	21,970	17,015	17,015	
	31	44,000	1,499	1,000	30,200	13,800	22,410	16,795	16,795	
	30	44,000	1,450	1,000	30,200	13,800	22,860	16,570	16,570	
	14*	44,000	1,400	1,000	30,200	13,800	23,330	16,335	16,335	
	29	44,000	1,350	1,000	30,200	13,800	23,830	16,085	16,085	
	28	44,000	1,300	1,000	30,200	13,800	24,350	15,825	15,825	
	12	44,000	1,700	0,500	30,200	13,800	20,750	11,750	23,500	
	13*	44,000	1,400	2,000	30,200	13,800	23,330	21,780	10,890	
	15*	44,000	1,400	0,500	30,200	13,800	23,330	10,890	21,780	
	16	44,000	0,801	2,000	30,200	13,800	31,100	16,600	8,300	
	17*	44,000	0,801	1,000	30,200	13,800	31,100	12,450	12,450	
	18	44,000	0,801	0,500	30,200	13,800	31,103	8,300	16,600	
	C	23*	54,000	1,397	1,000	37,180	16,820	19,190	13,405	13,405

*These slags were also used for the determination of electrical conductivity and later for reduction studies.

Liquidus Temperature and Primary Phase

Approximate values of the liquidus temperature were obtained from viscosity and resistivity measurements. The justification for such a technique is discussed in the detailed report on this work¹⁰.

So that the hot-stage microscope could be used for the measurement of liquidus temperature, the opaque slags resulting from premelting under argon were fully re-oxidized by being heated in pure oxygen at 1100°C for 1 hour. Welch¹¹ developed the arrangement in which the thermocouple functions as a generator of thermal e.m.f., sample-holder, and heating element. The instrument used for this work employed half-cycle heating and was constructed by Jochens¹². Details of the thermocouple used and the technique employed are given in reference 10.

The primary phase was identified by means of a Debye-Scherrer X-ray-diffraction camera.

Measurement of Viscosity

The rotating inner-cylinder technique was employed, a commercial Brookfield viscometer being used throughout. Both the spindle of the viscometer and the crucibles were made of molybdenum. The design and dimensions of these components have been described elsewhere^{10, 13}. The calibration of the viscometer was performed at a constant speed of 50 r/min, using three calibrating oils, S-600, S-60, and S-20 types A.S.T.M. oil standards (Channon Instrument Co. U.S.A.), at different temperatures. The calibration is represented by

$$\eta = -8,37 + 1,03N \quad (r=0,9998),$$

where η = viscosity in $\text{N.s/m}^2 \times 10^2$,

N = Brookfield viscosity number read from the scale,

r = correlation coefficient.

All viscosity measurements were conducted in an argon atmosphere. The molybdenum crucible with the slag was located consistently by means of a locating spigot fitting into the inner recrystallized-alumina tube shown in Fig. 1. The thermocouple junction was 2 mm above the crucible wall and vertically in line with it.

Measurement of Electrical Resistance

The crucibles and the arrangement for the temperature measurements were the same as those for the viscosity measurements. The electrodes were molybdenum wires of 1 mm diameter.

The a.c. bridge circuit that was used consisted of two equal standard resistances (R_s) and a non-reactive resistance box, R_m . A variable capacitance was connected in parallel to R_m . A sinusoidal input at 10 kHz was provided by a transistor-type oscillator. An oscilloscope was used to determine the balance point. It had a frequency response between 60 Hz and 60 kHz to minimize interference from the furnace and mains frequencies.

Standard solutions of NaCl and KCl at 25°C were used for calibration purposes, the conductivity values of these solutions being obtained from the work of Shedlovsky¹⁴ and Chambers *et al.*¹⁵.

The resistance of the ionic liquid in the cell is related to its electrical conductivity by

$$Rk = G,$$

where R = resistance of the liquid (Ω),

k = conductivity of the liquid (S/m),

G = cell constant (m^{-1}).

Thus, $\log k = \log G - \log R$, so that a graph of $\log R$ against $\log k$ should be a straight line with a slope of -1 , intersecting the $\log R$ axis at a point where $G = R$. In this particular case, the calibration gave

$\log R = 1,7158 - 0,9286 \log k$ ($r = -0,9989$), so that the cell constant was $51,97 \text{ m}^{-1}$.

Results and Discussion

Liquidus Temperature and Primary Phase

The results are given in Table II, and the approximate liquidus temperatures as obtained from the viscosity measurements are given as the curve tL in Figs. 2 to 9. The primary phases of the different slag compositions are also shown on the diagrams as either M (magnesium aluminium titanate) or P (perovskite).

The agreement among liquidus temperatures from different sources is reasonably good if it is borne in mind that the values derived from viscosity or resistance measurements would suffer from errors due to supercooling. Moreover, the slags used for indirect determination were in an atmosphere of pure argon and exhibited a small degree of reduction that could be measured in terms of a mass gain during complete re-oxidation in pure oxygen.

Members of slag series A, all having a CaO/MgO ratio of 1, showed a gradual increase in melting temperature with increase in basicity (Fig. 2). Figs. 3 and 4 show the liquidus temperatures of series B slags as a function of

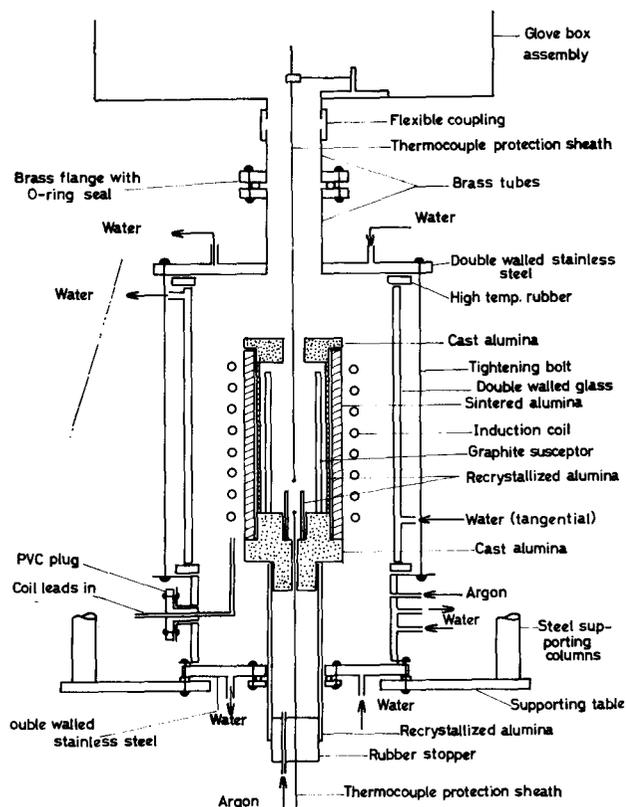


Fig. 1—Schematic representation of the furnace

TABLE II
LIQUIDUS TEMPERATURES, PRIMARY PHASES, VISCOSITIES, AND ELECTRICAL CONDUCTIVITIES OF SELECTED SLAGS WITHIN THE SYSTEM CaO-MgO-Al₂O₃-TiO₂-SiO₂

Slag	Liquidus temp.*		Primary phase†	Viscosity, N·s/m ² × 10 ³ Equation: $\ln \eta = a + b/T$				Electrical conductivity, S/m Equation: $\ln k = c - d/T$				
	HS °C	Vis °C		Res °C	a	b	r	$E\eta$ kJ/(mol. °C)	c	d	r	E_k kJ/(mol. °C)
A2		1388		-5,3398	16 693,4	0,9938	138,3	9,5247				
A5	1383	1361	1342	-2,9352	13 200,4	0,9931	109,8		8 488,9	0,9981	70,6	
A8		1322		-5,3801	18 042,9	0,9998	150,0					
B10	1454	1472		-4,4057	15 365,2	0,9878	127,7					
B11	1460	1455	1475	-2,7451	12 634,6	0,9787	105,0	9,3356	7 704,0	0,9944	64,1	
B34	1400	1402		-0,5435	8 544,9	0,9987	71,0					
B33	1358	1373		-2,8621	12 582,2	0,9984	104,7					
B32	1364	1369		-3,1999	13 285,7	0,9879	110,5					
B31	1350	1358		-2,5634	12 151,3	0,9830	101,0					
B30	1372	1358		-3,4409	13 781,1	0,9922	114,6					
B14	1365	1335	1340	-3,4380	13 673,9	0,9973	113,6	10,7409	10 075,0	0,9872	83,8	
B29	1360	1366		-2,2894	11 826,4	0,9802	98,3					
B28	1427	1440		-3,3402	14 611,0	0,9914	121,5					
B12	1461	1478		-6,2431	18 041,3	0,9893	150,0					
B13	1360	1337	1334	-6,4606	18 895,3	0,9979	157,1		13 131,8	0,9973	109,2	
B15	1499	1492	1478	-8,9873	24 588,7	0,9988	204,4		13 445,7	0,9923	111,8	
B16	1377	1388		-7,1895	21 785,8	0,9988	181,1					
B17	1405	1420	1401	-9,7258	23 186,0	0,9845	192,8		17 715,1	0,9976	147,3	
B18	1455	1473		-9,7258	26 271,7	0,9652	218,4					
C23	1473	1447	1461	-6,5594	19 473,9	0,9934	161,9		12 302,7	0,9969	102,3	

*Liquidus temperatures obtained from high-temperature microscopy (HS), viscosity measurements (Vis), and electrical-resistance measurements (Res).
†M is the magnesium aluminum titanate Mg₄Al₂Ti₃O₁₃, and P is perovskite (CaO.TiO₂).

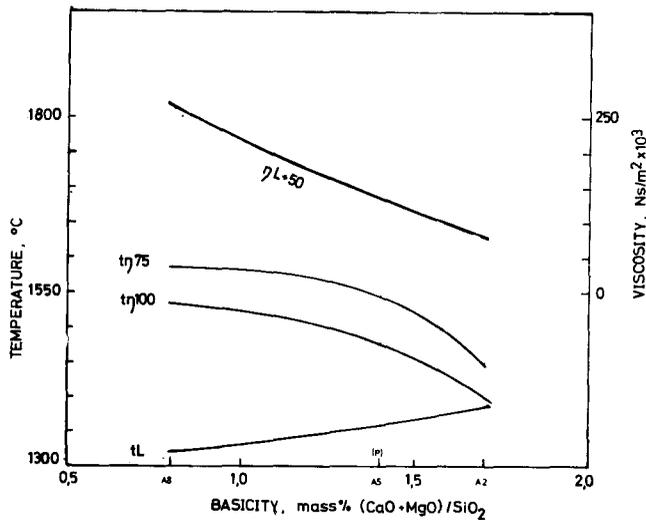


Fig. 2—The effect of basicity on the liquidus temperature and viscosity of slags with $(\text{TiO}_2 + \text{Al}_2\text{O}_3) = 36$ per cent and $\text{CaO}/\text{MgO} = 1$

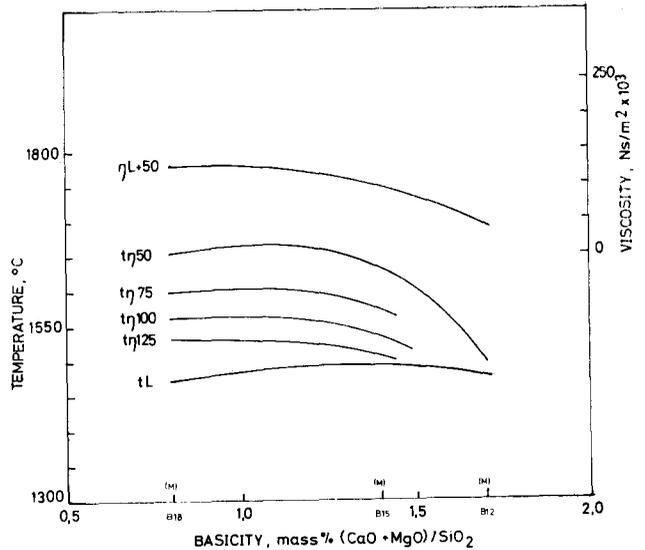


Fig. 5—The effect of basicity on the liquidus temperature and viscosity of slags with $(\text{TiO}_2 + \text{Al}_2\text{O}_3) = 44$ per cent and $\text{CaO}/\text{MgO} = 0.5$

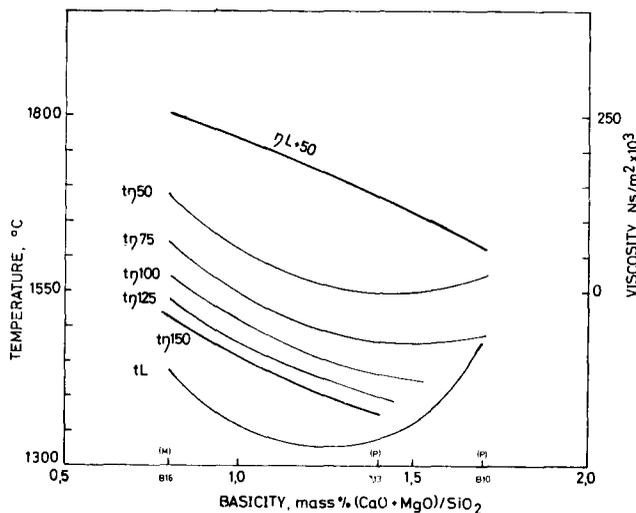


Fig. 3—The effect of basicity on the liquidus temperature and viscosity of slags with $(\text{TiO}_2 + \text{Al}_2\text{O}_3) = 44$ per cent and $\text{CaO}/\text{MgO} = 2$

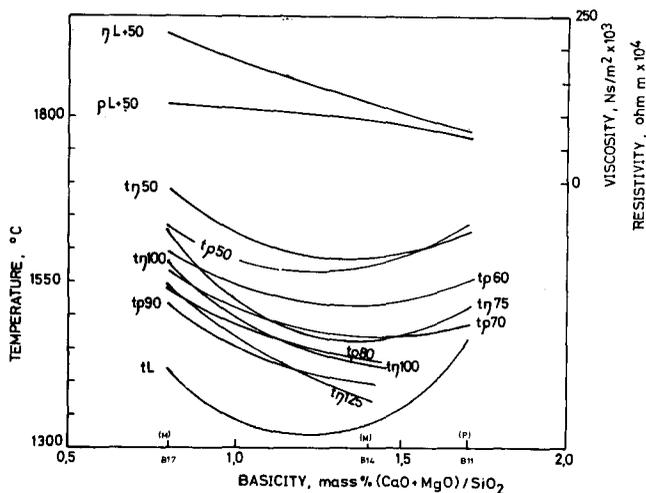


Fig. 4—The effect of basicity on the liquidus temperature, viscosity, and electrical resistivity of slags with $(\text{TiO}_2 + \text{Al}_2\text{O}_3) = 44$ per cent and $\text{CaO}/\text{MgO} = 1$

basicity at two values of the CaO/MgO ratio. For reasons of clarity, slags B30–B34 and B28–B29 have been omitted from Fig. 3. In both cases, an increase in the basicity caused an initial drop in liquidus temperature followed by a sharp rise. A change of primary phase from M to P occurred in both instances. For a CaO/MgO ratio of 0.5 where the primary phase was M for all three slags (Fig. 5), the variation in liquidus temperature was small.

With regard to the effect of the CaO/MgO ratio at different basicities, the results of this work can be compared with those of Jochens *et al.*⁴, although they studied slags of higher titania concentrations. For the system 19.69 per cent SiO_2 , 13.12 per cent Al_2O_3 , 37.19 per cent TiO_2 , 30 per cent $(\text{CaO} + \text{MgO})$ with CaO varying from 0 to 30 per cent, an increase in the MgO content from 0 to 12 per cent by mass was found to lower the liquidus temperature from 1520 to 1340°C. Further replacement of CaO by MgO caused a gradual rise in the liquidus temperature. There was also a change in primary phase from P (at MgO contents lower than that corresponding to the liquidus minimum) to M as the MgO was further increased. In a general way, the data presented in Figs. 6 and 7 agree with the trends above. Jochens also found that the minimum liquidus temperature shifted towards lower MgO contents with a decrease in the overall basicity. The absolute value of the minimum was reduced at the same time. These trends are also similar to those shown in Figs. 6 to 8 for slag groups of decreasing total basicity. This might imply that in Fig. 8, where all three slags have the same primary phase, the minimum must be situated at a basicity ratio greater than 2.

The series A5–B14–C23 differs only in $(\text{TiO}_2 + \text{Al}_2\text{O}_3)$ concentration (Fig. 9). Again, there may be a minimum liquidus temperature between A5 and B14 that is associated with a change of primary phase.

Viscosity and Electrical Conductivity

The results are presented in Table II according to the

Arrhenius relations

$$\ln \eta = a + b/T \text{ and}$$

$$\ln k = c - d/T,$$

where η = viscosity in $\text{N.s/m}^2 \times 10^3$,

k = electrical conductivity in S/m ,

T = absolute temperature, and

a, b, c, d are constants.

The equations were derived by the method of least-squares analysis, and the correlation coefficients are also given in the table, as well as the activation energies for viscous flow and for conduction.

In Figs. 2 to 9 the electrical conductivity is replaced by the resistivity to show the similarity of its dependence on any composition variable to that of viscosity. The results are given as temperatures of equal viscosity or resistivity, e.g. $t_{\rho 90}$ signifies the temperature at which the resistivity is $90 \text{ } \Omega \cdot \text{m} \times 10^4$. Viscosity is expressed as $\text{N.s/m}^2 \times 10^3$. The same diagrams also include curves of viscosity or resistivity at a fixed temperature interval of

50°C above the liquidus temperature. No points are given in the diagrams, but the curves go through the points predicted from the Arrhenius equations.

The effect of basicity (Figs. 2 to 5)

In those instances where the liquidus temperatures of the three members of the slag series vary only slightly with the basicity, the isoviscosity curves have the expected shape, showing increasing viscosity with increasing silica content. This applies to Figs. 2 and 5. It appears as though the basicity increase from 1,4 to 1,7 exerts a relatively larger effect than that from 0,8 to 1,4. The general trend is also evident when the viscosity is expressed as viscosity at 50°C above liquidus temperature ($\eta L+50$) and when the values of activation energy for viscous flow, E_η , are compared (Table II).

However, when an increasing basicity is accompanied by larger increases in liquidus temperature (Figs. 3 and 4), this is clearly reflected in the shape of the iso-viscosity curves. The curves representing $\eta L+50$ still show a

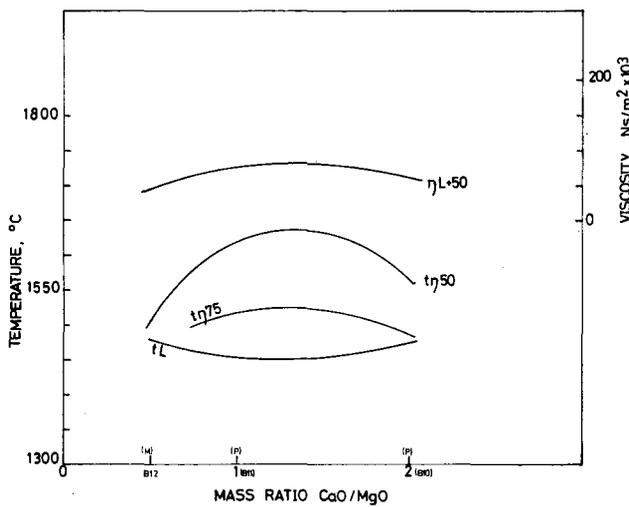


Fig. 6—The effect of lime-to-magnesia ratio on the liquidus temperature and viscosity of slags with $(\text{TiO}_2 + \text{Al}_2\text{O}_3) = 44$ per cent and $(\text{CaO} + \text{MgO})/\text{SiO}_2 = 1,7$

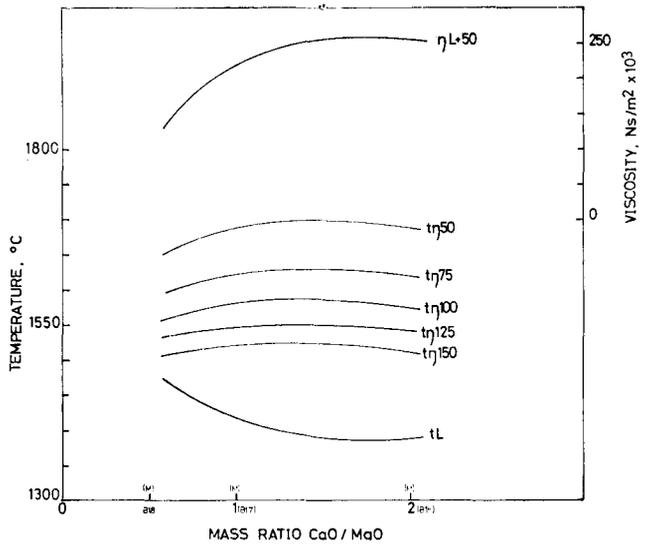


Fig. 8—The effect of lime-to-magnesia ratio on the liquidus temperature and viscosity of slags with $(\text{TiO}_2 + \text{Al}_2\text{O}_3) = 44$ per cent and $(\text{CaO} + \text{MgO})/\text{SiO}_2 = 0,8$

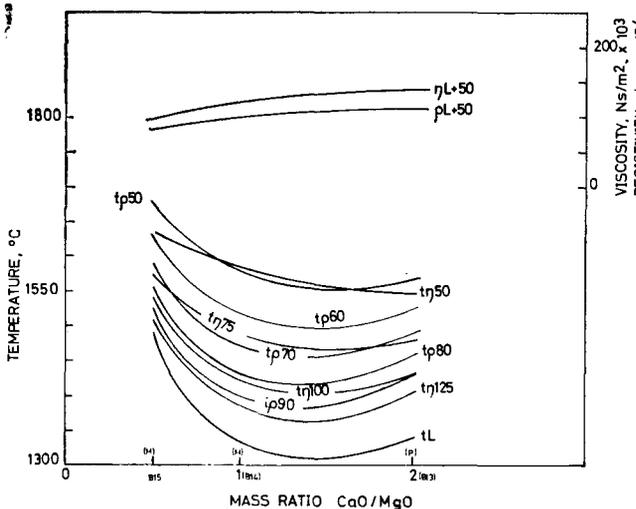


Fig. 7—The effect of lime-to-magnesia ratio on the liquidus temperature, viscosity, and electrical resistivity of slags with $(\text{TiO}_2 + \text{Al}_2\text{O}_3) = 44$ per cent and $(\text{CaO} + \text{MgO})/\text{SiO}_2 = 1,4$

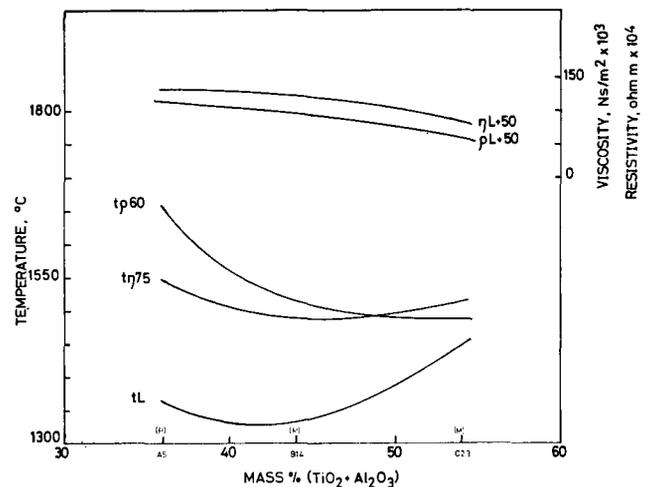


Fig. 9—Effect of $(\text{TiO}_2, \text{AlO}_3)$ content on the liquidus temperature, viscosity, and electrical resistivity of slags with $\text{CaO}/\text{MgO} = 1$ and $(\text{CaO} + \text{MgO})/\text{SiO}_2 = 1,4$

decrease in viscosity as the slag becomes more basic. An increasing silica concentration again has the effect of raising $E\eta$.

The available resistivity values for the series B11–B14–B17 are shown in Fig. 4. The curves in the diagram, as well as the trend shown by values of E_k , are very similar to those outlined above for the viscosity of the same series.

In attempts to predict the role of a particular metal oxide in a siliceous melt, the cationic field strength (I) has often been used. Accordingly, Table III gives the values of this parameter for the metal–oxygen bonds relevant to this study, as well as the cationic radii¹⁶.

TABLE III

PROPERTIES OF THE CATION–OXYGEN BONDS IN SOME METAL OXIDES

Oxide	Cationic radius $m \times 10^{10}$	Cationic field strength $m \times 10^{-20}$
CaO	0,99	0,70
MgO	0,65	0,95
Al ₂ O ₃	0,50	1,66
TiO ₂	0,68	1,85
SiO ₂	0,41	2,44

The fundamental tendency of Si⁴⁺ to enter into four-fold co-ordination with oxygen, a tendency that must give rise to polymerization in oxygen-deficient melts, is the result of the high field strength of the ion. Whether the Bockris postulate^{17, 18} of discrete silicate anions is valid, or whether liquid silicates contain an array of ions whose distribution is governed by chemical equilibrium^{19–21}, is immaterial in the present context. An increased silica content must give rise to the predominance of more-complex silicate anions. This is in accord with the trends shown in the diagrams.

The effect of the mass ratio CaO/MgO (Figs. 6 to 8)

The only instance where the viscosity at 50° above the liquidus temperature decreased substantially with an increase in the magnesia content is shown in Fig. 8 for the lowest basicity ratio of 0,8. For the higher basicities of 1,4 (Fig. 7) and 1,7 (Fig. 6), the variation of $\eta L + 50$ is small. With all the ratios calculated from concentrations in mass per cent, a decrease in the CaO/MgO ratio at 'constant basicity' actually represents an increase in the basicity on a molar basis if such a basicity ratio is still calculated as the ratio (CaO+MgO)/SiO₂. This may be part of the explanation for the effect of mass ratio CaO/MgO on the viscosity of acidic slags as shown in Fig. 8.

The curves for $\eta L + 50$ and for temperatures of equal viscosity have the same general shape when the liquidus temperature of the slag does not vary greatly (Figs. 6 and 8). Where the variation in liquidus temperature is more marked (Fig. 7), the isoviscosity curve is influenced by the liquidus temperature, particularly at high viscosity.

A feature common to all three graphs is that a high $\eta L + 50$ is associated with a low liquidus temperature.

According to Bockris, the smaller Mg²⁺ ion can be expected to exhibit a more pronounced 'bridging' tendency than Ca²⁺ and therefore be less effective than Ca²⁺ in breaking up the silicate network and lowering the

viscosity. However, it appears to be generally agreed that the replacement of lime by magnesia has no effect on viscosity if molar concentrations are used. This was illustrated by Turkdogan and Bills²² in their review of the viscosity data of CaO–MgO–Al₂O₃–SiO₂ melts. On these findings it would be reasonable to expect that an increase in molar basicity (by the addition of MgO or by a decrease in the mass ratio CaO/MgO at constant mass basicity) will lower the viscosity of a siliceous melt. The first alternative was verified by Freidenzon⁸ when he increased the magnesia content of CaO–MgO–Al₂O₃–SiO₂–TiO₂ melts, and the second by McRae⁹, who found (for the same overall system) that the replacement of CaO by MgO caused a slight drop in viscosity at a fixed temperature if mass ratios were used. In further agreement with the results in Figs. 6 to 8, McRae pointed out that a low viscosity (at a fixed temperature above liquidus) appeared to be associated with a high liquidus temperature.

Fig. 7 again illustrates the fact that viscosity and electrical resistivity follow very similar trends when both are regarded as functions of the same composition variable.

The effect of the (TiO₂+Al₂O₃) concentration (Fig. 9)

The diagram shows that an increase in (TiO₂+Al₂O₃) causes decreases in $\eta L + 50$ and $\rho L + 50$. The effect is also recognizable in the shapes of the curves for $t\rho$ 60 and $t\eta$ 75, in spite of the high liquidus temperature of the high titania slag (C23). The increased combined oxide content also caused increases in $E\eta$ and E_k (Table II).

In addition to references to the five-component system^{2, 5, 6–9}, there are numerous other examples in the literature^{23–30} of the effect of TiO₂ as one of lowering the viscosity of oxide melts. Kato and Minowa³¹ also reported an increase in the activation energy for viscous flow when small additions of titania were made to a CaO–SiO₂–Al₂O₃ slag.

No conclusion regarding the role of titanium oxide in siliceous melts can be reached on the basis of the few data presented in Fig. 9, mainly because the increase in titania content was accompanied by an increase in alumina. The Al³⁺ cation (of intermediate field strength) can enter the liquid structure of the CaO–SiO₂–Al₂O₃ system either in fourfold or in sixfold co-ordination, depending mainly on the Al₂O₃/CaO ratio³². Van der Colf¹⁰ pointed out there is no evidence that Ti⁴⁺ behaves in a similar manner, in spite of its high field strength. He also offered an explanation for the fact that titania normally lowers the viscosity and resistivity of siliceous melts, mainly on the basis of the atomistic approach of Marboe and Weyl³³ and the fact that titanium oxide loses oxygen readily at high temperature.

The relation between viscosity and electrical resistivity

For every slag for which both viscosity and resistivity values are available from this investigation, there is an obvious relationship between these properties. This is to be expected if it is accepted that viscosity is governed by the size of the anions while resistivity depends on the nature of the current-carrying cations. An increase in the temperature of a slag then causes progressive loosening of the liquid structure, a process that should be accompanied by a decrease in both viscosity and resistivity.

Fig. 10 is a graph of \ln (resistivity) against \ln (viscosity) for the slags of the investigation. Resistivity is expressed in $\Omega \cdot m \times 10^2$ and viscosity in $N \cdot s/m^2 \times 10$ (poise). The slopes of the lines vary considerably. The general form of the line is

$$\ln \rho = m \ln \eta + \ln C \text{ or } \rho = C \eta^m.$$

The constant C for a given slag has a value between 0,8 and 0,9 for the slags A5, B14, B13, B15 and B11, and is approximately 0,6 for slags B17 and C23.

The overall electrical conductance of these slags can be expected to incorporate some electronic conduction owing to the small oxygen deficiency at elevated temperatures. This electronic contribution will be common to all the slags, but differences in composition will alter its relative magnitude. The deviation of B17 and C23 above may be significant. The latter has a high $(TiO_2 + Al_2O_3)$ concentration (54 per cent), as compared with A5 (36 per cent) and B14 (44 per cent). An abnormally low value of resistivity corresponding to a viscosity of 1 poise appears to indicate relatively more electronic conduction. Slag B17 also has an appreciably lower resistivity than would be expected from its high silica

content of 31,1 per cent, as compared with 20,75 per cent for B11 and 23,33 per cent for B14. This again seems to indicate that electronic conduction becomes relatively more important as the silica content is increased.

At a constant temperature the two empirical equations $\ln \rho = \ln (A_k)^{-1} + E_k/RT$ (1) and $\ln \eta = \ln (A\eta) + E\eta/RT$ (2)

after combination lead to $\ln \rho = E_k/E\eta \ln \eta - E_k/E\eta \ln A\eta + \ln (A_k)^{-1}$. . . (3)

If $E_k/E\eta = x$ and $y = -E_k/E\eta \ln A\eta + \ln (A_k)^{-1}$ are constants, a graph of $\ln \rho$ against $\ln \eta$ should be a straight line of slope x and intercept y on the $\ln \rho$ axis. The relevant data for the investigated slags are shown in the first five columns of Table IV.

If slags B17 and C23 are omitted from the least-squares analysis, in the light of the observations based on Fig. 10 the remaining points give $x=0,696$ and $y=-0,169$ ($r=0,9316$). The figures in the last column of Table IV were calculated from equation (3) from the observed values of viscosity at 1500°C. The calculation

TABLE IV
VISCOSITIES AND RESISTIVITIES OF SLAGS AT 1500°C

Slag	η_{1500} $N \cdot s/m^2 \times 10$	ρ_{1500} $\Omega \cdot m \times 10^2$	$\ln \eta_{1500}$	$\ln \rho_{1500}$	ρ_{1500} (calc.) $\Omega \cdot m \times 10^2$
A5	0,91	0,88	-0,094	-0,128	0,79
B14	0,72	0,63	-0,329	-0,462	0,67
B13	0,66	0,66	-0,415	-0,415	0,63
B15	1,32	1,00	0,278	0,000	1,02
B11	0,80	0,68	-0,223	-0,386	0,72
B17	1,78	1,00			
C23	0,83	0,57			

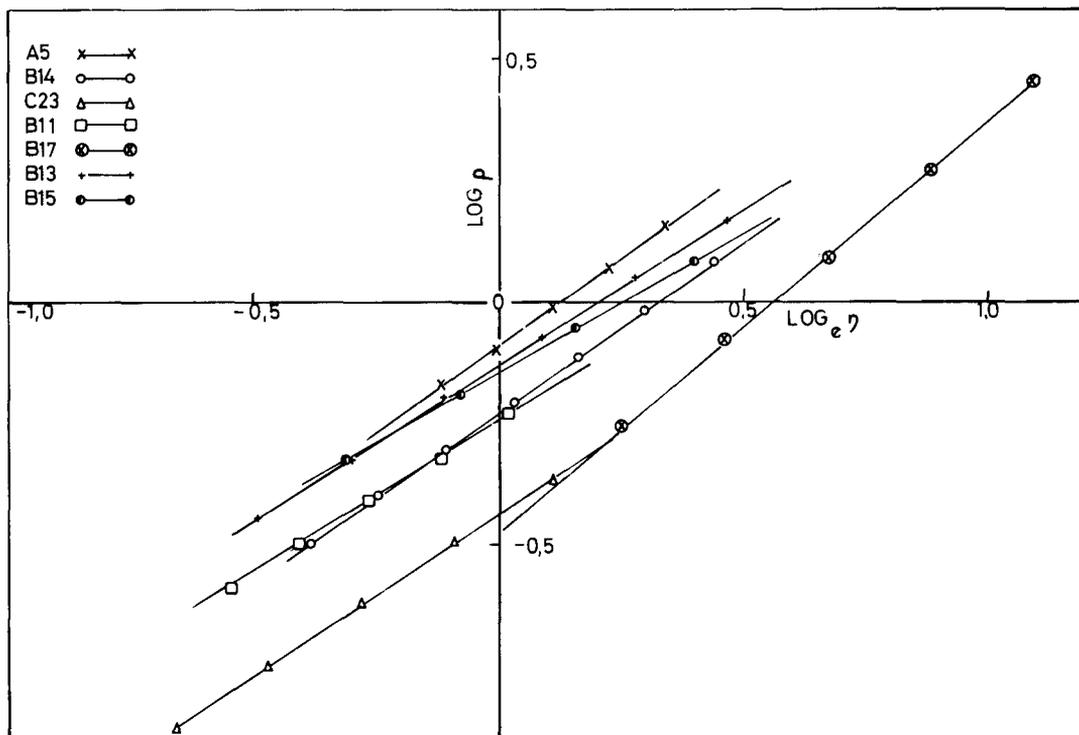


Fig. 10—Relation between viscosity (η) and resistivity (ρ) of the same slag

TABLE V

RESISTIVITIES CALCULATED FROM OBSERVED VALUES OF VISCOSITY AT 1500°C

Slag no.	η_{1500} (obs.) N.s/m ² × 10	ρ_{1500} (calc.) $\Omega \cdot m \times 10^2$	E_k kJ/mol. °C
A2	0,57	0,57	96
B10	0,71	0,66	89
B12	0,51	0,53	104

was then also made for the slags in Table V, for which the resistivity was not measured.

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