CHAPTER 5

DISCUSSION OF THE EFFECT OF VARIOUS PARAMETERS ON Cr_2O_3 REDUCTION

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This chapter is concerned with a discussion of the effect of various parameters on the reduction of Cr_2O_3 from slag. The parameters discussed are the effect of metal chromium content, the effect of temperature, the effect of melt geometry, the effect of surface-active elements, S, Se and Sb, and the effect of calcium fluoride. Scheme 4 is applied in determining rate constants as it gives meaningful results compared to scheme 5 as discussed in section 4.5.4.

5.1 Effect of metal chromium content.

The results from this investigation in which 15 and 4 wt% Cr were added to the metal and the runs conducted in an argon atmosphere, runs AS7 and AS8 respectively, are shown in Fig. 5.1. The figure shows that reduction of (Cr^{3+}) is not affected by metal chromium contents up to 15 wt%. The reduction rate of (Cr^{2+}) is decreased markedly by increasing the metal chromium content from 4 to 15 wt%. Figs. 5.2 and 5.3 show calculated concentration-time curves for the chromium species for

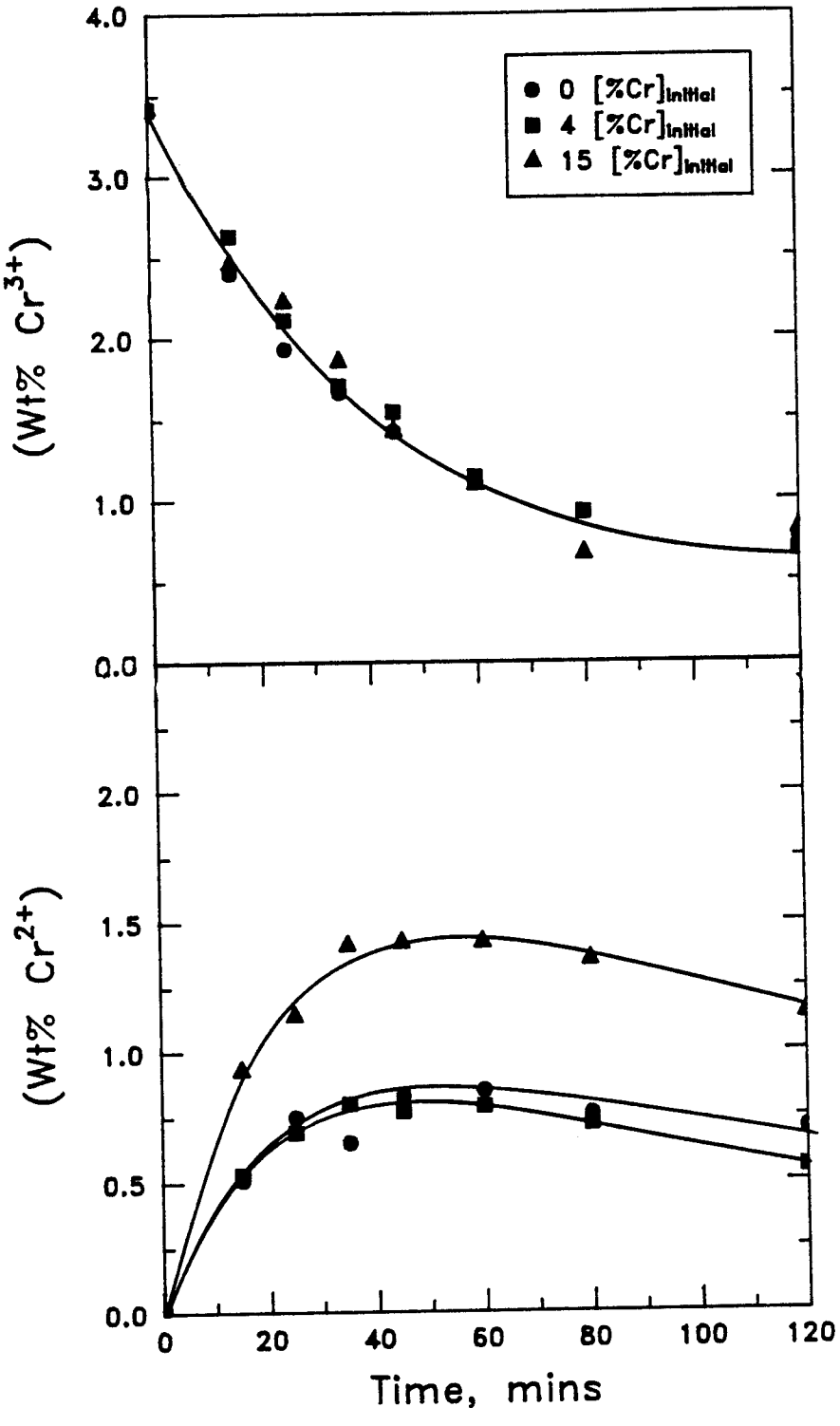
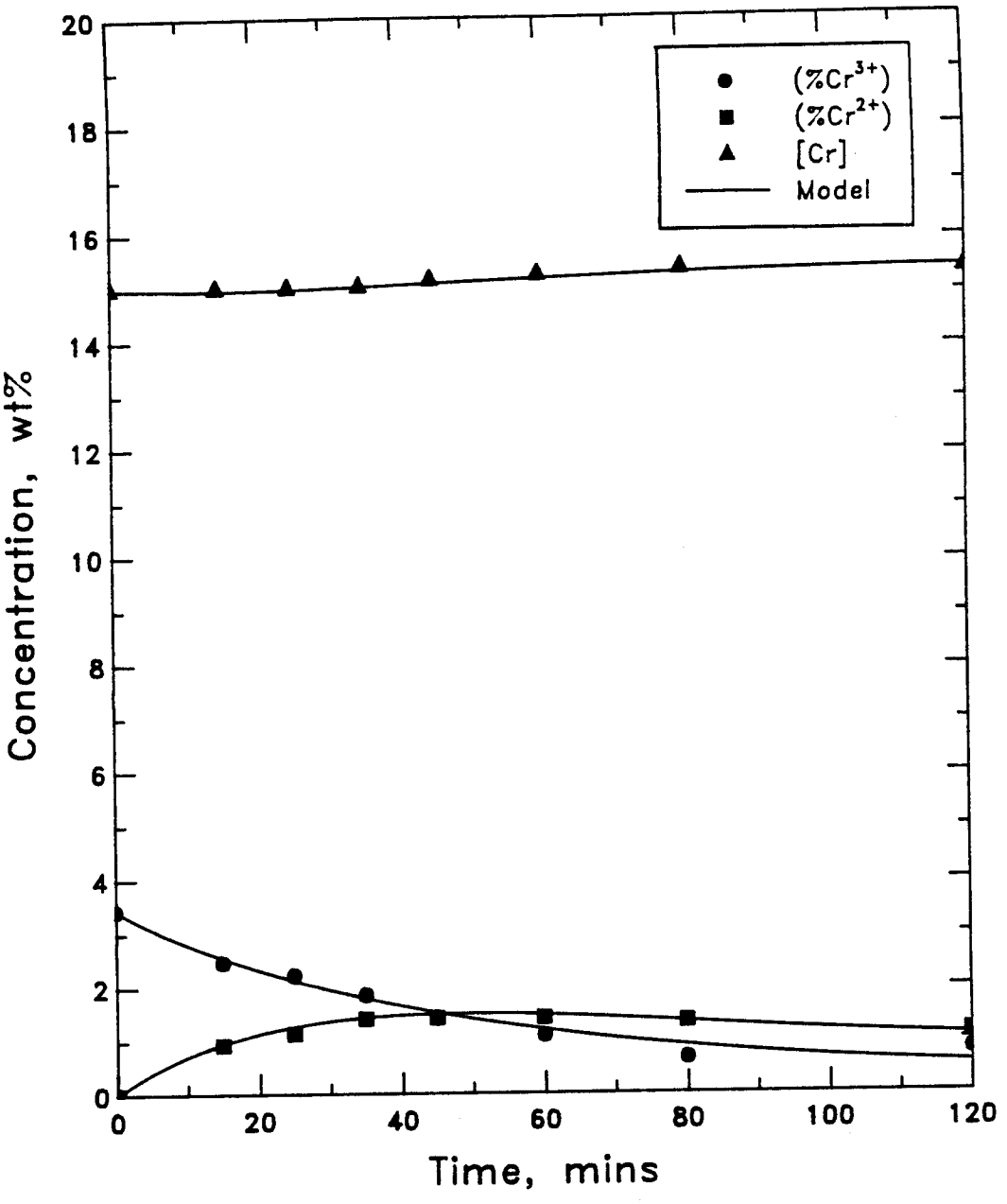


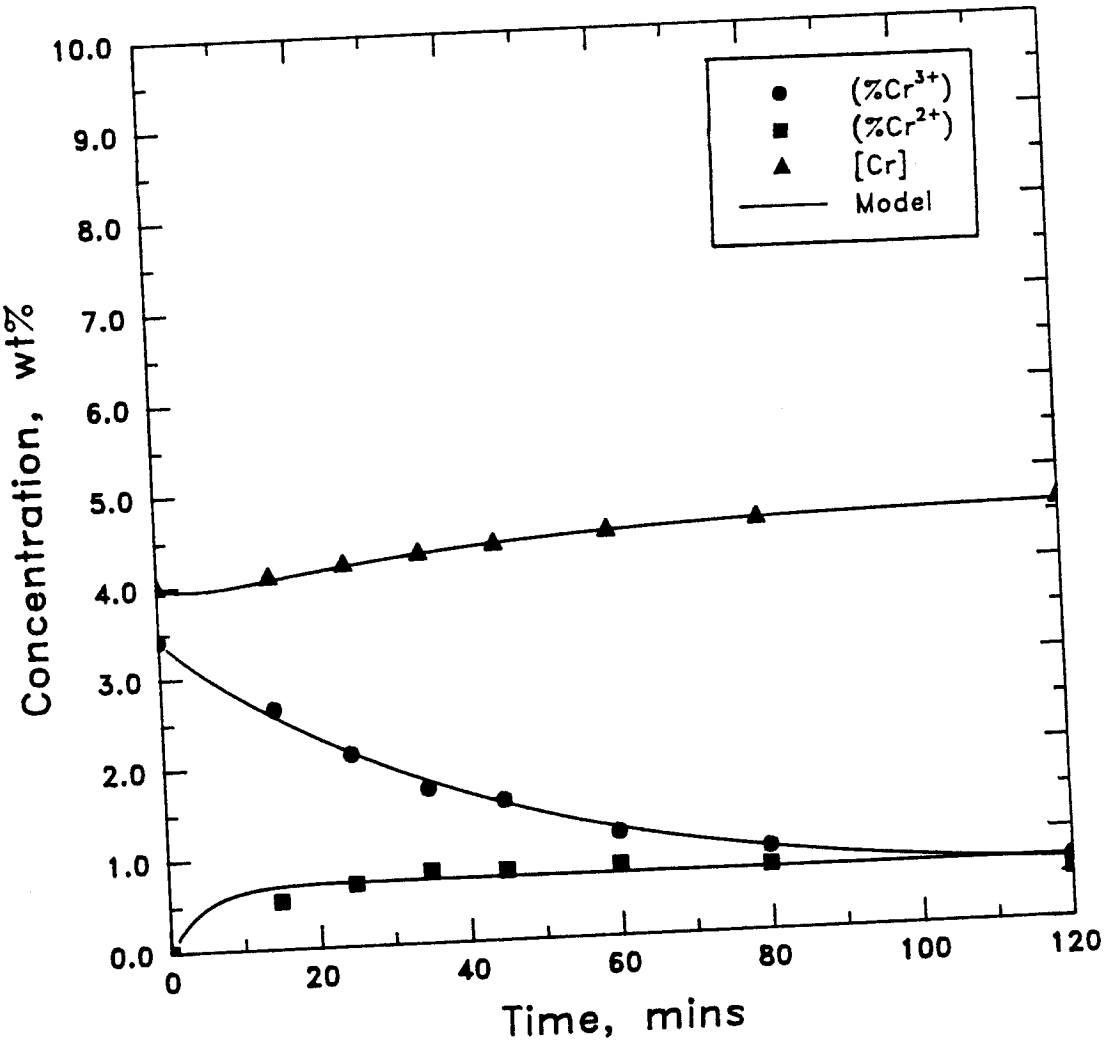
Fig. 5.1 Effect of metal chromium content on (Cr^{3+}) and (Cr^{2+}) reduction.



$k_1 = 0.0190\ cm.min^{-1}$. $k_2 = 0.0071\ cm.min^{-1}$.
$k_3 = 0.0222\ cm.min^{-1}$. $k_4 = 0.0011\ cm.min^{-1}$.

Sums of squares of deviations are:
$Cr^{3+} = 0.160$, $Cr^{2+} = 0.038$, $Cr_{Met.} = 0.009$.

Fig. 5.2 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run AS7.



$k_1 = 0.0203\ cm.min^{-1}$. $k_2 = 0.0163\ cm.min^{-1}$.
$k_3 = 0.1496\ cm.min^{-1}$. $k_4 = 0.0165\ cm.min^{-1}$.

Sums of squares of deviations are:
$Cr^{3+} = 0.019$, $Cr^{2+} = 0.068$, $Cr_{Met.} = 0.003$.

Fig. 5.3 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run AS8.

these runs using scheme 4. The rate constants obtained are shown in Table 5.1 together with those of run AS1 in which no chromium was initially added to the metal.

Table 5.1: Effect of metal chromium content on rate constants.

Initial [%Cr]	k_1	k_2	k_3	k_4
		$cm.min^{-1}$		
0	0.0239	0.0215	0.0609	0.0226
4	0.0203	0.0163	0.1496	0.0165
15	0.0190	0.0071	0.0222	0.0011

The similarity in the forward rate constant, k_1, for the three runs confirms the statement made above that the reduction of (Cr^{3+}) does not depend very much on the metal chromium content up to 15 wt%. In terms of the model, increasing the metal chromium content up to 15 wt% has no effect on the first-stage of the consecutive reaction i.e (Cr^{3+}) to (Cr^{2+}).

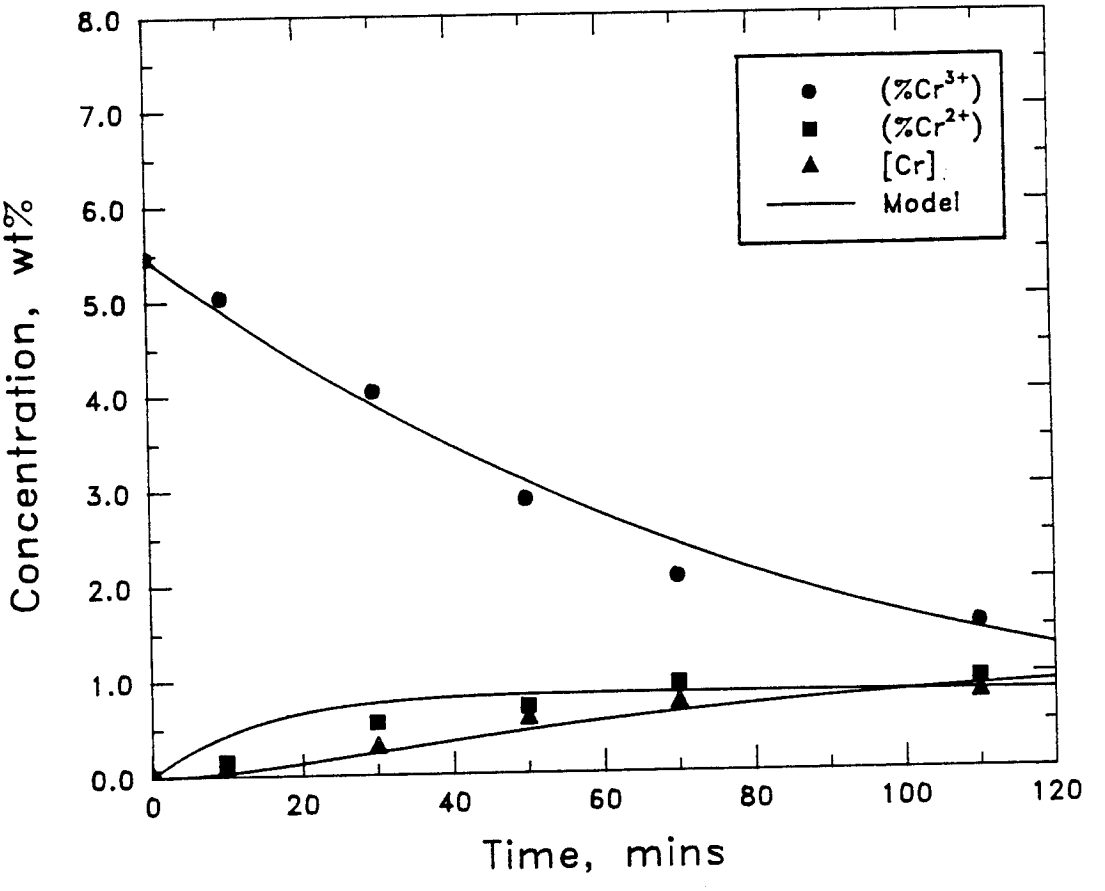
The forward rate constant, k_3, markedly reduced with an increase in metal chromium concentration from 4 to 15 wt%, an indication that the reduction of (Cr^{2+}) is dependent on the metal chromium content above 4 wt% when reduction is by carbon in metal. It is most probable that the increase in (Cr^{2+}) in the slag at 15 wt% is due to a reduction in the concentration gradient of (Cr^{2+})

between the bulk and interface which slows the reduction rate. Since the reduction of (Cr^{2+}) is a comparatively slow process[37], an accumulation of (Cr^{2+}) in slag occurs as shown in Fig. 5.1.

5.2 Effect of Temperature.

Concentration-time curves were drawn using scheme 4 and the results of Anyakwo[37] in which the experimental temperature was varied. Figs. 5.4, 5.5, 5.6 and 5.7 show the curves obtained and the corresponding observed concentrations at 1400, 1450, 1500 and 1550°C, respectively. In each case an initial concentration of 8 wt% Cr_2O_3 in slag was used and the runs were carried out in a CO atmosphere. Table 5.2 shows the variation of rate constants with temperature. A plot of the variation of the forward rate constants, k_1 and k_3, with temperature is shown in Fig. 5.8. An increase in the rate constant values with increase in temperature is apparent, indicating that the rate of Cr_2O_3 reduction increases with an increase in temperature. This is in good accord with the finding of other investigators into the reduction rate of Cr_2O_3 from slag[31,69].

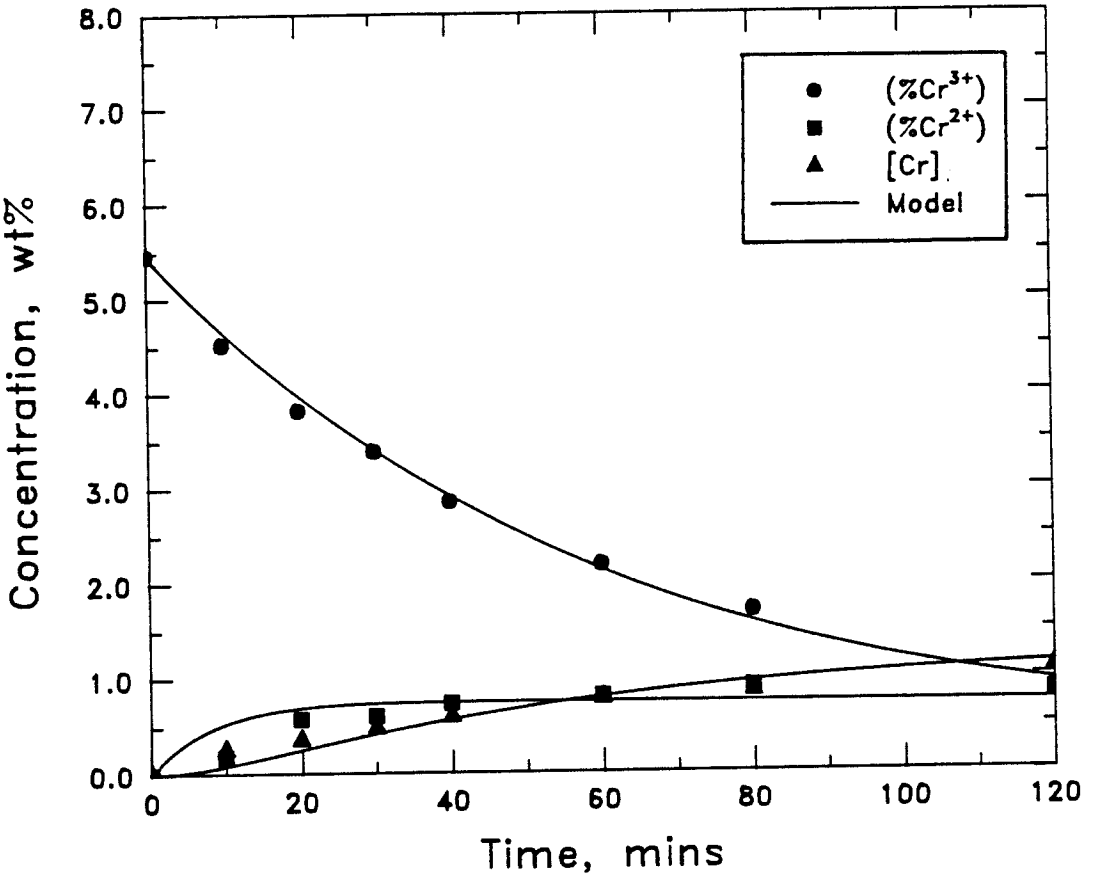
Arrhenius plots for (Cr^{3+}), (Cr^{2+}) and Cr_2O_3 reduction were generated using the forward rate constants (Table 5.2) and are shown in Fig. 5.9. Activation energies of



$k_1 = 0.0098\ cm.min^{-1}.\quad k_2 = 0.0031\ cm.min^{-1}.$
$k_3 = 0.0483\ cm.min^{-1}.\quad k_4 = 0.0088\ cm.min^{-1}.$

Sums of squares of deviations are:
$Cr^{3+} = 0.470,\quad Cr^{2+} = 0.180,\quad Cr_{Met.} = 0.069.$

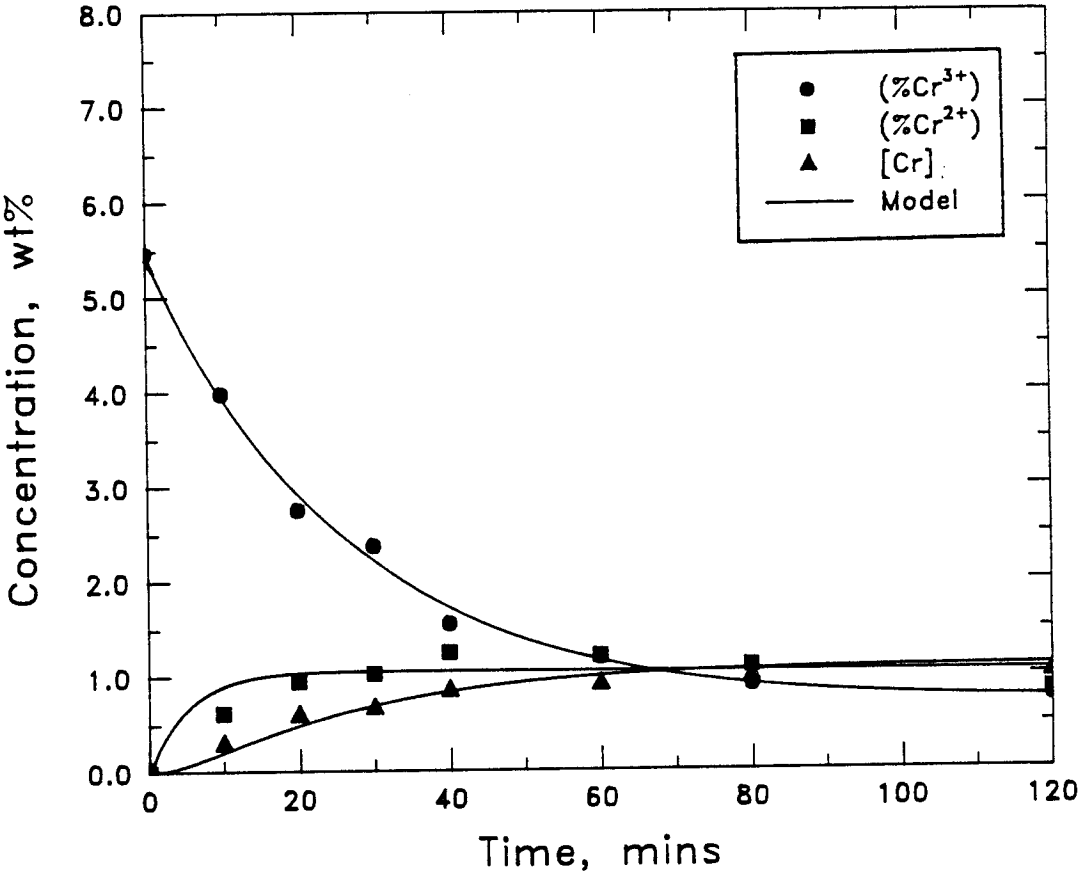
Fig. 5.4 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] at 1400°C , data from Ref (37).



$k_1 = 0.0148\ cm.min^{-1}$. $k_2 = 0.0080\ cm.min^{-1}$.
$k_3 = 0.0815\ cm.min^{-1}$. $k_4 = 0.0137\ cm.min^{-1}$.

Sums of squares of deviations are:
$Cr^{3+} = 0.069$, $Cr^{2+} = 0.203$, $Cr_{Met.} = 0.061$.

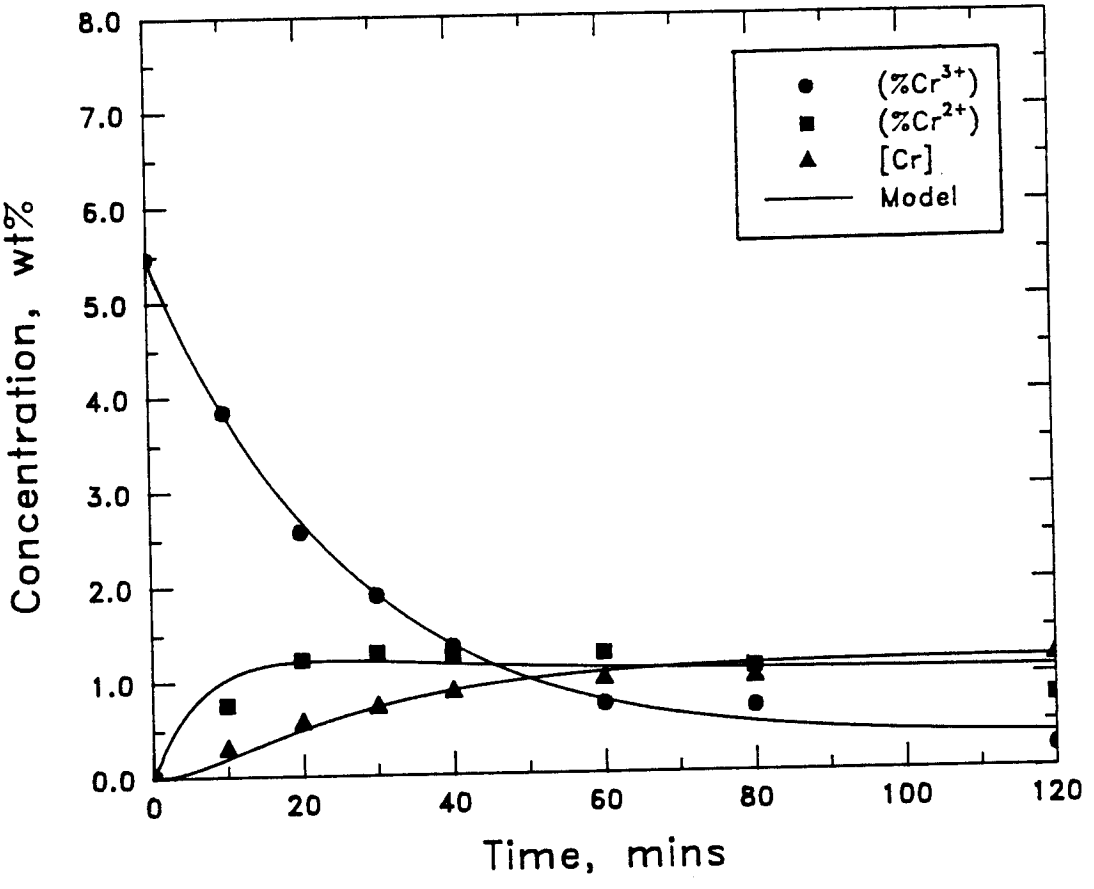
Fig. 5.5 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] at 1450°C , data from Ref (37).



$k_1 = 0.0321\ cm.min^{-1}$. $k_2 = 0.0223\ cm.min^{-1}$.
$k_3 = 0.1086\ cm.min^{-1}$. $k_4 = 0.0309\ cm.min^{-1}$.

Sums of squares of deviations are:
$Cr^{3+} = 0.081$, $Cr^{2+} = 0.204$, $Cr_{Met.} = 0.048$.

Fig. 5.6 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] at 1500°C , data from Ref (37).



$k_1 = 0.0334\ cm.min^{-1}$. $k_2 = 0.0108\ cm.min^{-1}$.
$k_3 = 0.0915\ cm.min^{-1}$. $k_4 = 0.0242\ cm.min^{-1}$.

Sums of squares of deviations are:
$Cr^{3+} = 0.065$, $Cr^{2+} = 0.212$, $Cr_{Met.} = 0.047$.

Fig. 5.7 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] at 1550°C , data from Ref (37).

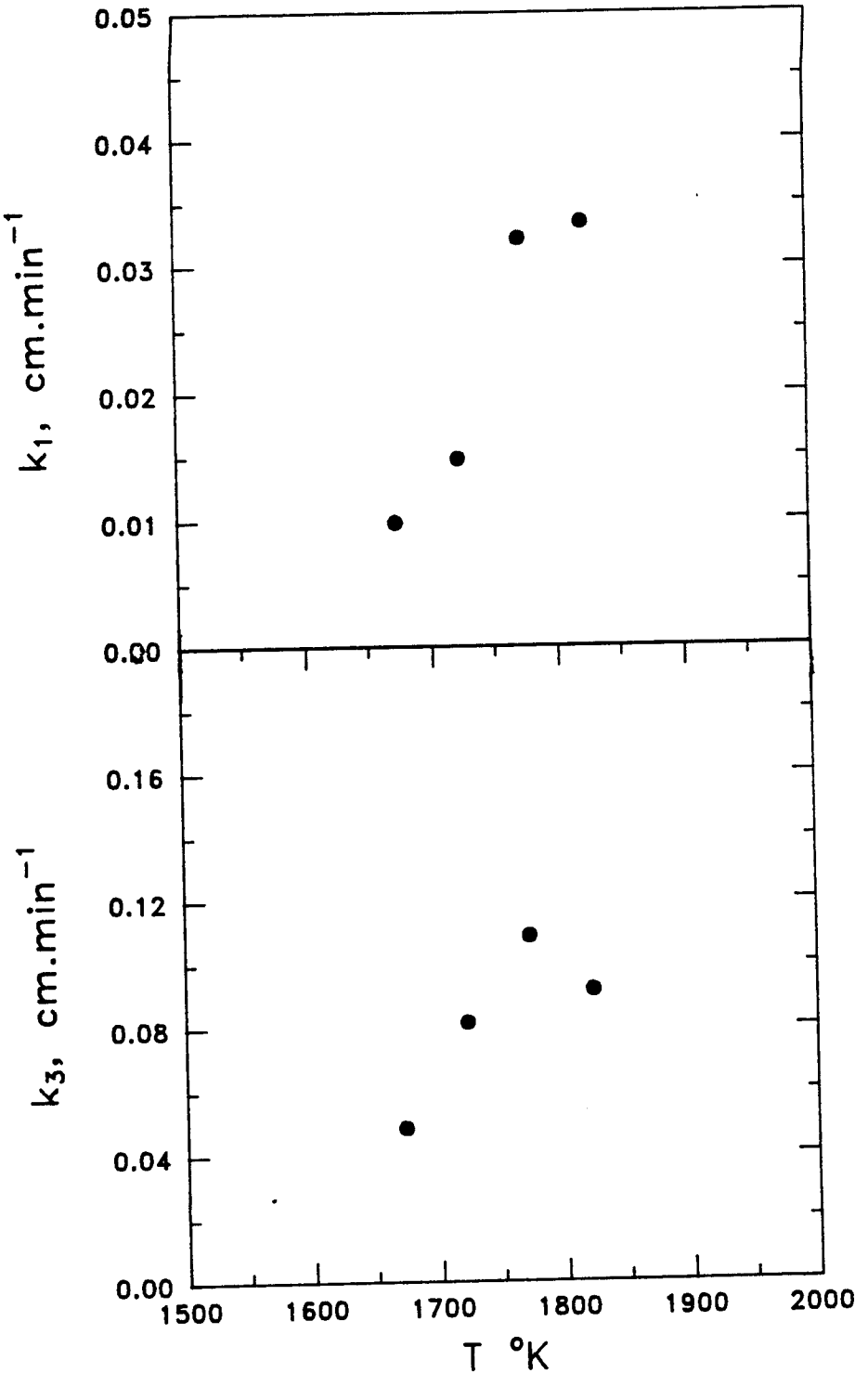


Fig. 5.8 Effect of temperature on forward rate constants k_1 and k_3.

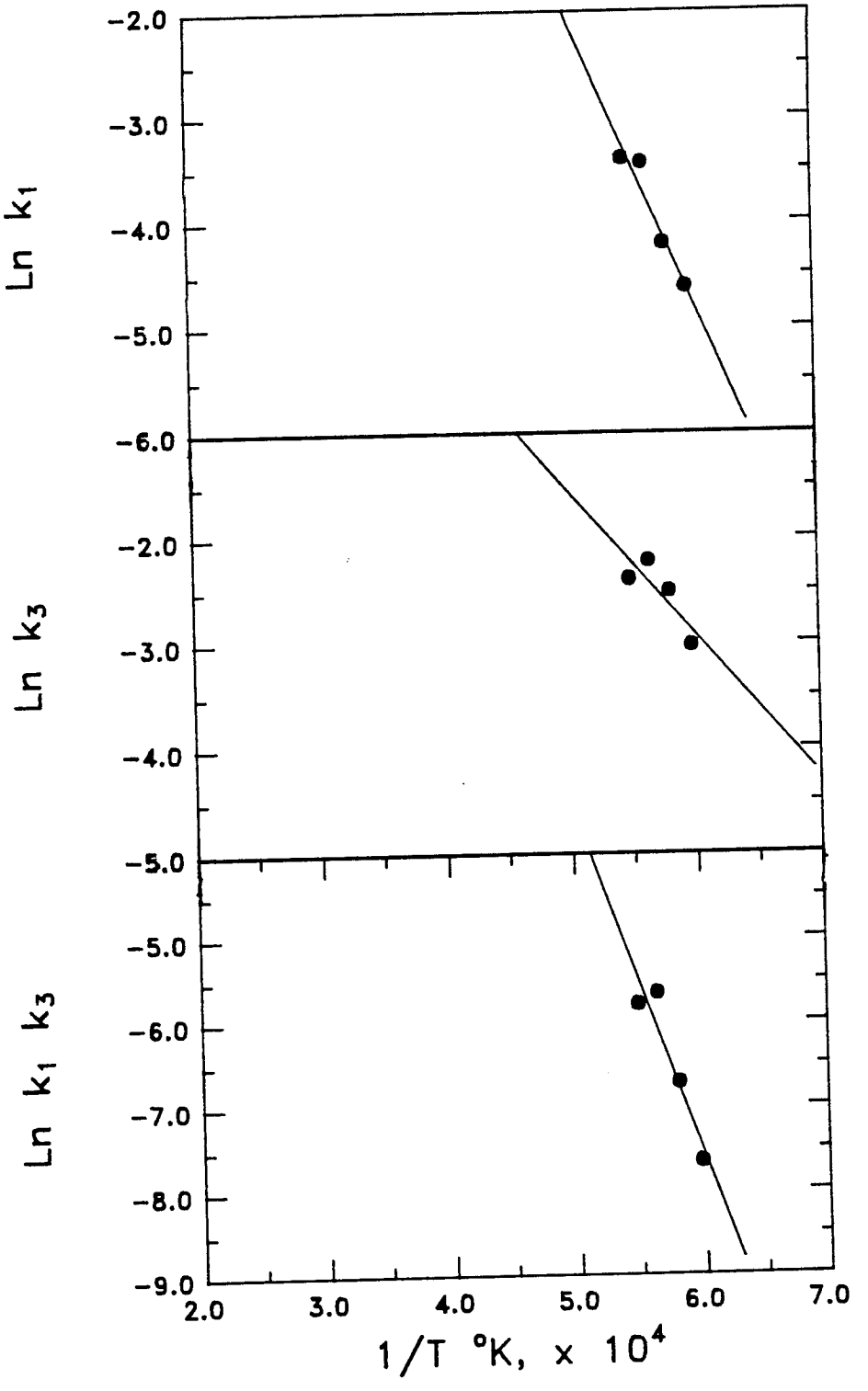


Fig. 5.9 Arrhenius plots for (Cr^{3+}), (Cr^{2+}) and Cr_2O_3 reduction.

the reduction of the chromium species and Cr_2O_3 were

Table 5.2: Variation of rate constants with temperature.

Temp. ^oC	k_1	k_2	k_3	k_4
		$cm.min^{-1}$		
1400	0.0098	0.0031	0.0483	0.0088
1450	0.0148	0.0080	0.0815	0.0137
1500	0.0321	0.0223	0.1086	0.0309
1550	0.0334	0.0108	0.0915	0.0242

determined according to equation (1.37). The activation energy for Cr_2O_3 reduction was obtained by plotting Ln k_1k_3 against 1/T (table 5.3) as shown in Fig. 5.9. The product, k_1k_3, represents the overall reduction of Cr_2O_3 to [Cr]. The activation energies obtained for (Cr^{3+}), (Cr^{2+}) and Cr_2O_3 reduction were 54.16, 27.15 and 81.33 kcal/mol, respectively. A comparison of the activation energies obtained is made with those from other investigators in Table 5.4.

Table 5.3: Data for arrhenius plots of (Cr^{3+}), (Cr^{2+}) and Cr_2O_3 reduction.

T ^oK	1/T x 10^4	k_1	Ln k_1	k_3	Ln k_3	Ln k_1k_3
1673	5.977	0.0098	-4.625	0.0483	-3.030	-7.656
1723	5.804	0.0148	-4.213	0.0815	-2.507	-6.720
1773	5.640	0.0321	-3.439	0.1086	-2.220	-5.659
1823	5.485	0.0334	-3.399	0.0915	-2.391	-5.791

A variation in the activation energy for the reduction of (Cr^{3+}), (Cr^{2+}) and Cr_2O_3 can be seen from the table. This could be due to the different temperatures and systems used. In some cases, such as Ref. (31), either mass transport in slag or an interfacial chemical reaction was assumed to be rate-controlling when determining the activation energy. However, the activation energy obtained in this study for the reduction of (Cr^{3+}) is in good accord with that obtained

Table 5.4: Activation energy of Cr_2O_3 reduction.

Ref.	Temp. range ^oC	System	Species reduced	Activation energy kcal/mol
20	1710-1820	Fe-C	Cr^{2+}	106.75
29	1130-1490	H_2	Cr_2O_3	26.60
31	1550-1625	Fe-Si	Cr^{3+}	100.00 MTS
"	"	"	Cr^{2+}	130.00 ICR
36	1520-1720	C	Cr_2O_3	54.70
37	1400-1550	Fe-C	Cr^{3+}	52.00
"	"	"	Cr^{2+}	80.00
40	1500-1680	Fe-C	Cr_2O_3	46.00
Present study	1400-1550	Fe-C	Cr^{3+}	54.16
	"	"	Cr^{2+}	27.15
	"	"	Cr_2O_3	81.33

MTS = Mass transport in slag ICR = Interfacial chemical Reaction

by Anyakwo[37], though an integration method for the determination of rate constants was used in his case and the reduction of (Cr^{3+}) and (Cr^{2+}) were separated in the kinetic analysis of the system.

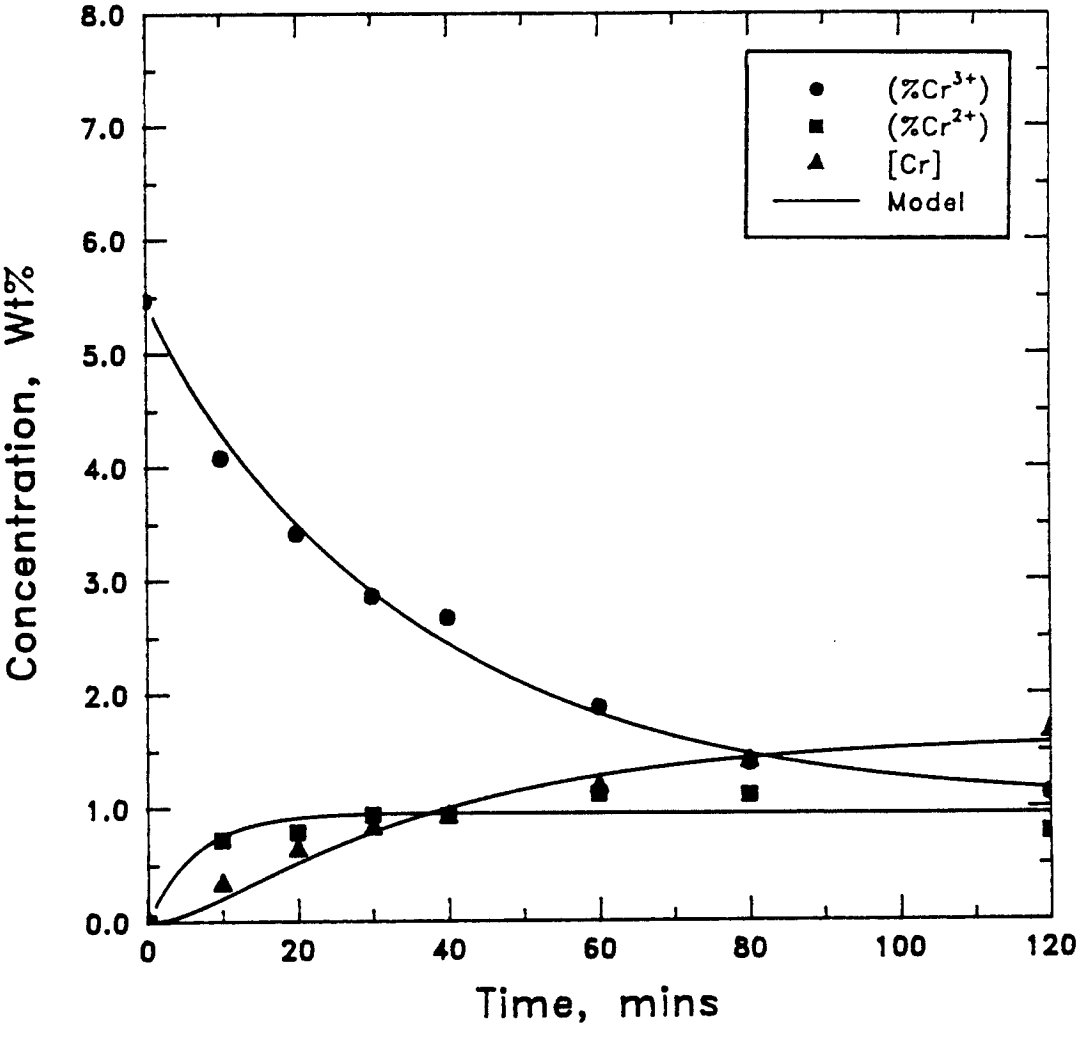
Typically the activation energy for rate limitation by mass transport in the slag may vary from 65 to 100 kcal/mol[31]. The activation energy for rate limitation by an interfacial chemical reaction may vary from a few kilocalories per mole to several hundred kilocalories per mole, depending on the complexity of the interfacial reaction. While activation energies may not distinguish definitely between mass transport control and chemical reaction control, they will identify the phase in which the rate-limiting mechanism occurs for mass transport rate-limitation[31]. King[27] stated that the activation energies for the reactions which are transport controlled by diffusion in liquid metal are between 5 and 30 kcal/mol and presumably between 30 and 70 kcal/mol if diffusion in slags is the rate-controlling process.

The 54.16 kcal/mol activation energy obtained for (Cr^{3+}) reduction is consistent with mass transport control in the slag phase. This is in accord with the results of Robison and Pehlke[31] who found the rate of (Cr^{3+}) reduction to increase with increase in stirring rate of the melt, indicating a mass transport limitation of

(Cr^{3+}) in the slag phase. The low value of the activation energy of (Cr^{2+}) reduction obtained indicates that its reduction is not limited by mass transport in the slag phase but probably by an interfacial chemical reaction at the slag/metal interface. Robison and Pehlke[31] also found the reduction of (Cr^{2+}) to be controlled by an interfacial chemical reaction. They observed an increase in stirring rate to have no effect on the rate of (Cr^{2+}) reduction an indication that its reduction was not controlled by mass transport in the slag phase.

5.3 Effect of melt geometry.

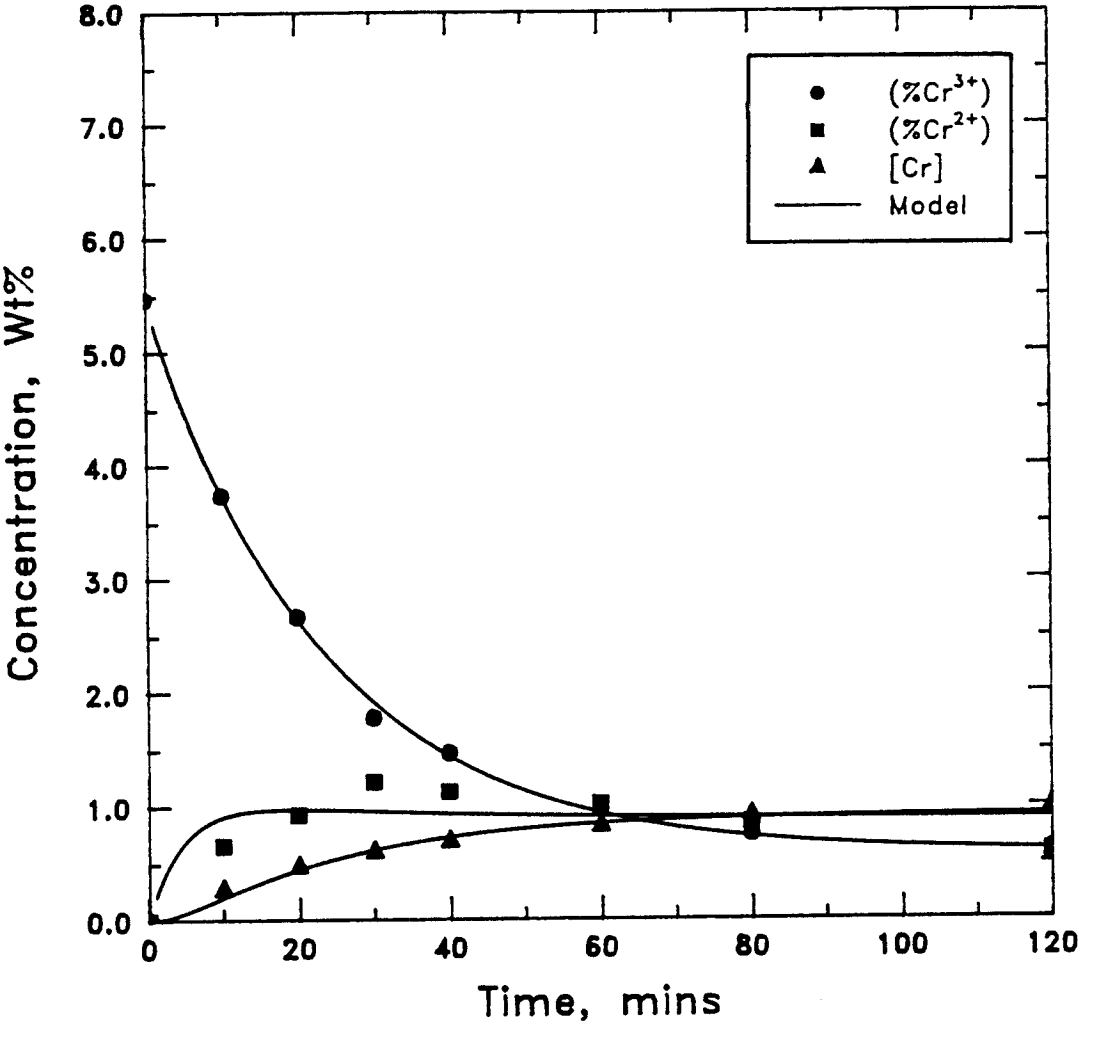
The results of Anyakwo[37] are used to discuss the effect of melt geometry since he used conditions similar to those in this study except for the experimental temperature of 1500°C as opposed to 1470°C in this study. The experimetal variables for this investigation are summarised in Table 5.5. Run CRS25 was used as the reference run. The calculated concentration-time curves for runs CRS24, CRS25 and CRS26 are shown in Figs. 5.10, 5.11 and 5.12, respectively



$k_1 = 0.0478\ cm.min^{-1}.\ k_2 = 0.0318\ cm.min^{-1}.$
$k_3 = 0.1307\ cm.min^{-1}.\ k_4 = 0.0365\ cm.min^{-1}.$

Sums of squares of deviations are:
$Cr^{3+} = 0.120,\ Cr^{2+} = 0.101,\ Cr_{Met.} = 0.056.$

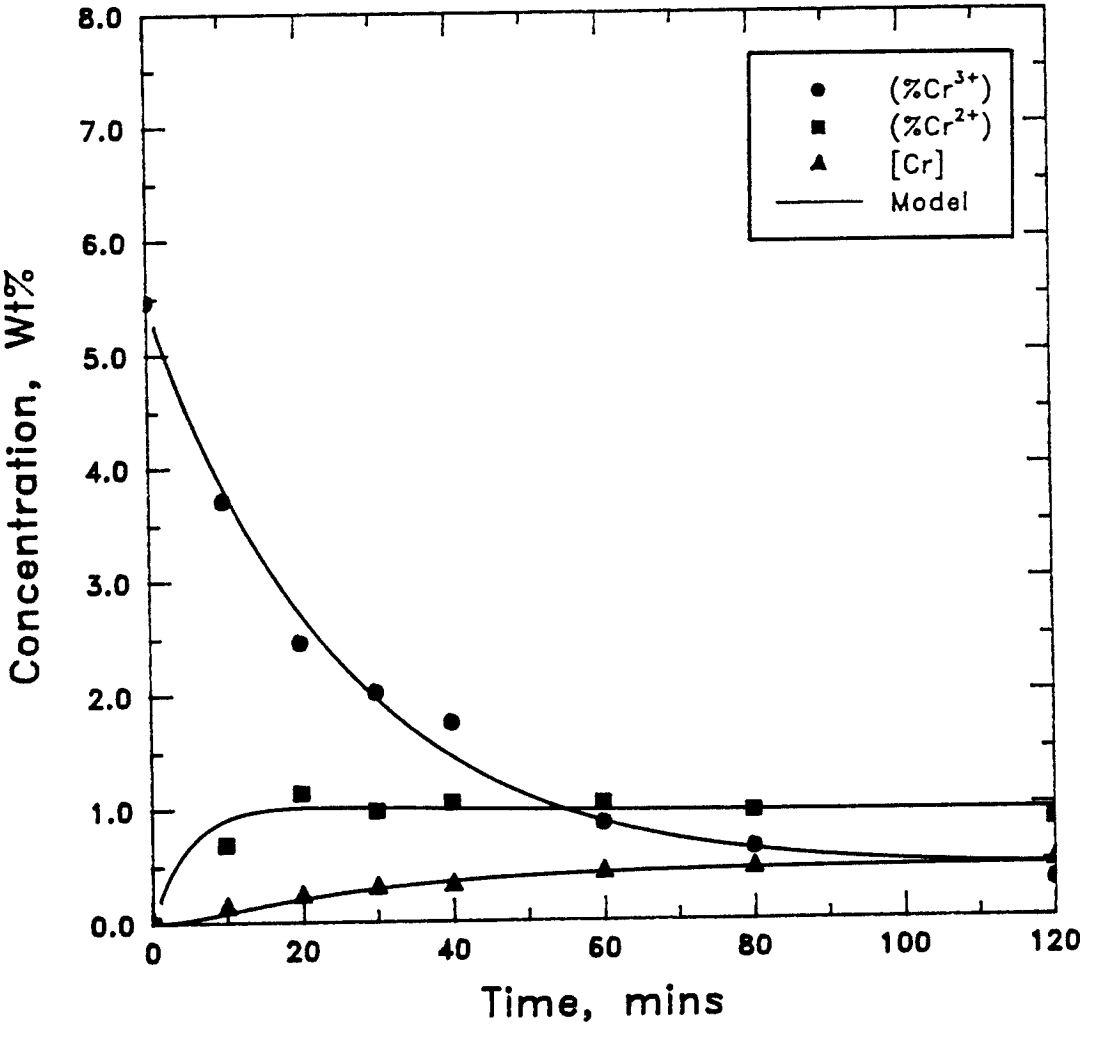
Fig. 5.10 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run CRS24, Ref (37).



$k_1 = 0.0373\ cm.min^{-1}$. $k_2 = 0.0245\ cm.min^{-1}$.
$k_3 = 0.1330\ cm.min^{-1}$. $k_4 = 0.0298\ cm.min^{-1}$.

Sums of squares of deviations are:
$Cr^{3+} = 0.023$, $Cr^{2+} = 0.281$, $Cr_{Met.} = 0.013$.

Fig. 5.11 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run CRS25, Ref (37).



$k_1 = 0.0339\ cm.min^{-1}$. $k_2 = 0.0154\ cm.min^{-1}$.
$k_3 = 0.1233\ cm.min^{-1}$. $k_4 = 0.0289\ cm.min^{-1}$.

Sums of squares of deviations are:
$Cr^{3+} = 0.189$, $Cr^{2+} = 0.089$, $Cr_{Met.} = 0.004$.

Fig. 5.12 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run CRS26, Ref (37).

Table 5.5: Effect of melt geometry[37].

Run No.	Initial ($wt\%Cr_2O_3$)	Metal wt. (g)	Slag wt. (g)
CRS24	8	80	40
CRS25	8	80	20
CRS26	8	160	20

The rate constants obtained from these runs using scheme 4 are shown in Table 5.6. From the table it can be seen that increasing the slag volume slightly increases the value of k_1 while increasing the volume of the metal bath has no effect on k_1. This shows that the rate-limiting process for (Cr^{3+}) reduction is associated with the slag phase and not the metal phase. The slight increase in k_1 is in good accord with the finding that changes in slag height has a slight effect on the reduction rate of the chromium species. The rate constant, k_3, does

Table 5.6: Effect of melt geometry on rate constants.

Run No.	k_1	k_2	k_3	k_4
		$cm.min^{-1}$		
CRS24	0.0478	0.0318	0.1307	0.0365
CRS25	0.0373	0.0245	0.1330	0.0298
CRS26	0.0339	0.0154	0.1233	0.0289

not change with increase in slag volume, showing that the reduction of (Cr^{2+}) is not dependent on stirring rate of the slag phase. Doubling the volume of the metal bath does not markedly change the value of k_3 either. These results show that the reduction of (Cr^{2+}) is not limited by mass transport in either the slag or metal phase, but by an interfacial chemical reaction.

If the reaction rate is limited by an interfacial chemical reaction, stirring will not alter the reaction rate as long as the effective reactive surface area is not changed. The interfacial surface area would not be altered in this study since there was no form of mechanical stirring employed, hence the nearly constant values of k_3 obtained for changes in slag and metal volume.

5.4 Effect of surface-active elements: sulphur, selenium and antimony.

In the investigation of heterogeneous kinetics at high temperature, one of the most interesting effects is that of strong adsorbed species retarding the rates of chemical reactions on surfaces. Surface-active elements are known to segregate on the reaction interface in heterogeneous systems, and hence retard the rate of

interfacial reactions. This is due to surface poisoning. It is thought that a segregation of a surface-active element to the interface could cause a reduction in the mass transfer coefficient. The influence of surface-active elements on the kinetics of oxide reduction from slags has been little studied for slag/metal systems. The object of this study was to investigate the effect strongly adsorbed species could have on the kinetics of reduction of Cr_2O_3 from slag. The surface-active elements used were sulphur and selenium. Sulphur was either added to the metal or to the slag, whereas selenium was only added to the metal. The results from these studies are discussed in the following paragraphs. The results from Anyakwo[37] on the effect of antimony addition to metal are also discussed.

5.4.1 Effect of Sulphur addition to the metal.

To investigate the effect of sulphur additions to the metal on the reduction of Cr_2O_3 from slag, runs AS11 and AS12 were carried out in which 0.05 and 0.10 wt% S were initially added to metal, respectively. The results from these runs are presented in Table 3.1. Fig. 5.13 shows concentration-time curves for (Cr^{3+}) and (Cr^{2+}) reduction from the above runs and that from a run where no sulphur was added to the metal (run AS5). It can be

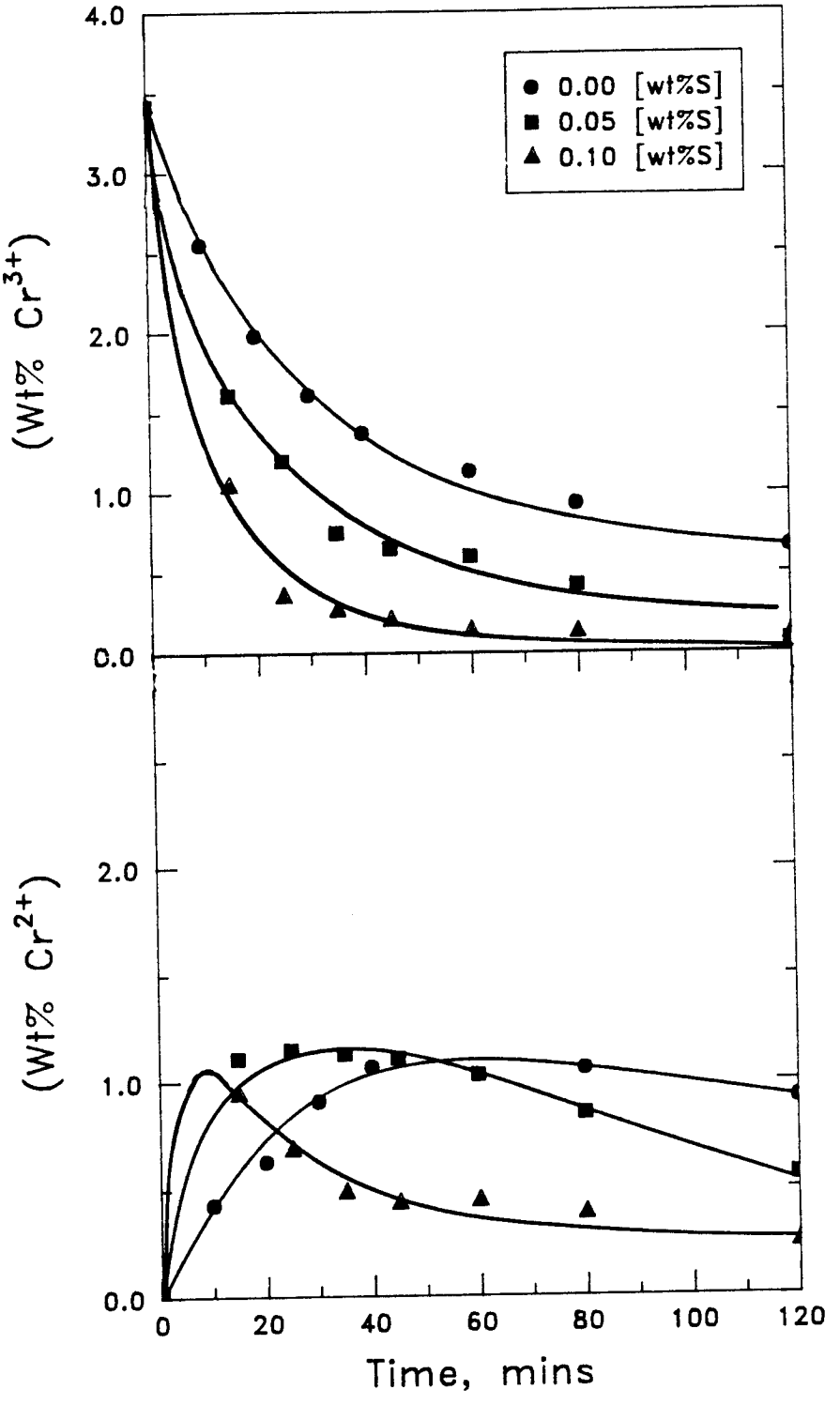


Fig. 5.13 Effect of sulphur addition to metal on (Cr^{3+}), and (Cr^{2+}) reduction.

seen from the figure that the reduction rate of (Cr^{3+}) increased as the metal sulphur content increased. The production rate of (Cr^{2+}) and its subsequent rate of reduction increased with an increase in the sulphur content of the metal. The sulphur content of the slag showed a gradual increase and remained more or less constant after about 60 minutes (Fig. 5.14). Most of the sulphur transfer to slag occurred during the initial stages of reduction. More sulphur was transfered to the slag in the run where 0.1 wt%S was added to the metal. High iron levels were recorded in the slag and they increased as the metal sulphur content increased (Fig. 5.15). Numerous metal droplets were found in the slag samples for these runs, as outlined in section 3.2. Outgrowths visible on most of the droplets suggested that the metal droplets were torn away from the metal bath.

The increase in the rate of reduction of Cr_2O_3 from slag when sulphur is added to the metal could be due to the following: Sulphur strongly decreases the surface tension of liquid iron to such an extent that the slag wets the sulphur containing iron. A small amount of mechanical work (CO bubbling) is sufficient to cause emulsification of the metal by surface break up, resulting in small metal particles moving into the slag phase. An enormous contact area between slag and metal is thus created for the reduction reactions to take

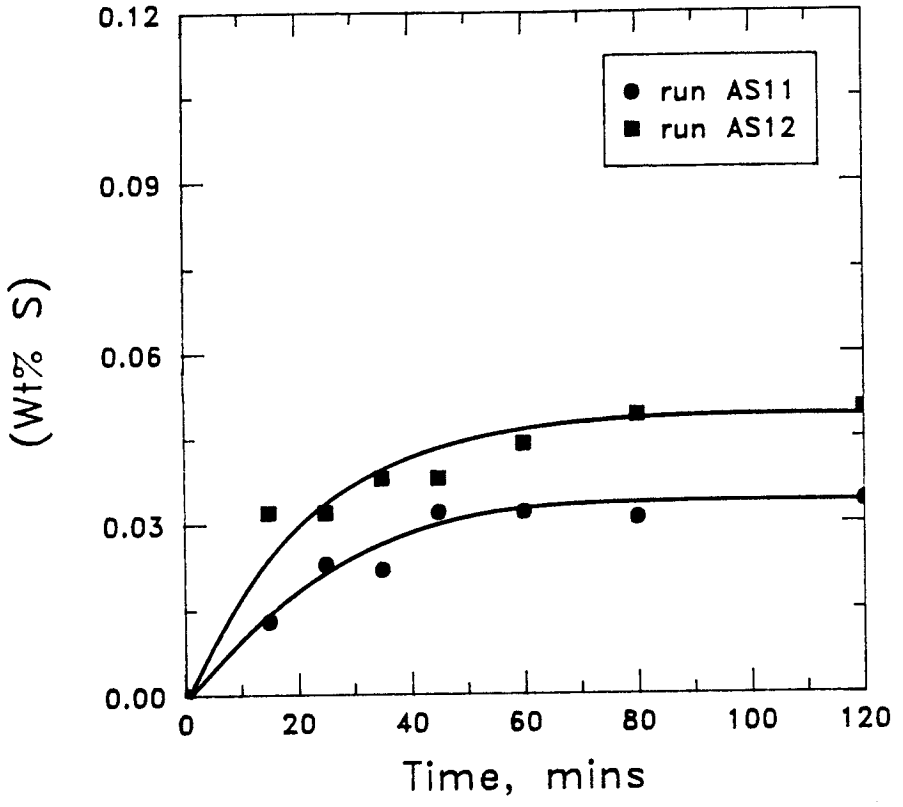


Fig. 5.14 Variation of sulphur in slag for 0.05 (run AS11) and 0.10 [wt%S] (run AS12) addition to metal.

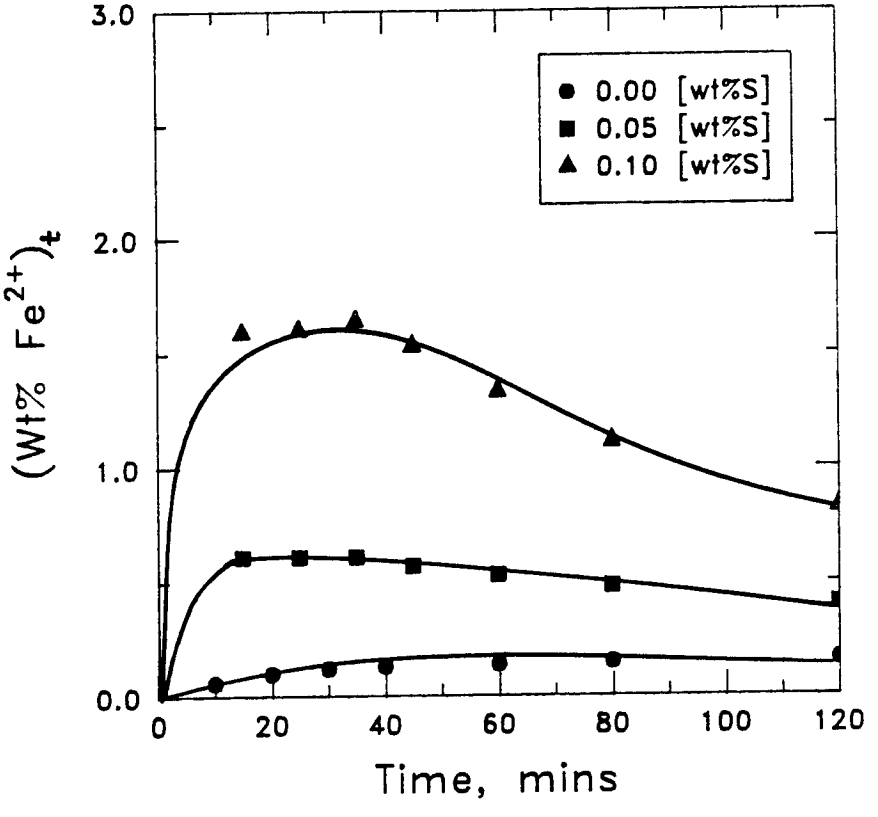


Fig. 5.15 Effect of sulphur addition to metal on Fe_t^{2+} content in slag.

place, leading to an increase in the rate of Cr_2O_3 reduction. This phenomenon varied with the amount of sulphur in the metal, the decrease in interfacial tension and the extent of emulsification increasing with increase in the sulphur content of the metal up to 0.1 wt% S. The numerous small metal droplets, because of their high surface area, quickly lose most of their carbon in the reaction with Cr_2O_3 in slag and because of their high residence time, the exposed iron then reacts with Cr_2O_3 by the reaction

$$(Cr_2O_3) + 3[Fe] = 2[Cr] + 3(FeO) \qquad (5.1)$$

This reaction takes place simultaneously with that due to carbon oxidation

$$(Cr_2O_3) + 3[C] = 2[Cr] + 3CO(g) \qquad (5.2)$$

The following reaction could also take place under these conditions

$$2(Cr^{3+}) + 3(S^{2-}) = 2[Cr] + 3[S] \qquad (5.3)$$

Reactions (5.1), (5.2) and (5.3) can be split up into two reactions to include the intermediate, (Cr^{2+}). These reactions are assumed to be taking place simultaneously, leading to increased rates of Cr_2O_3 reduction.

Reaction (5.4) is delayed probably because the presence

$$(FeO) + [C] = [Fe] + CO(g) \qquad (5.4)$$

of large quantities of small metal droplets provide a more favourable condition for reaction (5.1) to proceed faster and concurrently with reaction (5.2). This situation may probably be responsible for the accumulation of Fe in slag. At longer times, more than 60 minutes, the (Cr^{3+}) and (Cr^{2+}) concentration-time curves level off showing a decrease in the rates of reduction reactions. This may be due to a reduction in the oxygen potential of the system and thus a more quiescent metal bath. Emulsification then is destroyed and the reactions take place only at the slag/metal interface and only carbon is involved in the reactions.

There are two possibilities which may account for the accumulation of Fe in the slag: that due to transfer from the metal bath as FeS during mass transfer in the initial stages of reduction and that due to direct reduction of Cr_2O_3 in the slag by equation (5.1). To clarify this point, graphs showing the variation of Fe^{2+}, in form of (FeO) and that in form of (FeS) with time, were drawn for runs AS11 and AS12. The Fe^{2+} in form of (FeS) was determined from the sulphur content of the slag. These graphs are shown in Fig. 5.16. Examination of the figure shows that the bulk of the iron in slag is

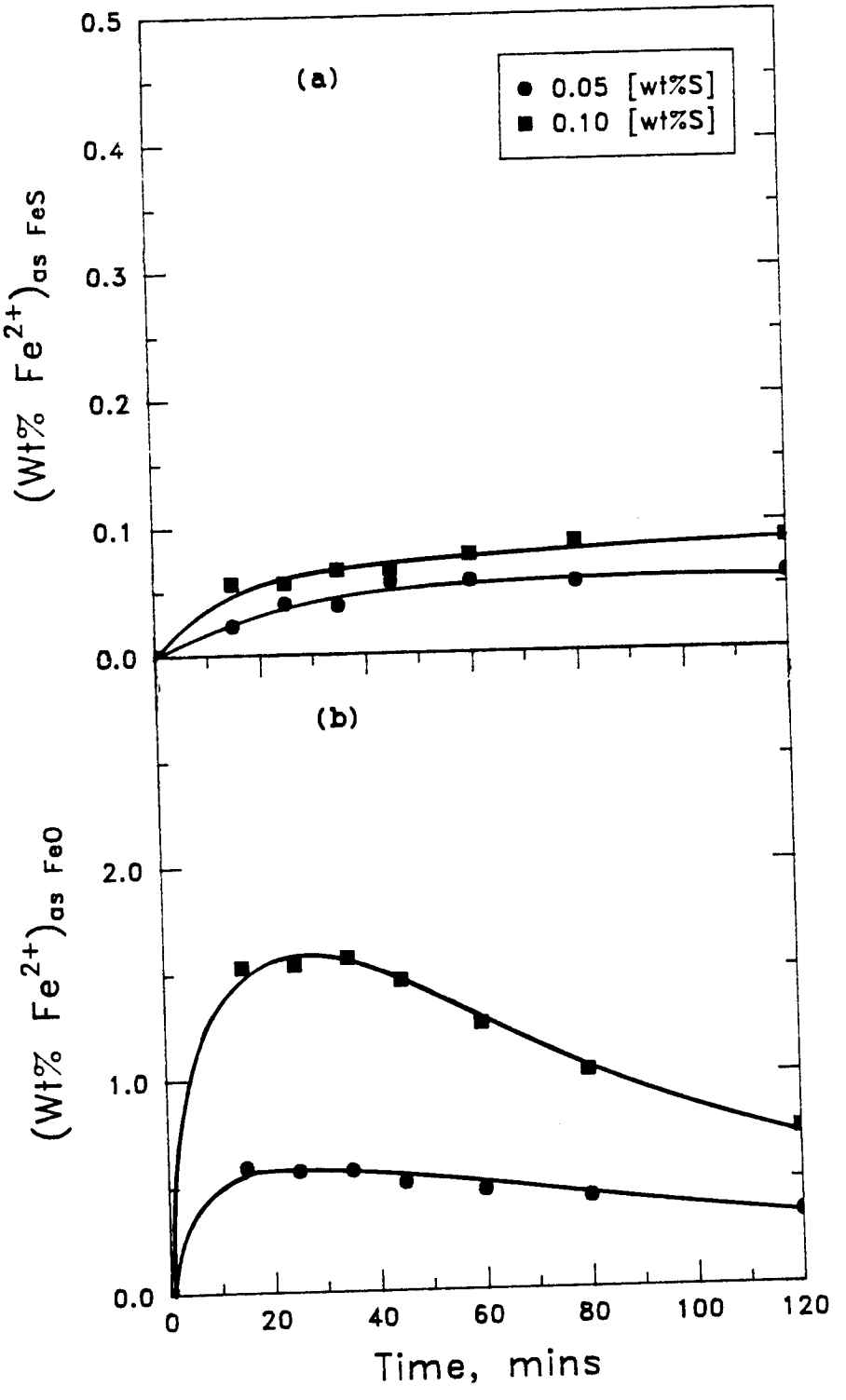


Fig. 5.16 Effect of sulphur addition to metal on Fe^{2+}, in form of FeS (a) and FeO (b) in slag.

in form of FeO. The shape of the curves shows that there is FeO accumulation in slag in the initial stages of reduction and decreases at longer times. The reduction of FeO levels at longer times could probably be due to a reduction in the extent of emulsification as a result of low oxygen potential which enables the reactions to take place at the slag/metal interface and only carbon is involved in the reduction reactions, as a result FeO reduction takes place concurrently with Cr_2O_3 reduction.

Assuming that Fe transfers to the slag as a result of sulphur transfer from the metal, then according to Ramachandran et al[63], metal desulphurisation, which has been shown to be a cathodic reduction process at the slag/metal interface, can be represented by the reaction

$$[S] + 2\,e^- = (S^{2-}) \qquad (5.5)$$

To preserve neutrality in the system used, either negative ions such as O^{2-} must be discharged at the interface, resulting in CO evolution as

$$[C] + (O^{2-}) = CO(g) + 2\,e^- \qquad (5.6)$$

or electropositive atoms such as Fe must transfer to the slag as

$$[Fe] = (Fe^{2+}) + 2\,e^- \qquad (5.7)$$

giving the overall molar solute transfer equivalent of

$$2n_S = 2n_{Fe} + 2n_C \qquad (5.8)$$

and the overall sulphur transfer equation is

$$[S] + (O^{2-}) = (S^{2-}) + [O] \qquad (5.9)$$

The Fe transfered to the slag due to this process in these runs is not adequate to account for the increased levels as can be seen from Fig. 5.16. The only explanation, therefore, for the increase in Fe levels in the slag with sulphur addition to metal is that due to equation (5.1). Reactions (5.3) and (5.9) represent the sulphur cycle. Reaction (5.3) is responsible for the non-accumulation of sulphur in the slag as a result of reaction (5.9). It is assumed that reaction (5.3) is very fast with respect to reaction (5.9). It follows, therefore, that desulphurisation could take place after reaction (5.3) has gone to completion.

The postulation for the increase in the reduction rate of Cr_2O_3 presented in the preceeding paragraphs is supported by the work of Kozakevitch et al[64] who observed metal emulsification to take place during the desulphurisation reaction. They explained this phenomenon by saying that a large decrease in the interfacial tension causes the

metal layer to separate into spherical drops which segregate in the slag. Gaye and Riboud[65], in their study of various alloy-slag systems, observed the rate of decarburisation of Fe-C-S alloy droplets in calcium aluminosilicate melts containing iron oxide to be affected in two opposing ways: the presence of sulphur lowers the specific rate of interfacial reaction, but on the other hand, also accelerates the global kinetics by enhancing metal emulsification. They concluded that a result specific to slag/metal emulsion is that the enhanced tendency for emulsification of the metal due to sulphur or any surface-active element, creating an increase in interfacial area, can counterbalance the decrease in specific reaction rate. This explained the high initial decarburisation rates they observed with the alloy initially containing 0.064 wt%S.

To substantiate the postulation presented above, two runs, AS18 and AS19, were carried out using the same conditions but with no sulphur in the metal and 0.10 wt%S initial metal content, respectively. After 25 minutes the runs were terminated by withdrawing the crucible from the hot zone and quenching the contents by passing argon through the reaction tube. The slag was then crushed and metal droplets collected by magnetic separation and weighed. The results from these runs are shown in Table 3.1. Table 5.7 shows the weights of the

metal droplets collected from each run.

Table 5.7: Metallic iron droplets recovered from slag

Run No.	[wt% S]	Weight of metal droplets recovered (g)
AS 18	0.00	0.03
AS 19	0.10	0.36

The metal droplets varied in size from less than 0.1 mm to about 2 mm. The droplets from run AS19 are shown in plate 3.3 of section 3.2.

The table above shows that the weight of the metal droplets recovered from the slag was higher in the run where sulphur was added to the metal. The increase in metal droplets in run AS19 is due to metal emulsification in the slag. This is in accord with the earlier postulation that metal emulsification, which is a result of the lowering of the interfacial tension, increases the metal droplets in the slag which, because of their high surface area and residence time, leads to an increase in the rate of Cr_2O_3 reduction. Comparison of the results for (Cr^{3+}) reduction between runs AS18 and AS19 (Table 3.1) shows that the reduction in run AS19 is higher because of the low value of (Cr^{3+}) realised after 25 minutes.

Anyakwo[37], in his investigation of the effect of sulphur addition to metal on the reduction rate of Cr_2O_3 obtained similar results. The increase in the reduction rates of Cr_2O_3 was attributed to metal emulsification.

5.4.2 Effect of high sulphur additions to metal.

To investigate whether additions of sulphur to the metal above 0.10 wt% would further increase the rate of Cr_2O_3 reduction, runs AS13 and AS14 were carried out in which 0.30 and 0.50 wt% S were added to the metal, respectively. The results for (Cr^{3+}) and (Cr^{2+}) reduction are shown in Fig. 5.17 together with the results from runs AS11 and AS12. The figure shows that the concentrations of (Cr^{3+}) and (Cr^{2+}) for run AS13 and AS14 are similar to those of run AS12 in which 0.10 wt%S was added to the metal. This clearly shows that increasing the sulphur content of the metal above 0.10 wt% does not increase the rate of Cr_2O_3 reduction any further.

Since the increase in the reduction rate with sulphur addition to the metal is a result of metal emulsification, which is a consequence of the lowering of interfacial tension, the results above show that there may not be any marked reduction in the interfacial

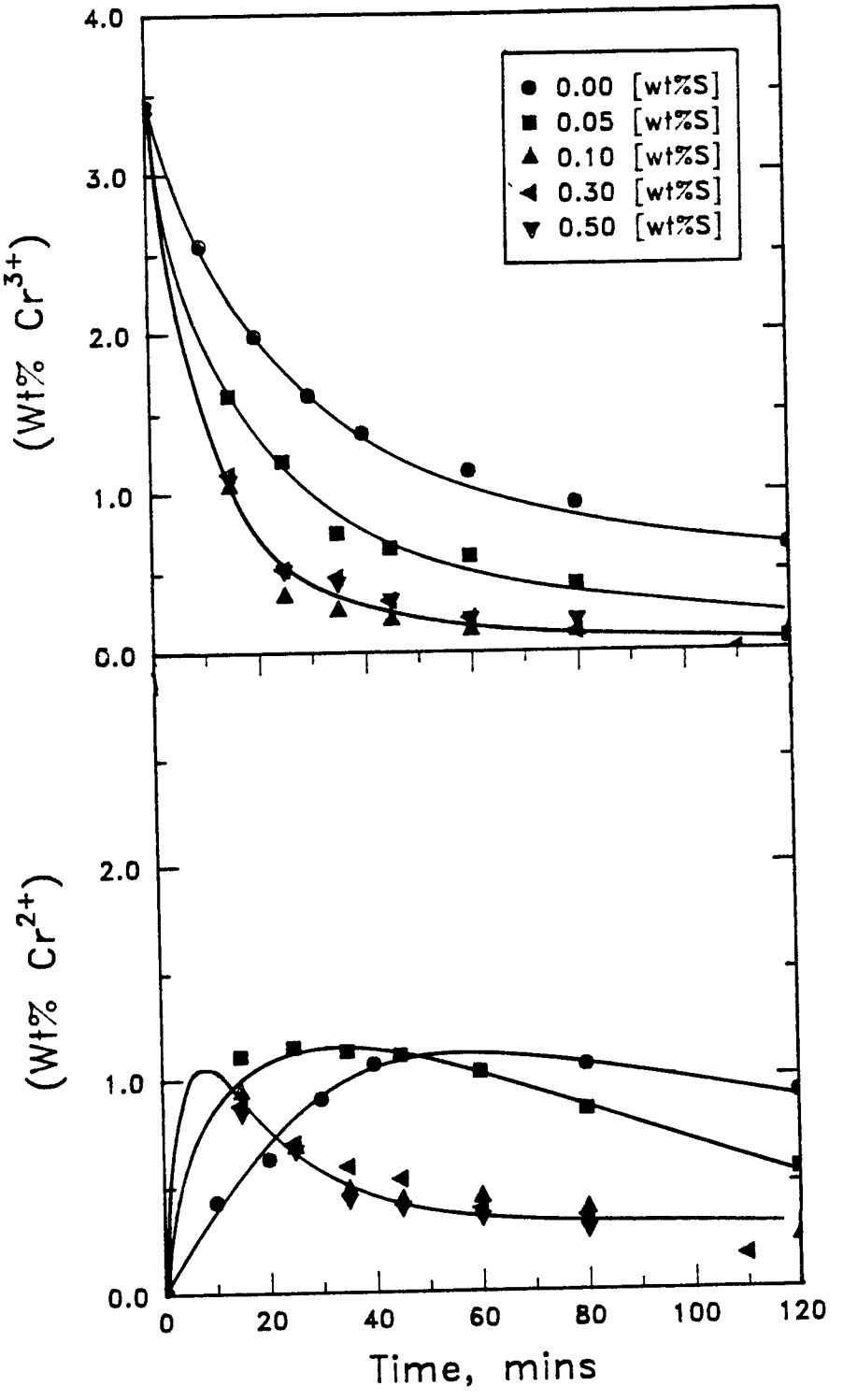


Fig. 5.17 Effect of high sulphur additions to metal on (Cr^{3+}) and (Cr^{2+}) reduction.

tension at metal sulphur contents higher than 0.10 wt%. The result is having rates of Cr_2O_3 reduction similar to those for the case where 0.10 wt% S was added to the metal as depicted in Fig. 5.17. This interpretation is supported by the work of Kozakevitch et al[66] who studied the depression of surface tensions of iron-carbon alloys by sulphur. Their results are shown in Fig. 5.18 for Fe-4wt%C-S alloys at 1450°C. These alloys are similar to those used in this study. The figure shows that the depression of surface tension for this alloy is highest up to about 0.10 wt% S in the metal. Above this, the depression in surface tension is minimal and shows no marked change. Therefore, it can be assumed that addition of sulphur to the metal at concentrations higher than 0.10 wt% would not have a marked increase in the depression of the surface tension of the alloy. As the extent of metal emulsification would not markedly change either, the rate of Cr_2O_3 reduction would not be expected to increase. This is in accord with the findings from this study and explains why no increase in the rate of reduction was recorded at higher than 0.10 wt% S in the metal.

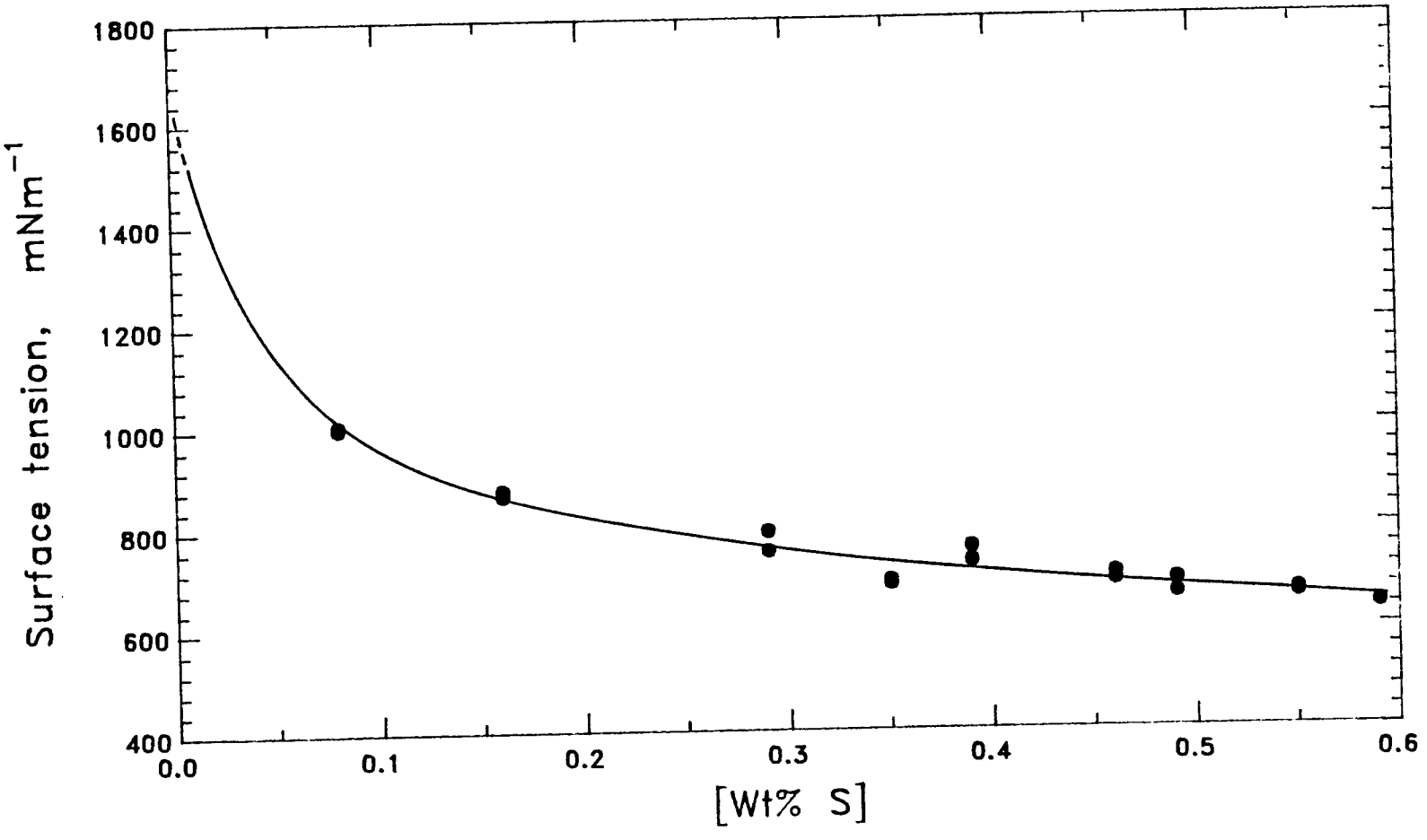


Fig. 5.18 Surface tension-[wt% S] curve for Fe-4wt%C-S alloys at 1450°C (after Kozakevitch et al(66)).

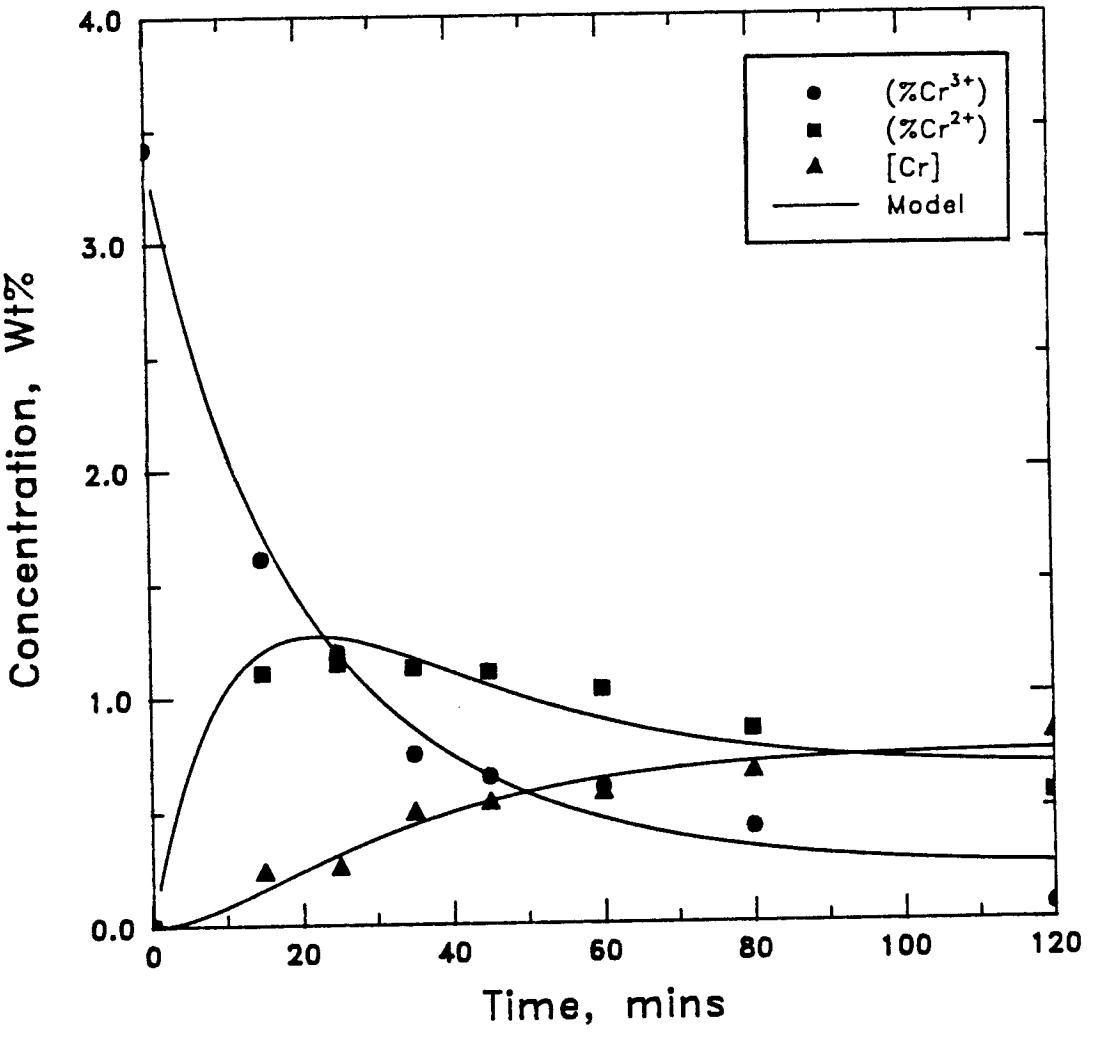
5.4.3 First-order, consecutive, reversible two-stage reaction curves for runs AS11, AS12, AS13 and AS14.

The calculated concentration-time curves of the chromium species for runs AS11, AS12, AS13 and AS14, using scheme 4, are shown in Figs. 5.19 through 5.22, respectively. The observed experimental values for these runs are also shown. The rate constants obtained for these runs are shown in Table 5.8.

Table 5.8: Variation of rate constants with metal sulphur content.

Wt% [S]	k_1	k_2	k_3	k_4
	$cm.min^{-1}$			
0.00	0.0248	0.0191	0.0434	0.0233
0.05	0.0460	0.0158	0.0386	0.0103
0.10	0.0869	0.0235	0.1127	0.0136
0.30	0.0800	0.0317	0.0965	0.0104
0.50	0.0941	0.0318	0.1033	0.0093

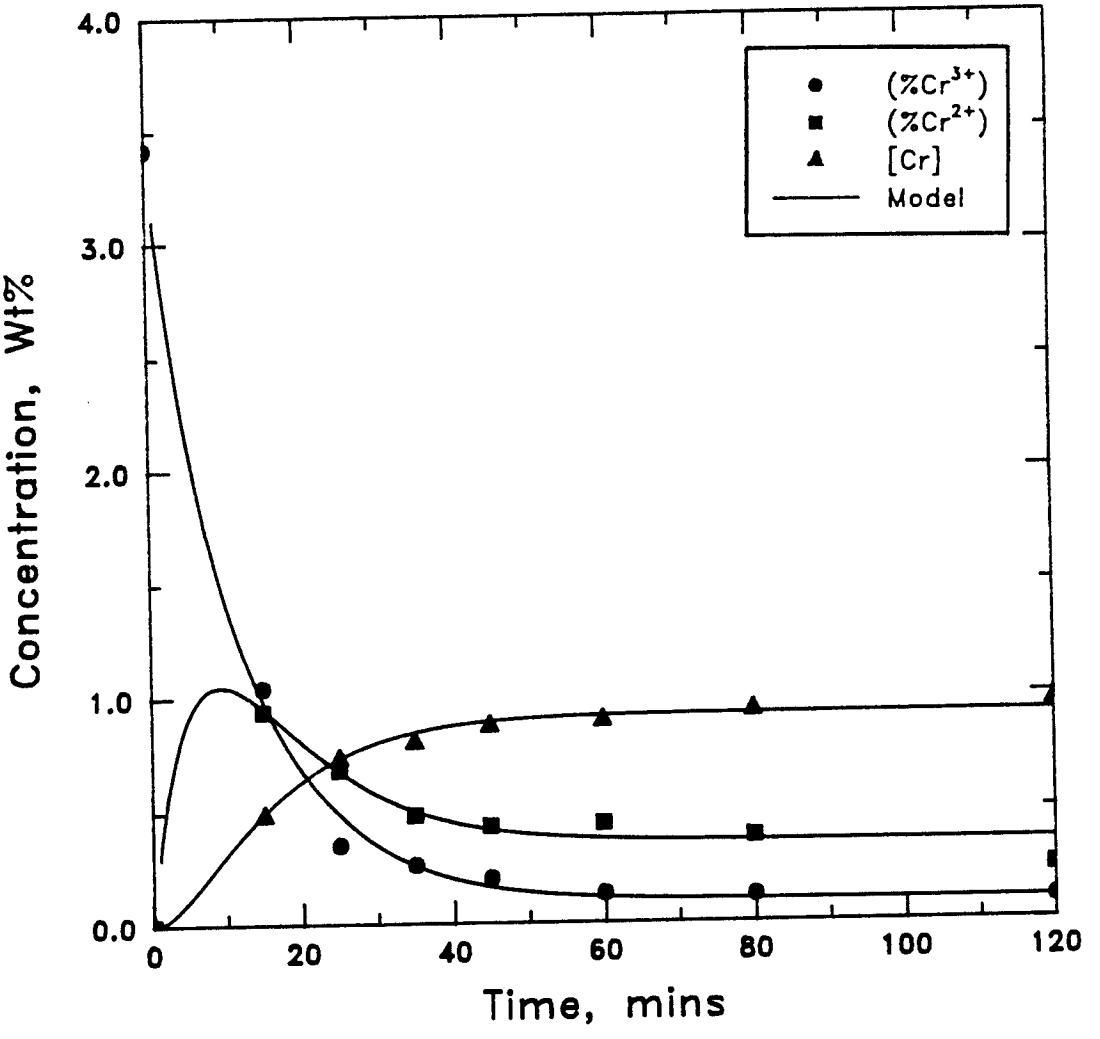
Fig 5.23 shows a plot of the effect of sulphur additions to metal on the forward rate constants k_1 and k_3. The figure shows that k_1 increases with metal sulphur content reaching a maximum at 0.1 wt% after which it remains nearly constant, within the bounds of experimental error. Similarly, k_3 increases up to a metal sulphur content of



$k_1 = 0.0460\ cm.min^{-1}$. $k_2 = 0.0158\ cm.min^{-1}$.
$k_3 = 0.0386\ cm.min^{-1}$. $k_4 = 0.0103\ cm.min^{-1}$.

Sums of squares of deviations are:
$Cr^{3+} = 0.085$, $Cr^{2+} = 0.071$, $Cr_{Met.} = 0.024$.

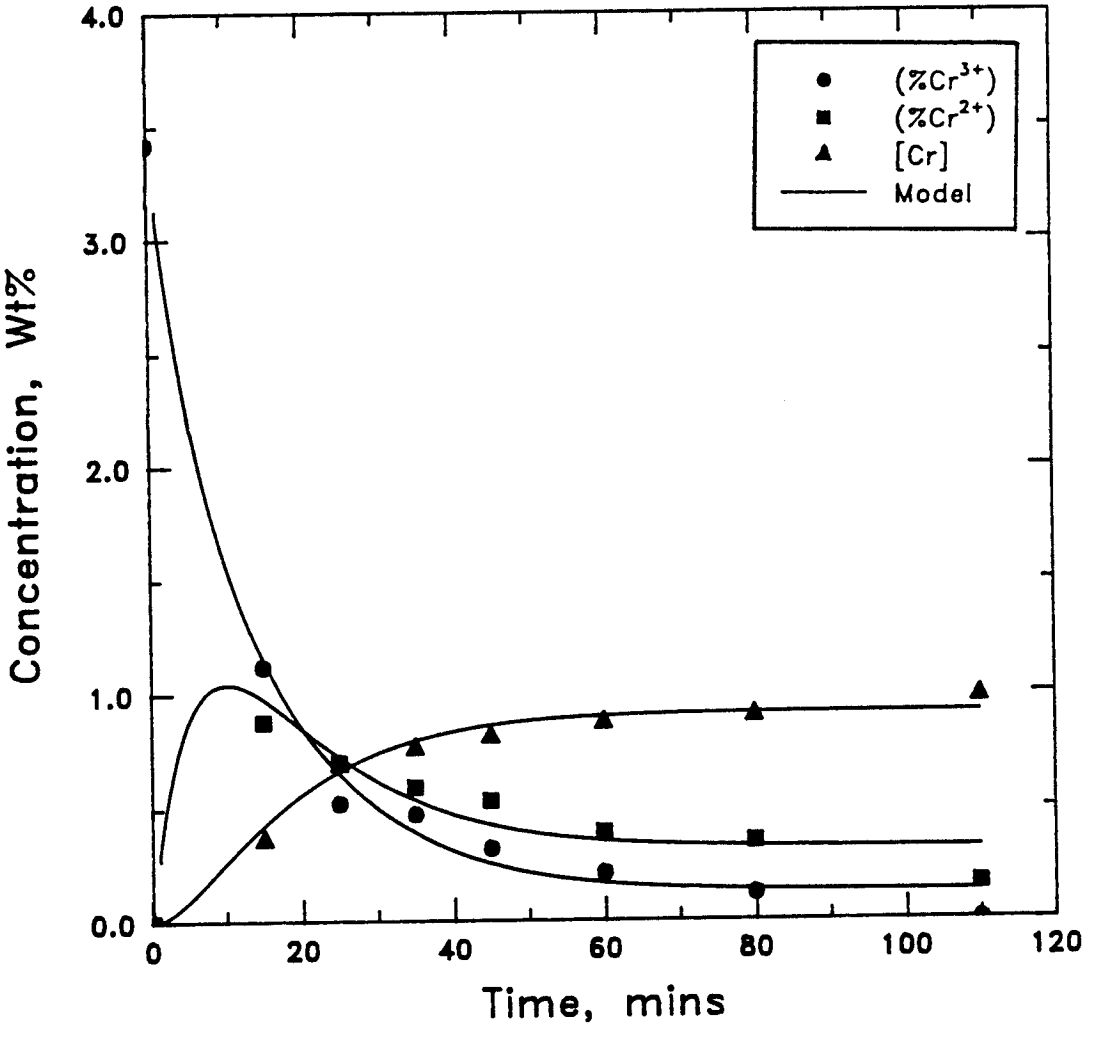
Fig. 5.19 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run AS11.



k_1 = 0.0869 cm.min^{-1}. k_2 = 0.0235 cm.min^{-1}.
k_3 = 0.1127 cm.min^{-1}. k_4 = 0.0136 cm.min^{-1}.

Sums of squares of deviations are:
Cr^{3+} = 0.024, Cr^{2+} = 0.019, $Cr_{Met.}$ = 0.005.

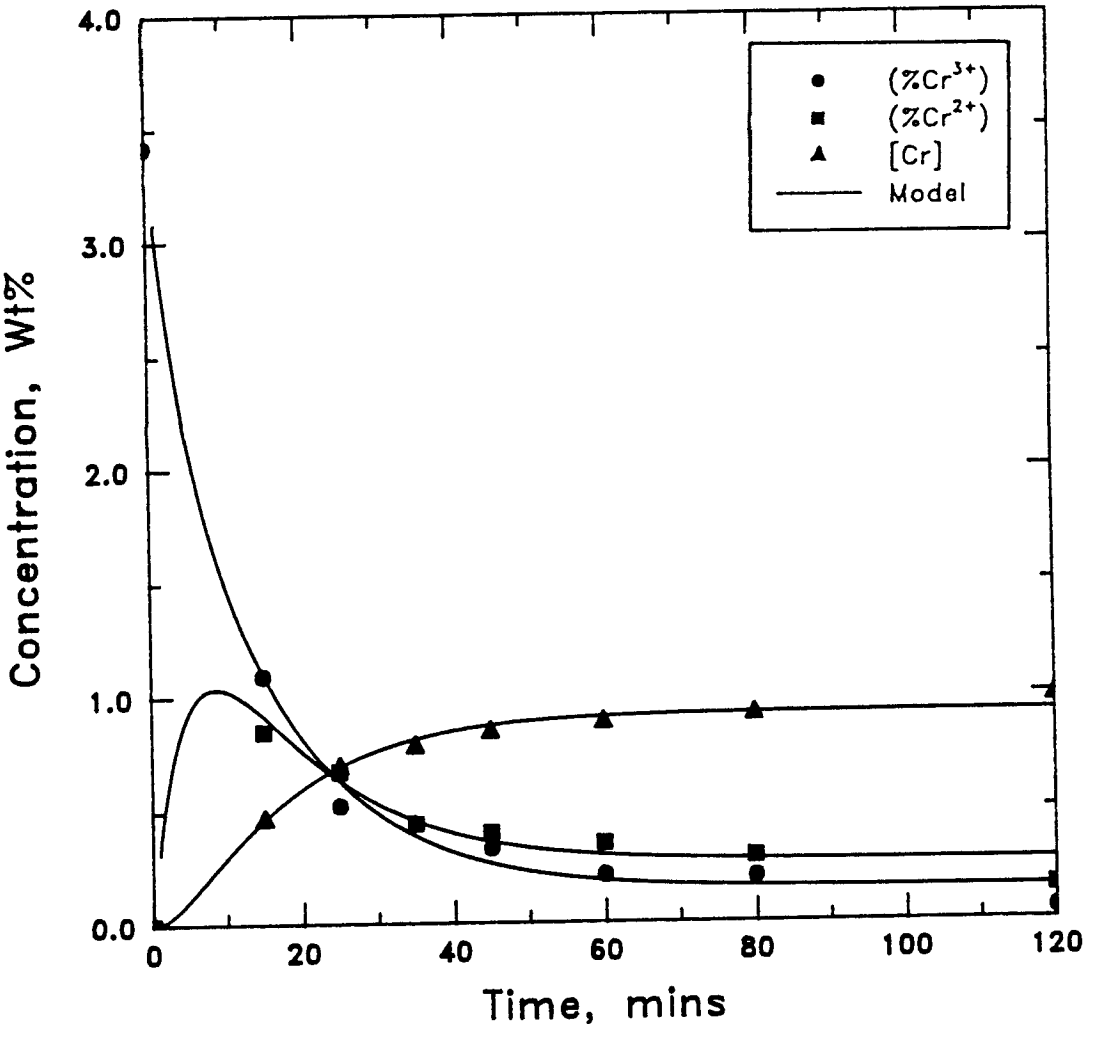
Fig. 5.20 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run AS12.



k_1 = 0.0800 $cm.min^{-1}$. k_2 = 0.0317 $cm.min^{-1}$.
k_3 = 0.0965 $cm.min^{-1}$. k_4 = 0.0104 $cm.min^{-1}$.

Sums of squares of deviations are:
Cr^{3+} = 0.047, Cr^{2+} = 0.053, $Cr_{Met.}$ = 0.015.

Fig. 5.21 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run AS13.



$k_1 = 0.0941\ cm.min^{-1}.\ k_2 = 0.0318\ cm.min^{-1}.$
$k_3 = 0.1033\ cm.min^{-1}.\ k_4 = 0.0093\ cm.min^{-1}.$

Sums of squares of deviations are:
$Cr^{3+} = 0.032,\ Cr^{2+} = 0.025,\ Cr_{Met.} = 0.007.$

Fig. 5.22 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run AS14.

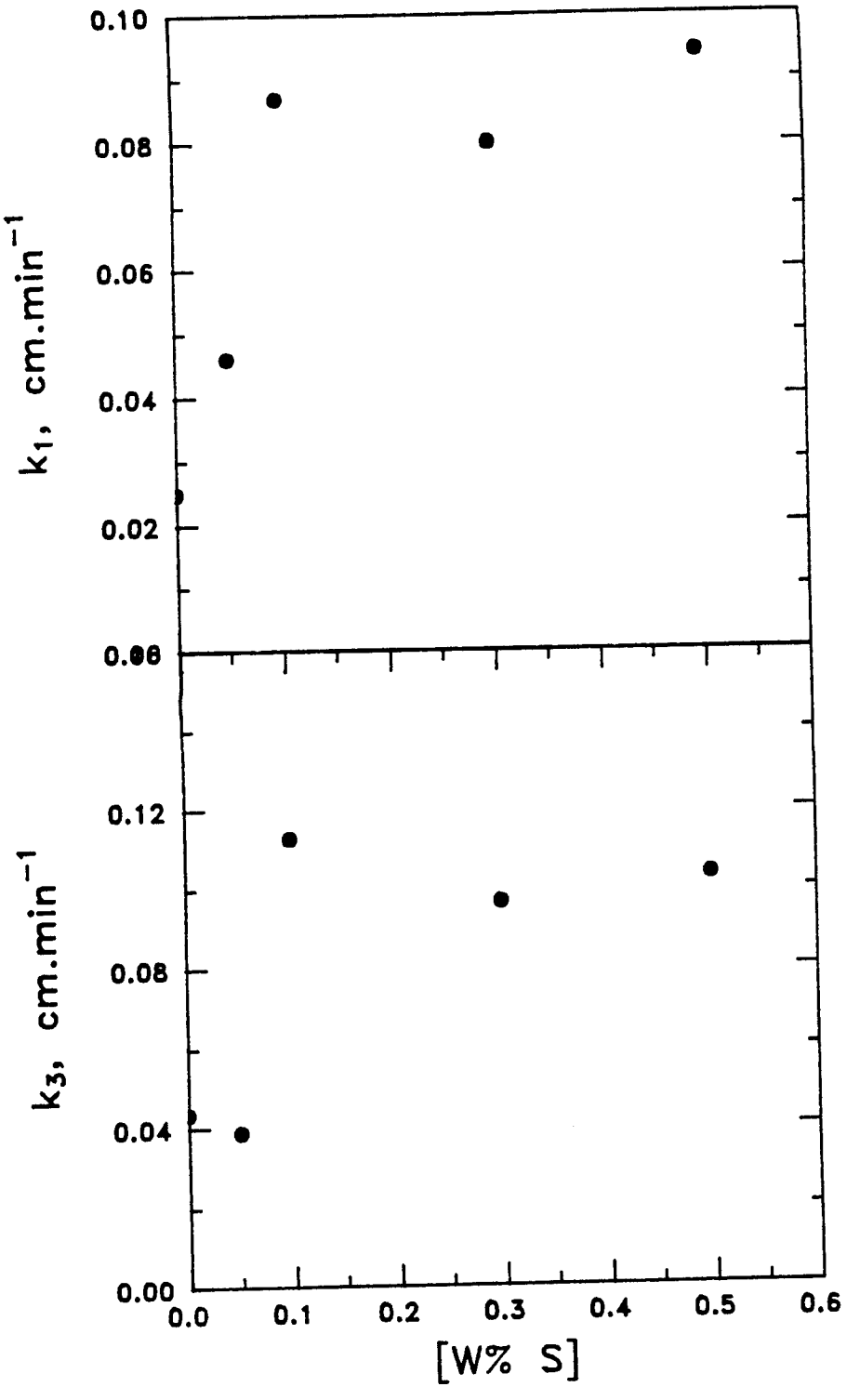


Fig. 5.23 Effect of Sulphur addition to metal on the forward rate constants k_1 and k_3.

0.10 and remains nearly constant at metal sulphur contents above this value. The behaviour of the rate constants above with metal sulphur additions of up to 0.50 wt% gives further evidence that additions of sulphur to metal above 0.10 wt% does not increase the rate of Cr_2O_3 reduction any further. The reason for this has already been highlighted in section 5.4.2.

Using the results of Kozakevitch et al[66] shown in Fig. 5.18, surface tension values for the sulphur levels used in this study were obtained and plotted against k_1 and k_3. The plots are shown in Fig. 5.24. The figure is a mirror image of Fig. 5.23 and shows the variation of the rate constants with alloy surface tension. The figure shows that high values of rate constants, k_1 and k_3, are obtained at low surface tensions, below about 1000 mNm^{-1}.

5.4.4 Effect of sulphur addition to slag.

To illustrate the effect of sulphur additions to slag on the rate of Cr_2O_3 reduction , the results from runs AS15 and AS16, in which 0.20 wt% S was added to the slag in form of CaS and FeS, respectively, are plotted in Fig. 5.25. The figure shows that the reduction rate of (Cr^{3+}) increases with sulphur addition to slag. The production rate of (Cr^{2+}) and its subsequent reduction also shows an

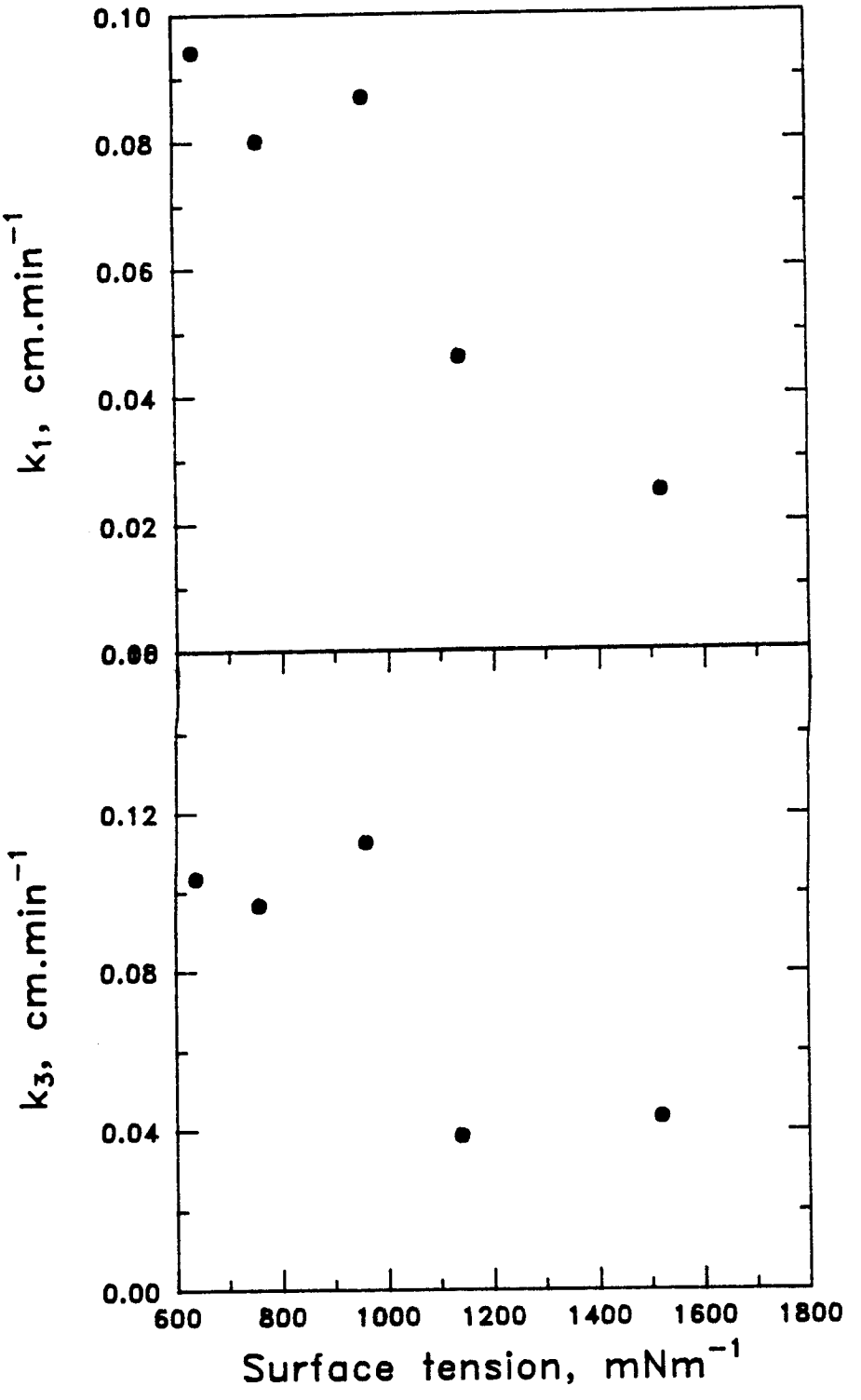


Fig. 5.24 Effect of Surface-tension on the forward rate constants k_1 and k_3.

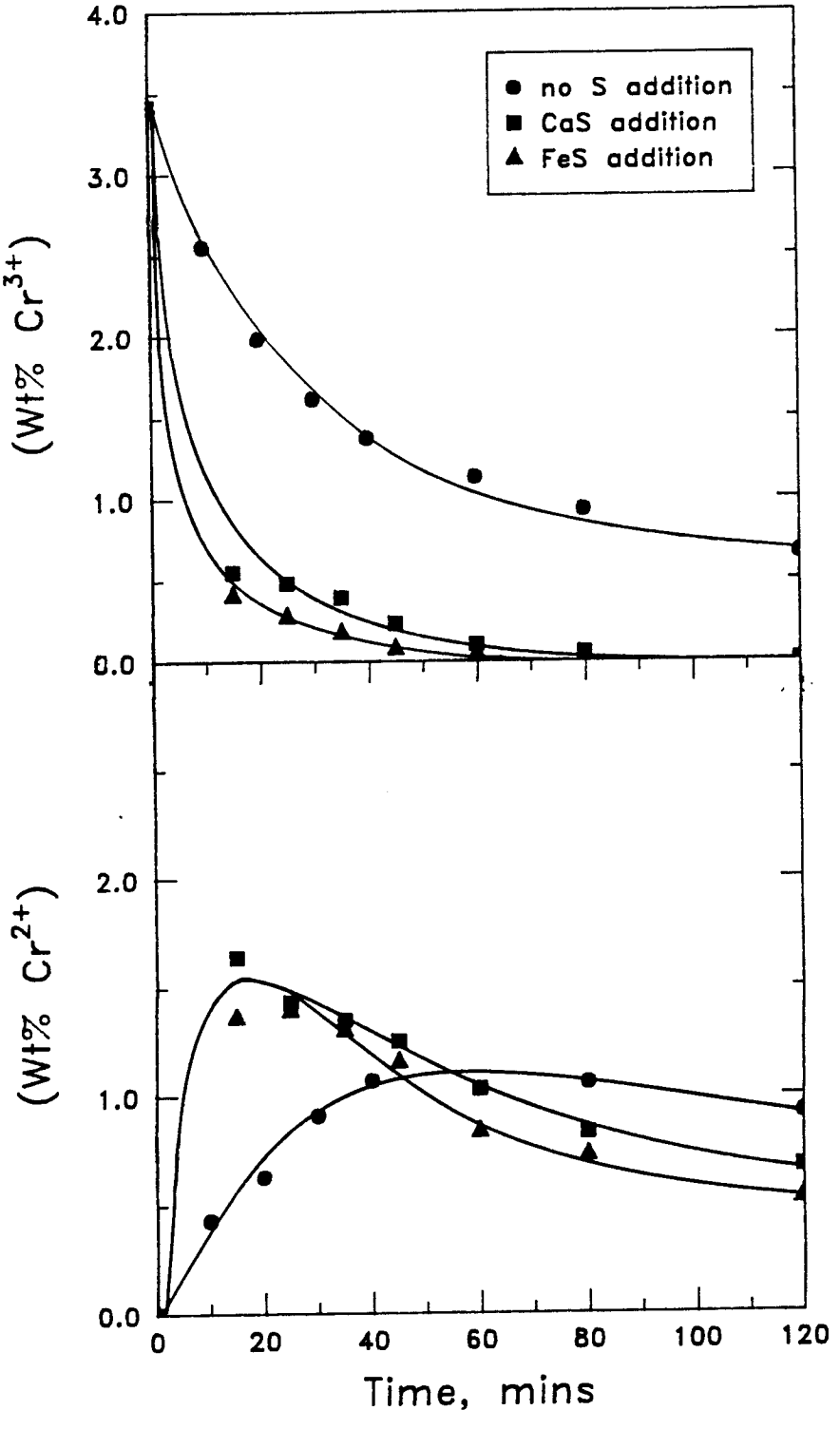


Fig. 5.25 Effect of Sulphur addition to slag on (Cr^{3+}) and (Cr^{2+}) reduction.

increase. However, the run where sulphur was added as FeS, run AS16, shows a slightly higher reduction rate for both chromium species than where it was added as CaS. This is probably due to the presence of Fe^{2+} ions in slag, in the case of run AS16, which react with Cr_2O_3, this reaction taking place concurrently with that due to carbon oxidation, resulting in increased rates of reduction of the chromium species. The higher FeO levels achieved in run AS16 (Fig. 5.26) is an indication that there was a reaction between Cr_2O_3 and Fe from FeS, with FeO as one of the products. In Fig. 5.26, the Fe in slag of run AS15 is assumed to be present as FeO. The reason for the increase in the reduction rate of Cr_2O_3 with sulphur addition to metal has already been outlined. The same effect is thought to be taking place in this case. The mass transfer across the interface which brings about the reduction in interfacial tension is the transfer of sulphur from the slag to metal. This is evidenced by the reduction in sulphur levels in slag with time, Fig. 5.27, and the final sulphur content in the metal which was 0.030 and 0.038 wt% for run AS15 and AS16, respectively. There was a drastic decrease in the sulphur content of the slag in both cases during the initial 20 minutes of the run. This corresponded with a high reduction and production rate of (Cr^{3+}) and (Cr^{2+}), respectively. The slag sulphur content remained nearly constant thereafter.

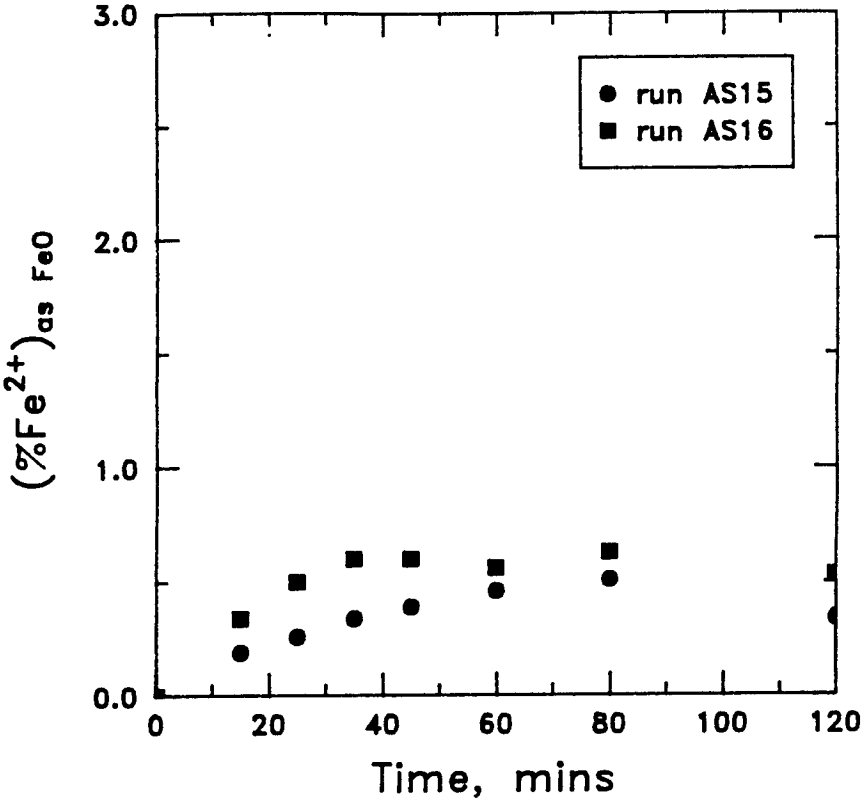


Fig. 5.26 Variation of FeO in slag for runs AS15 and AS16.

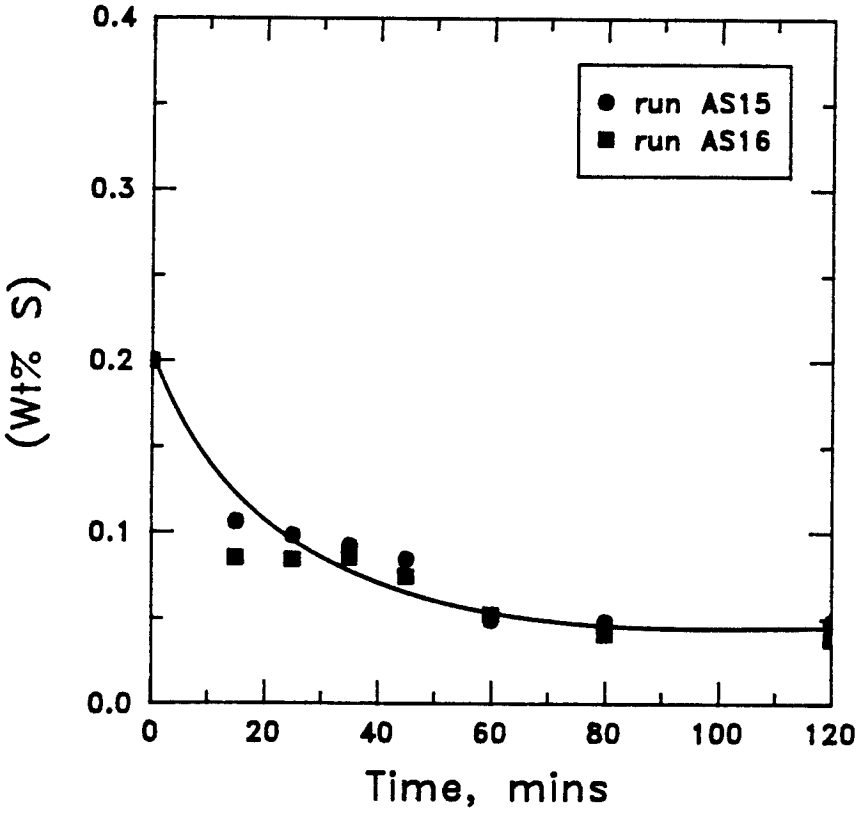


Fig. 5.27 Variation of Sulphur in slag for runs AS15 and AS16.

High iron levels in the slag were recorded in both runs as shown in Fig. 5.28, with run AS16 showing higher concentrations. The reason for the increase in Fe content of the slag has already been outlined in section 5.4.1. Fig. 5.29 shows a plot of total Fe, Fe^{2+} in form of FeS and FeO in slag as a function of time for run AS16. It is clear from the figure that by subtracting the Fe^{2+} occurring as FeS in slag from the total Fe^{2+}, the Fe^{2+} in form of FeO is still high.

Figs. 5.30 and 5.31 show concentration-time curves obtained for runs AS15 and AS16, respectively. Table 5.9 shows the rate constants obtained for these runs together with those of run AS5. The rate constant values show that there was a drastic increase in k_1 in both cases, an indication that probably reaction (5.3) was taking place simultaneously with that due to reduction by carbon thereby increasing the reduction rate of (Cr^{3+}). The shapes of the (Cr^{2+}) curves in both cases, in contrast to

Table 5.9: Rate constants for runs AS15 and AS16

Run	k_1	k_2	k_3	k_4
		$cm.min^{-1}$		
AS5	0.0248	0.0191	0.0434	0.0233
AS15	0.1174	0.0205	0.0396	0.0136
AS16	0.1087	0.0058	0.0562	0.0171

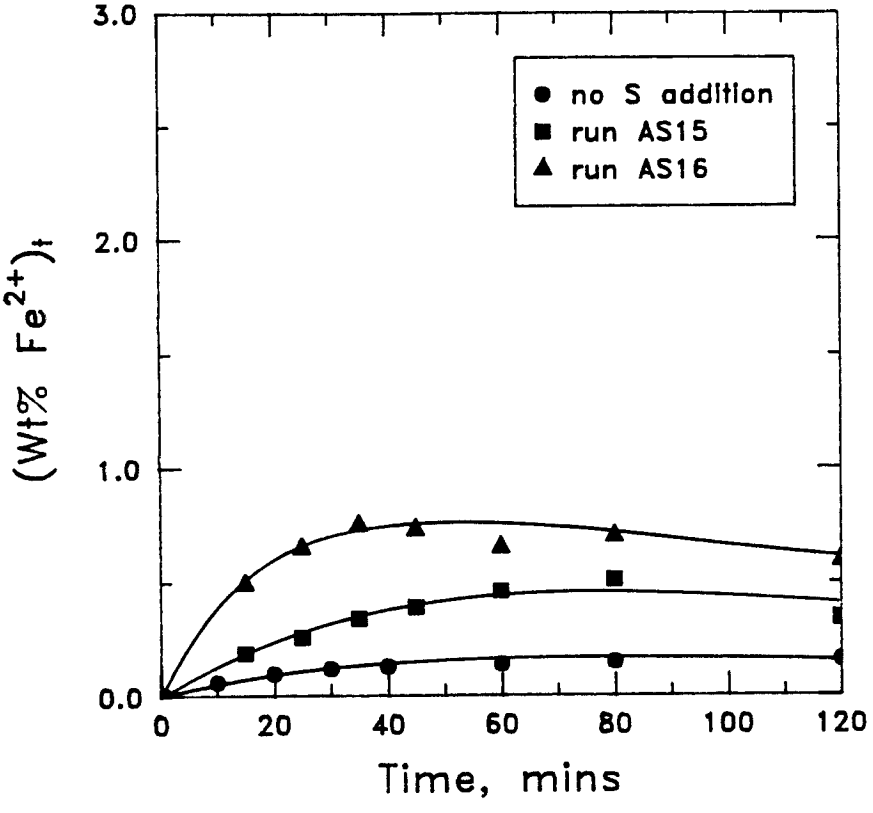


Fig. 5.28 Effect of Sulphur addition to slag on Fe_t^{2+} content of slag.

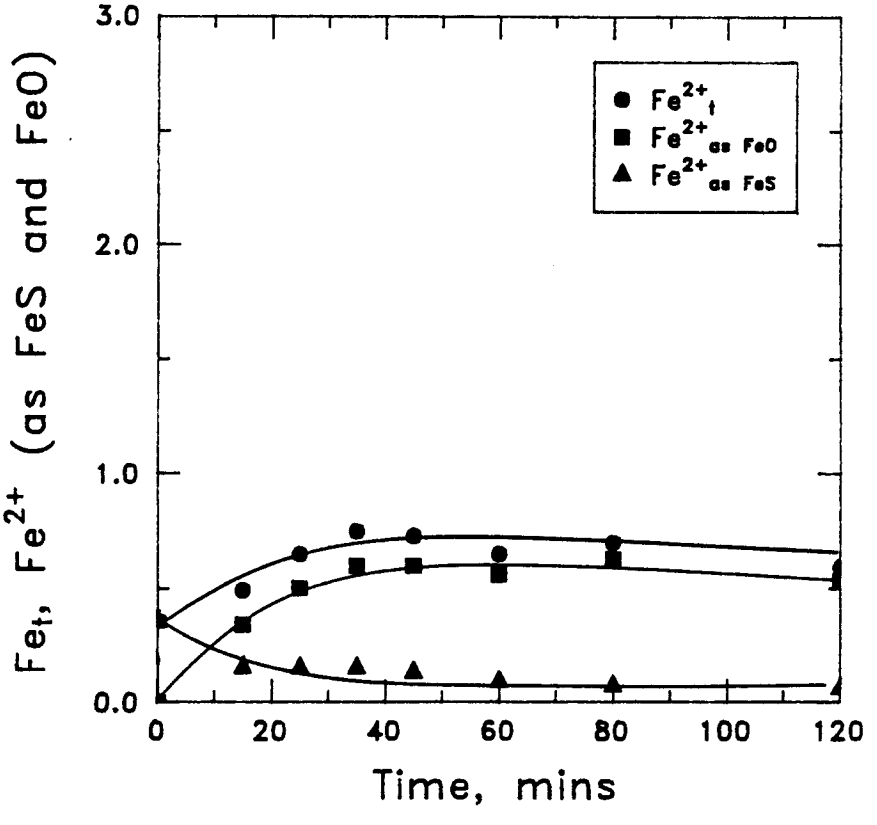
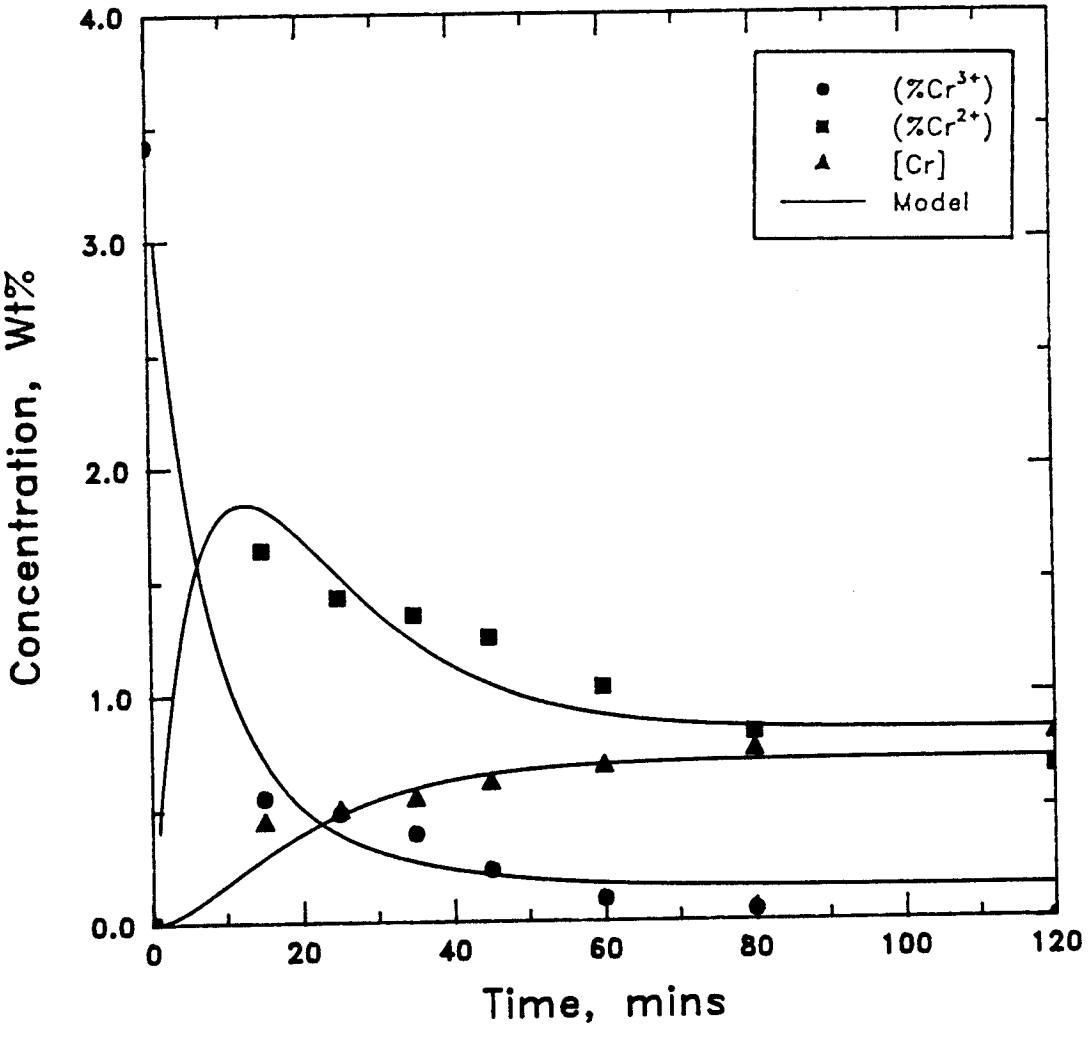


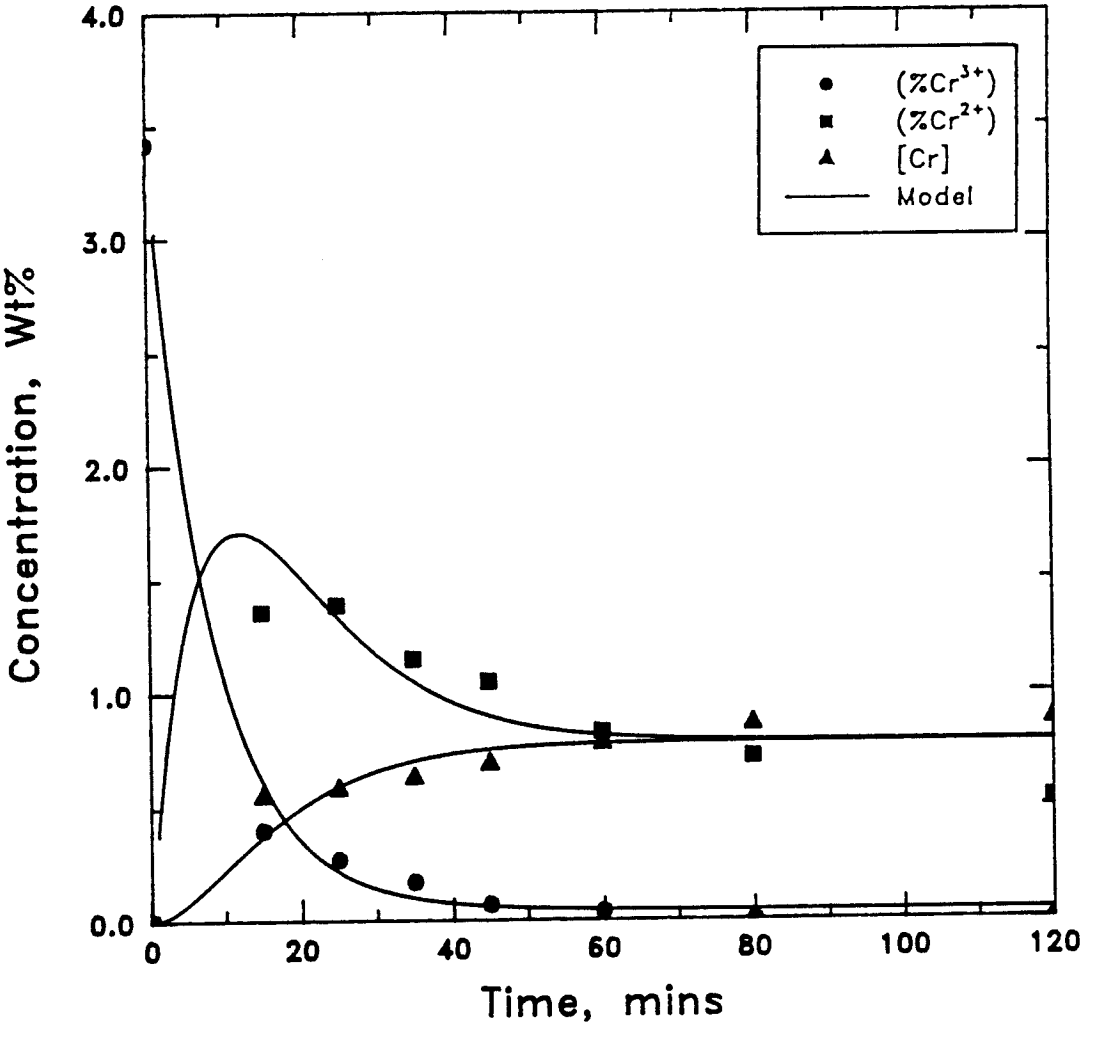
Fig. 5.29 Variation of Fe^{2+} in slag in form of FeS and FeO for run AS16.



$k_1 = 0.1174\ cm.min^{-1}$. $k_2 = 0.0205\ cm.min^{-1}$.
$k_3 = 0.0396\ cm.min^{-1}$. $k_4 = 0.0136\ cm.min^{-1}$.

Sums of squares of deviations are:
$Cr^{3+} = 0.088$, $Cr^{2+} = 0.144$, $Cr_{Met.} = 0.037$.

Fig. 5.30 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run AS15.



$k_1 = 0.1087\ cm.min^{-1}$. $k_2 = 0.0058\ cm.min^{-1}$.
$k_3 = 0.0562\ cm.min^{-1}$. $k_4 = 0.0171\ cm.min^{-1}$.

Sums of squares of deviations are:
$Cr^{3+} = 0.056$, $Cr^{2+} = 0.300$, $Cr_{Met.} = 0.055$.

Fig. 5.31 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run AS16.

those of Figs. 5.20 to 5.22 point to the fact that the reduction rate of (Cr^{2+}) does not increase as much, as shown by the values of k_3 in Table 5.9. The (Cr^{2+}) curves in Figs. 5.30 and 5.31 are similar to those of Fig. 5.19 in which 0.05 wt%S was added to the metal. This is expected as the sulphur transfer to the metal was 0.030 and 0.038 wt% in runs AS15 and AS16, respectively.

5.4.5 Effect of FeO addition to slag.

In section 5.4.4, the increase in the rates of reduction of the chromium species, in the case where FeS was added to the slag as opposed to CaS addition, was attributed to the presence of Fe^{2+} ions in the slag which take part in the reduction reactions. To explore this further, run AS26 was carried out in which the same stoichiometric amount of Fe as in run AS16 (added as FeS) was added to the slag as FeO. Fig. 5.32 shows rate curves for (Cr^{3+}) and (Cr^{2+}) reduction for run AS5, in which no FeO was added to slag, and run AS26. The figure shows that the reduction rates of the chromium species decrease on addition of FeO to slag. This is due to competition for carbon between Cr_2O_3 and FeO, thereby decreasing the reduction rates of the chromium species. Fig. 5.33 shows a rate curve for FeO reduction for run AS27 in which the

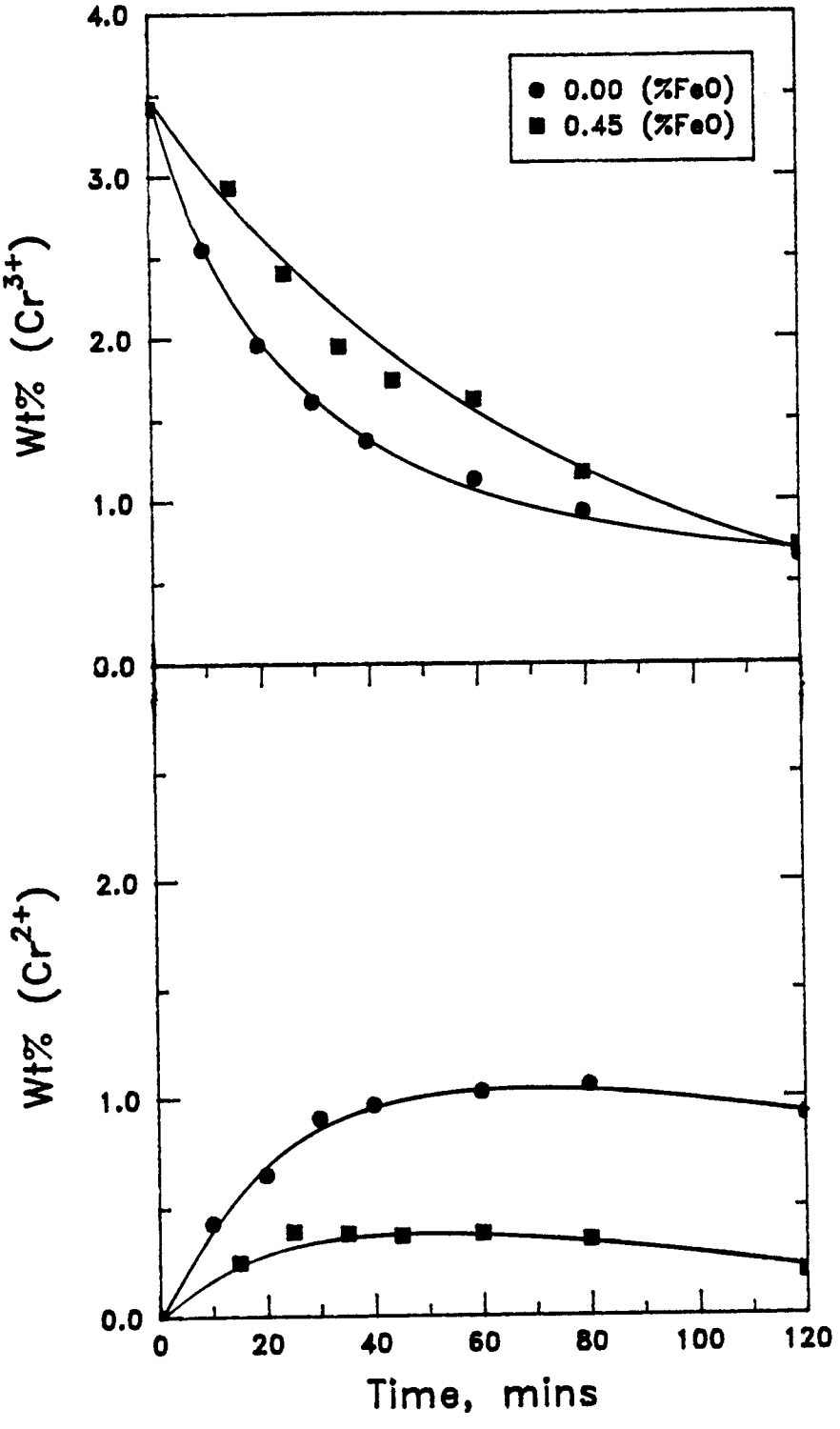


Fig. 5.32 Effect of FeO addition to slag on (Cr^{3+}) and (Cr^{2+}) reduction.

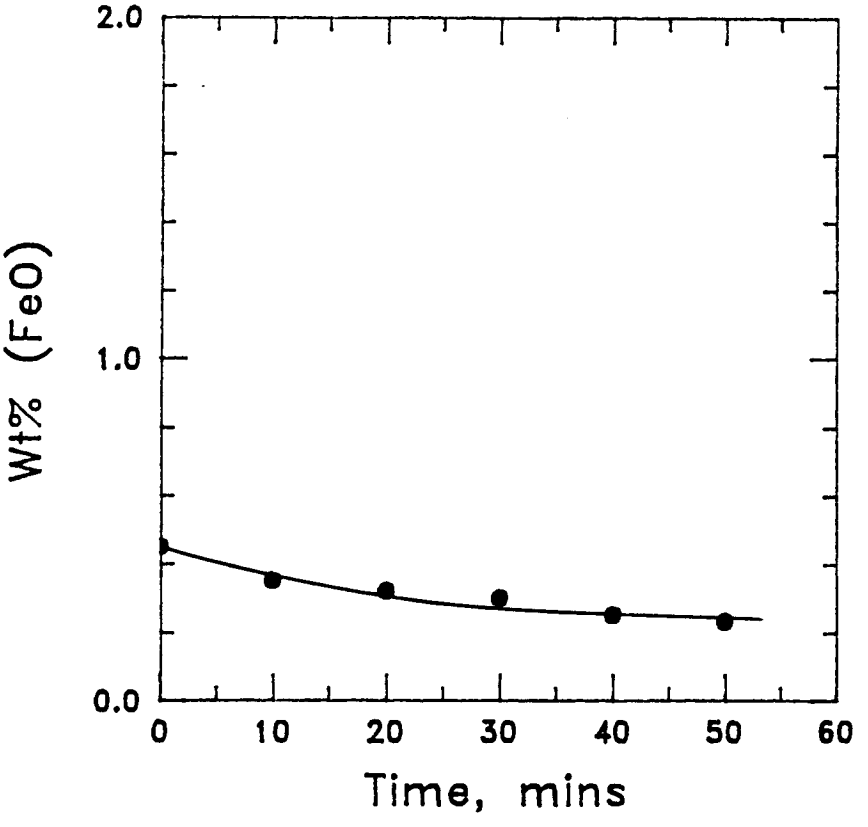


Fig. 5.33 Concentration-time curve for FeO reduction from slag.

same amount of FeO as in run AS26 was added to the slag containing no Cr_2O_3. It is clear from the figure that FeO is also reduced. This gives support to the statement above that the reduced rates of reduction of the chromium species is due to competition of Cr_2O_3 and FeO for carbon during reduction. However, this could not account for the increase in the reduction rates of the chromium species when Fe was added to slag as FeS as opposed to CaS addition, as discussed in section 5.4.4.

5.4.6 Effect of Selenium and Antimony addition to metal.

In order to further explore the effect of surface-active elements on the rate of Cr_2O_3 reduction from slag, runs AS20 and AS21 were carried out in which 0.005 and 0.02 wt% Se, another surface-active element in liquid iron, were added to the metal. Fig. 5.34 shows the concentration-time curves for (Cr^{3+}) and (Cr^{2+}) reduction. The figure shows that the reduction rate of (Cr^{3+}) increases with selenium addition. The rate of (Cr^{2+}) production and its subsequent reduction also increases with selenium addition. High iron levels were recorded in slag in both cases (Fig. 5.35). The reason for the increase in the reduction rates of the chromium species and the subsequent increase in slag iron levels has been outlined in section 5.4.1. Metal emulsification

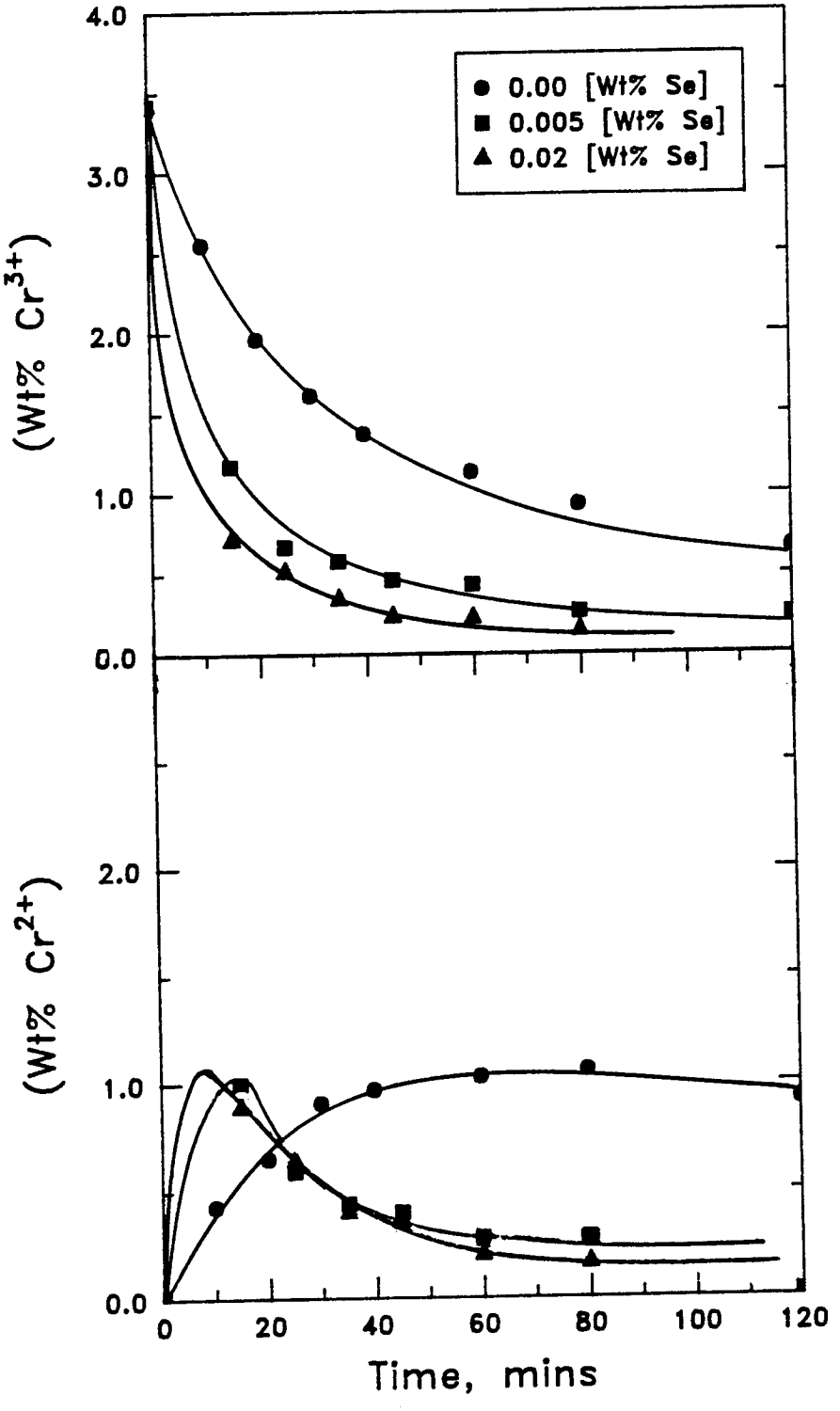


Fig. 5.34 Effect of Selenium addition to metal on (Cr^{3+}) and (Cr^{2+}) reduction.

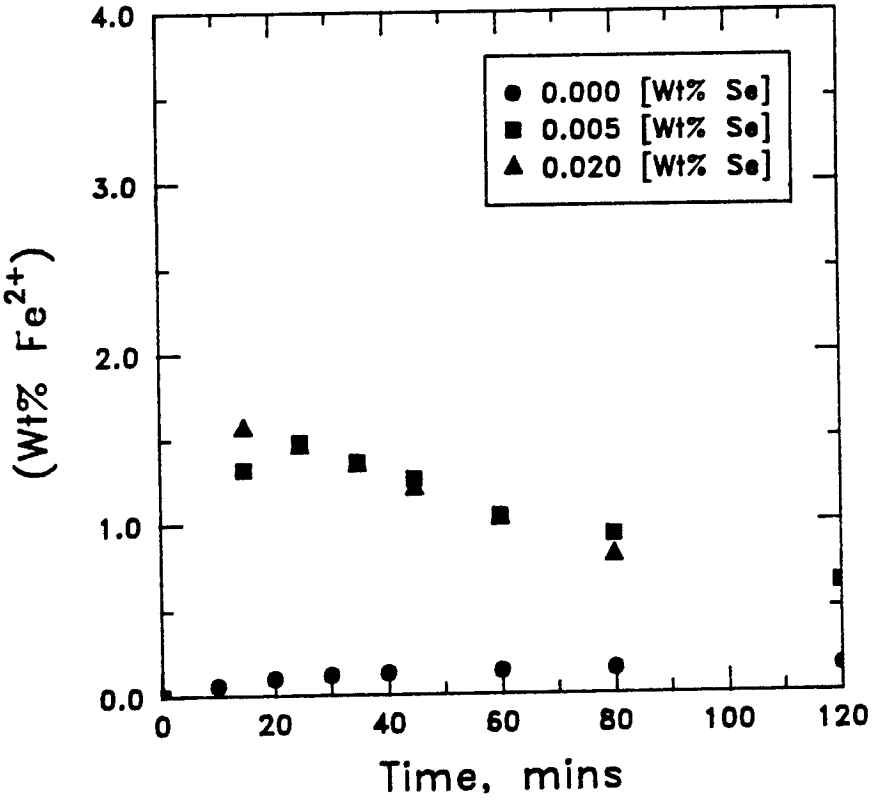


Fig. 5.35 Variation of Fe^{2+} in slag for runs AS20 and AS21.

in this case is brought about by a reduction in the surface tension of iron due to surface coverage of selenium and there is no transfer of selenium to the slag. Note that even at very low selenium additions to the metal, 0.005 wt%, the reduction rate of the chromium species is high. This is in accord with the results of Kozakevitch and Urbain[67] who found selenium to be highly surface-active than sulphur and oxygen as shown in Fig. 5.36.

Figs. 5.37 and 5.38 show concentration-time curves for runs AS20 and AS21, respectively. The rate constants obtained are shown in Table 5.10 together with those of run AS5. The table shows that the rate constants, k_1 and k_3, increase with selenium addition to metal up to 0.02 wt%, indicating that the reduction rates of the chromium species are increased when selenium is added to metal. This is in accord with the observation made ealier. An increase in k_2 with selenium addition can also be seen from the table. This is due to the slow process of (Cr^{2+}) reduction which leads to an increase in the rate of the reverse reaction.

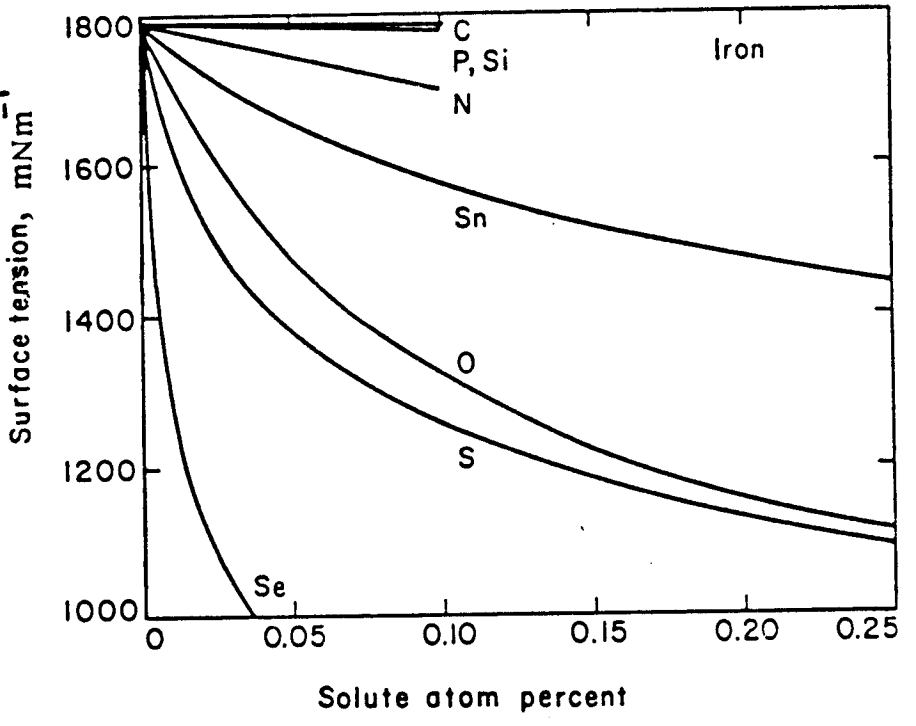
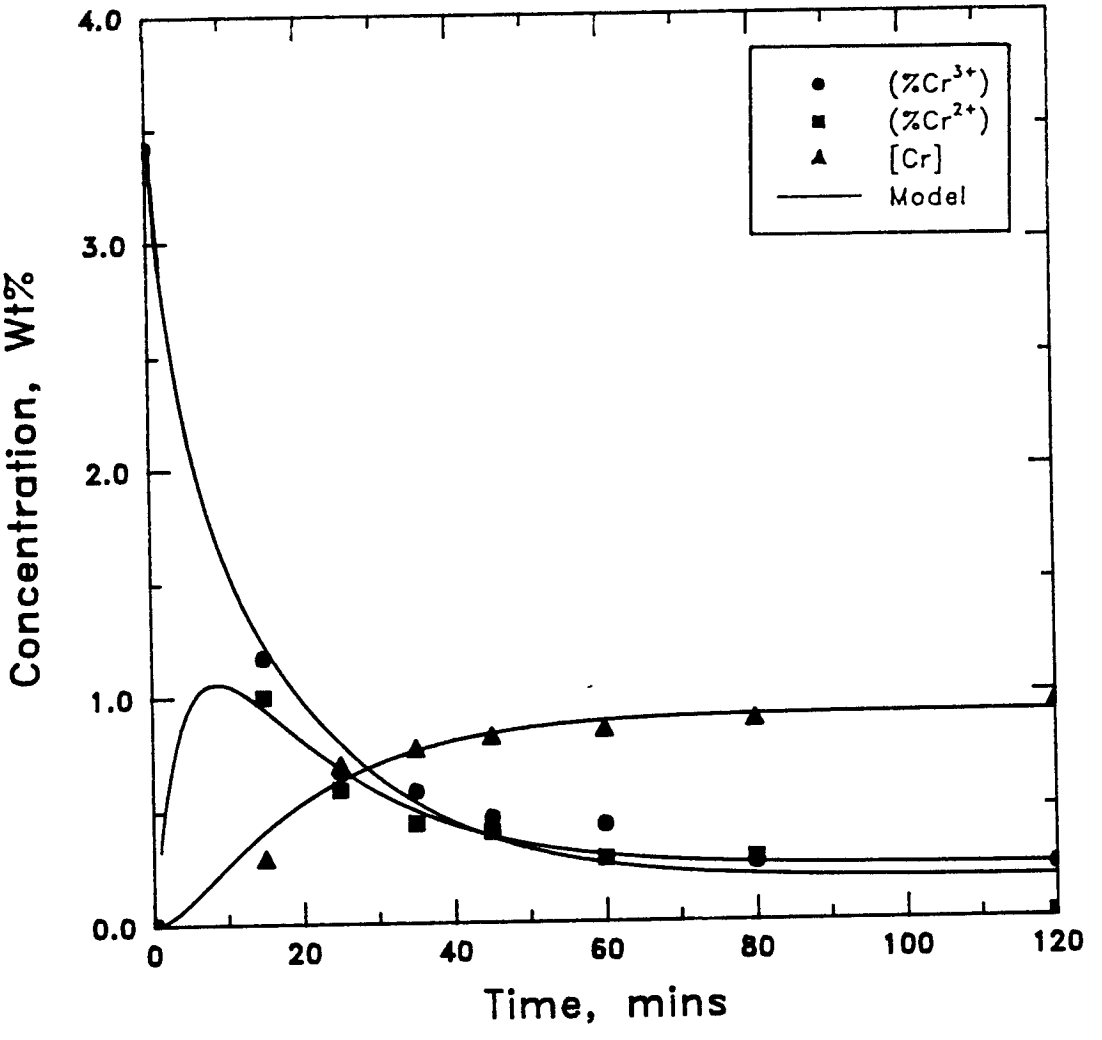


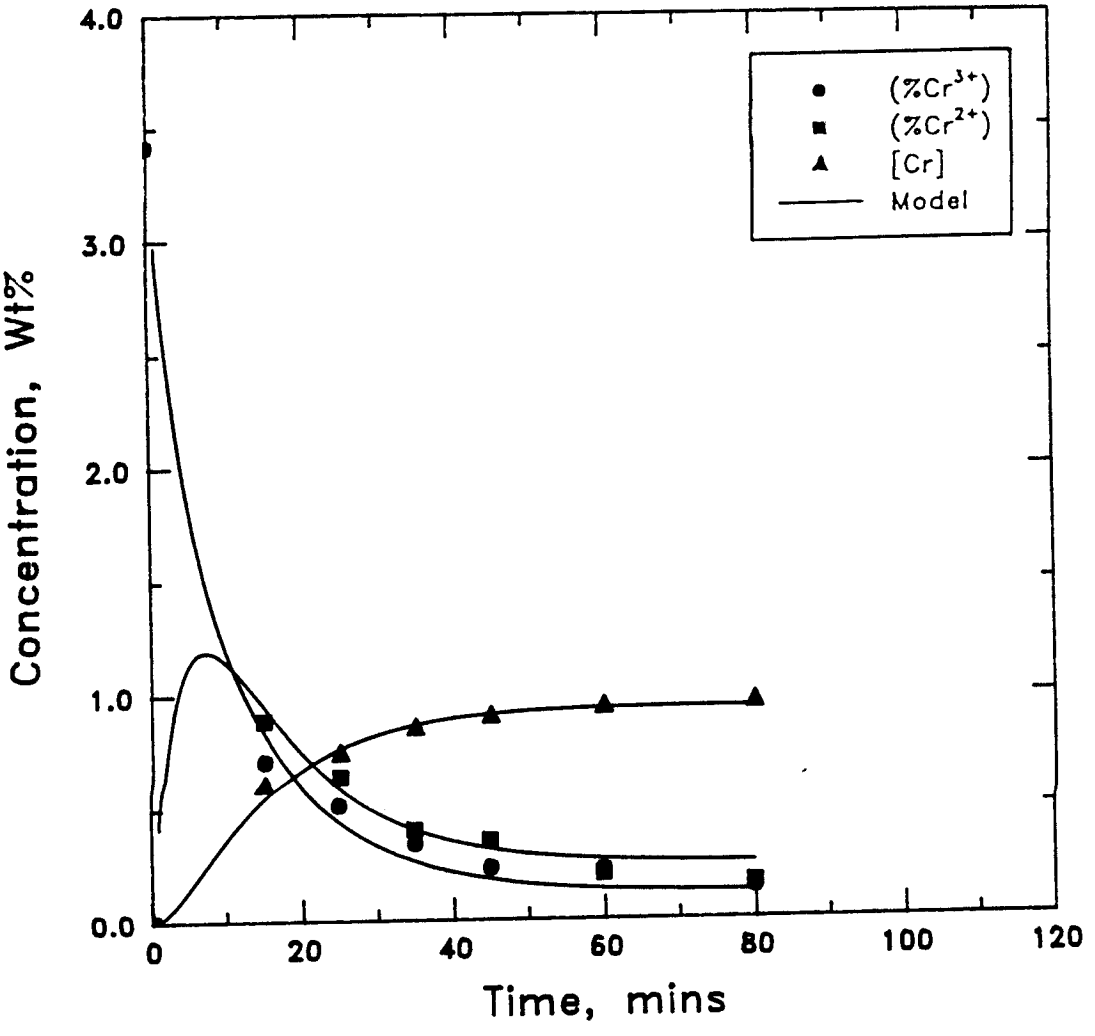
Fig. 5.36 Effect of added elements on surface tension of pure iron (66).



k_1 = 0.0986 cm.min^{-1}. k_2 = 0.0751 cm.min^{-1}.
k_3 = 0.0874 cm.min^{-1}. k_4 = 0.0070 cm.min^{-1}.

Sums of squares of deviations are:
Cr^{3+} = 0.067, Cr^{2+} = 0.063, $Cr_{Met.}$ = 0.026.

Fig. 5.37 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run AS20.



$k_1 = 0.1272\ cm.min^{-1}$. $k_2 = 0.0602\ cm.min^{-1}$.
$k_3 = 0.1042\ cm.min^{-1}$. $k_4 = 0.0084\ cm.min^{-1}$.

Sums of squares of deviations are:
$Cr^{3+} = 0.038$, $Cr^{2+} = 0.019$, $Cr_{Met.} = 0.005$.

Fig. 5.38 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run AS21.

Table 5.10: Rate constants for runs AS20 and AS21

Run	k_1	k_2	k_3	k_4
		$cm.min^{-1}$		
AS5	0.0248	0.0191	0.0434	0.0233
AS20	0.0986	0.0751	0.0874	0.0070
AS21	0.1272	0.0602	0.1042	0.0084

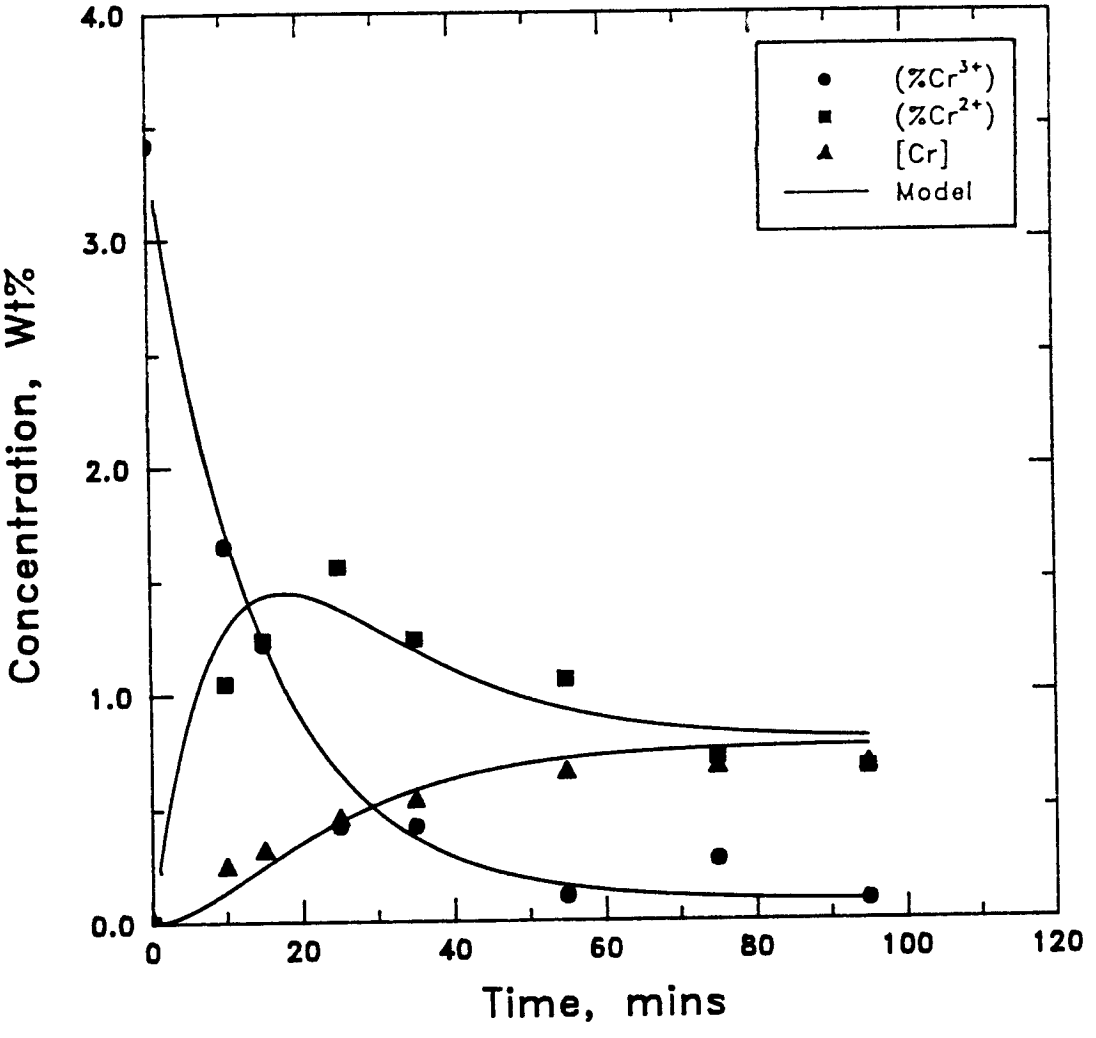
Anyakwo[37] added antimony to metal in his investigation of the effect of surface-active elements on the rate of Cr_2O_3 reduction. He carried out two runs in which 0.05 and 0.20 wt% Sb were added to the metal. The concentration-time curves for these runs are shown in Figs. 5.39 and 5.40 for 0.05 and 0.20 wt% Sb metal addition, respectively. An increase in the forward rate constants, k_1 and k_3, on addition of 0.20 wt% Sb to metal is apparent. These results give further evidence on the increase in the reduction rates of the chromium species with addition of surface-active elements to the system.

5.5 Effect of Calcium Fluoride addition to slag.

Calcium fluoride has primarily a twofold action in slags:

(1) It lowers the melting point of slags, so that slags of higher basicity can be used.

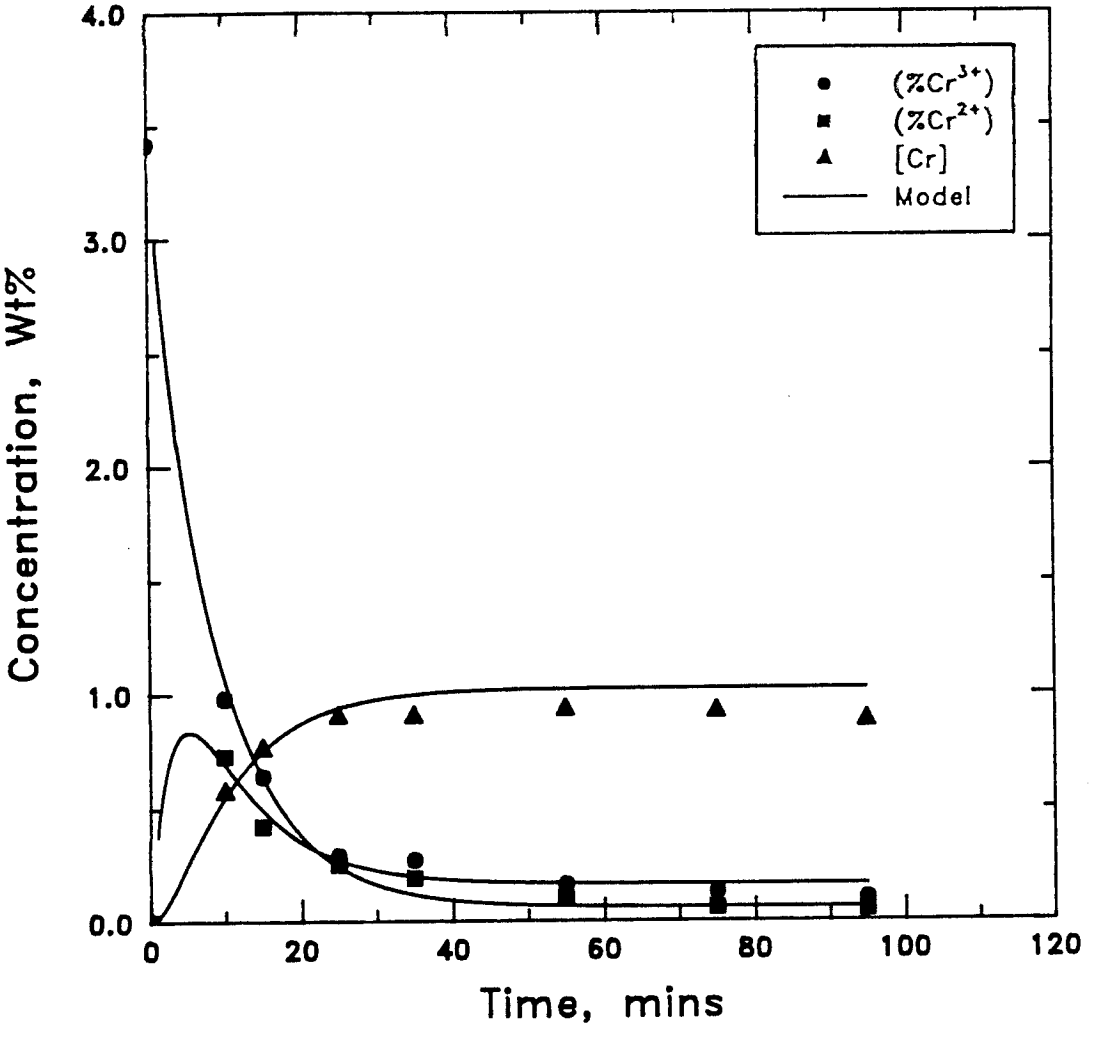
(2) It decreases the viscosity.



$k_1 = 0.0631\ cm.min^{-1}$. $k_2 = 0.0064\ cm.min^{-1}$.
$k_3 = 0.0486\ cm.min^{-1}$. $k_4 = 0.0151\ cm.min^{-1}$.

Sums of squares of deviations are:
$Cr^{3+} = 0.092$, $Cr^{2+} = 0.177$, $Cr_{Met.} = 0.039$.

Fig. 5.39 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for 0.05 [wt% Sb] addition to metal, data from Ref (37).

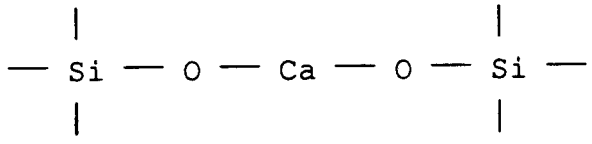


k_1 = 0.1220 cm.min^{-1}. k_2 = 0.0450 cm.min^{-1}.
k_3 = 0.2259 cm.min^{-1}. k_4 = 0.0115 cm.min^{-1}.

Sums of squares of deviations are:
Cr^{3+} = 0.049, Cr^{2+} = 0.033, $Cr_{Met.}$ = 0.055.

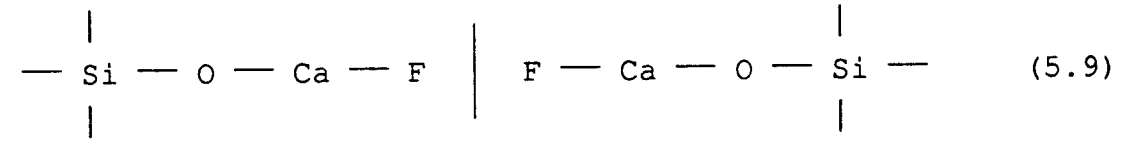
Fig. 5.40 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for 0.2 [wt% Sb] addition to metal, data from Ref (37).

Molecularly, the action of calcium fluoride in silicate slags can be looked at in the following way. The fluoride ion has a valence of -1, while the oxygen has a valence of -2. Each oxygen ion which is not bonded between two silicon ions joins with the calcium ion. This calcium ion in turn is attached to another oxygen according to the scheme



(5.8)

With the introduction of calcium fluoride, the bonding can be thought to occur as follows:



(5.9)

We have solvatation of the silicate by the calcium fluoride. No new compound is formed, but the different silicate units are shielded from each other by unstable CaF^+ ions, which behave like a lubricant between the larger anion units and leads to a reduction in viscosity. Kozakevitch[68] studied the effect of calcium and magnesium fluoride additions on the viscosity of $CaO-SiO_2-Al_2O_3-MgO$ slags. Some of the results from this study are shown in Fig. 5.41. The pronounced effect of additions of fluoride-bearing fluxes on the viscosity of slags is clearly shown in the figure.

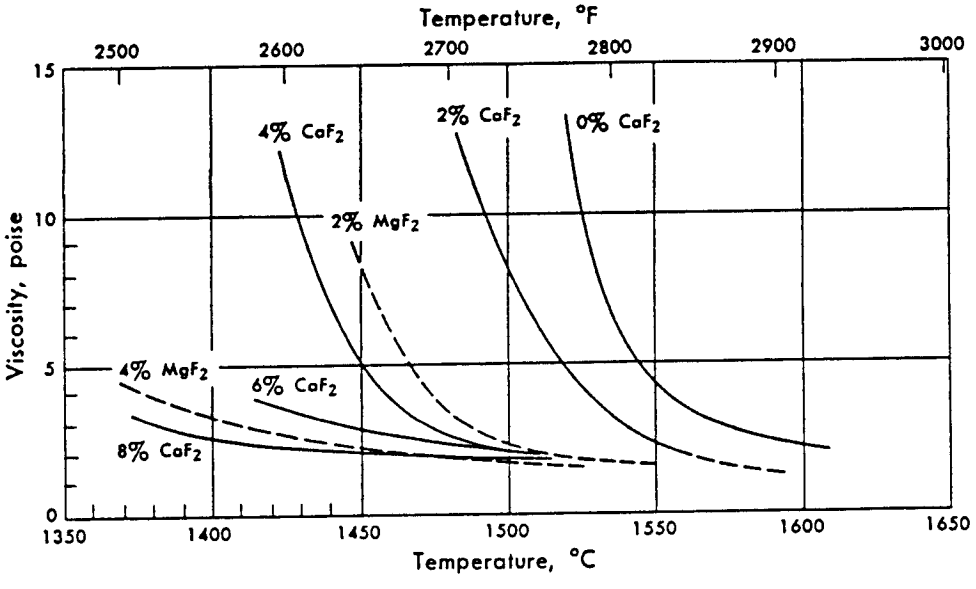


Fig. 5.41 Effect of CaF_2 and MgF_2 additions on the Viscosity of a synthetic slag of the composition 51.7% CaO, 3.2% MgO, 12.7% Al_2O_3, 32.4% SiO_2 and a CaO/SiO_2 ratio of 1.6 (67).

In view of this, runs AS22, AS23 and AS24 were carried out in which 2, 3.5 and 5 wt% CaF_2 were added to the slag, respectively, to determine its effect on the reduction rate of Cr_2O_3. The results from these runs are shown in Fig. 5.42. The figure shows that the reduction rates of the chromium species increase with CaF_2 addition to slag up to 5 wt%.

The reduction in slag viscosity with CaF_2 addition to slag is thought to be responsible for the increased rates of reduction of the chromium species. A low viscosity of slag allows easy mixing of the metal and slag during CO bubbling thereby increasing the slag/metal contact area and consequently the rates of reactions. Vigorous bubbling of the slag bath during these runs was observed due to fluid slags. Examination of the alumina crucible from a run in which 5 wt% CaF_2 was added to slag revealed little or no corrosion. High iron levels in slag were recorded with increase in CaF_2 content as shown in Fig. 5.43. The large slag/metal contact area created, which is a result of easy mixing of the slag and metal due to low slag viscosity allows reaction (5.1) to proceed simultaneously with that due to carbon oxidation. This leads to high Fe levels in slag. As in the case of addition of surface-active elements, the Fe levels decreases at longer times indicating the onset of FeO reduction from slag.

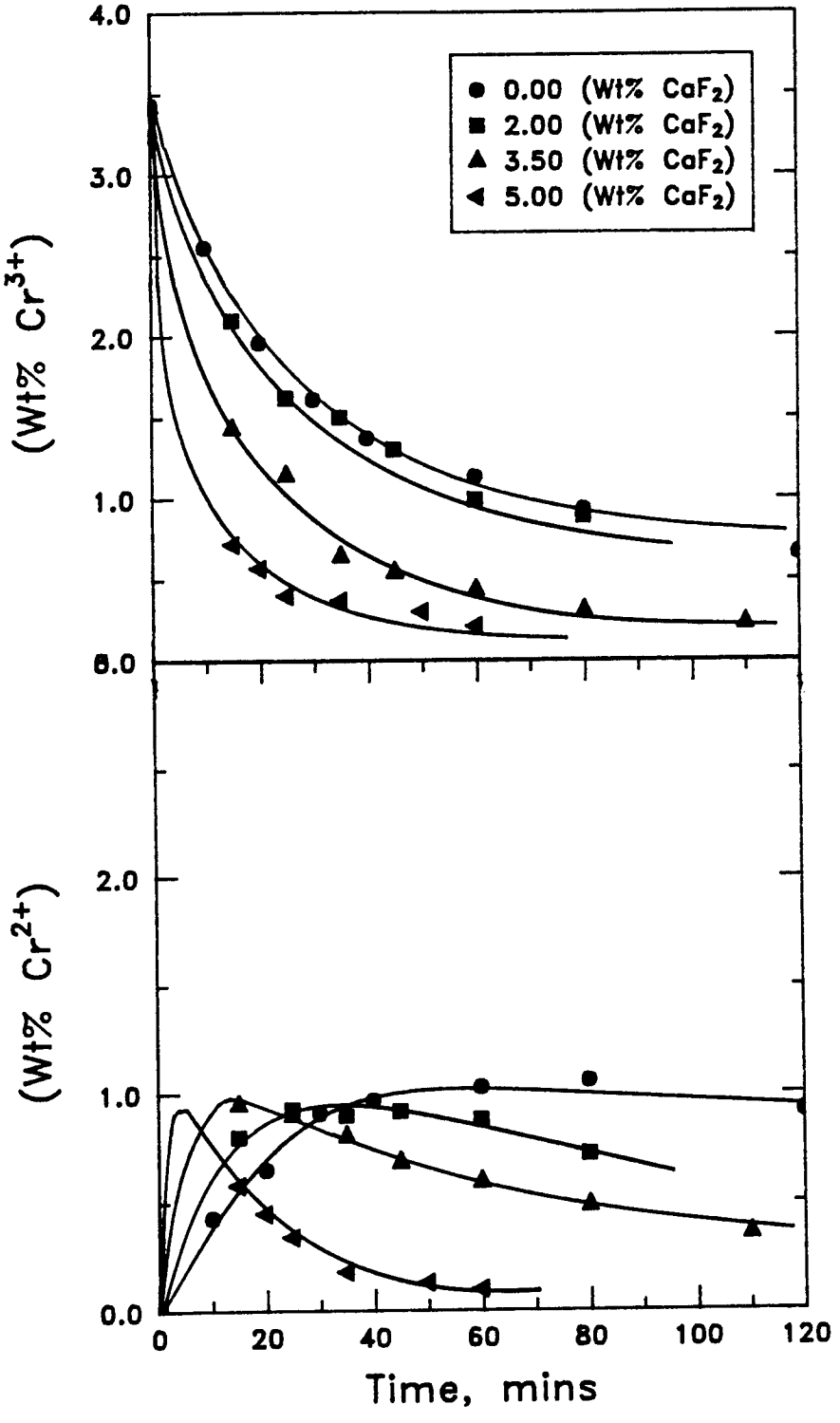


Fig. 5.42 Effect of Calcium Fluoride additions on (Cr^{3+}) and (Cr^{2+}) reduction.

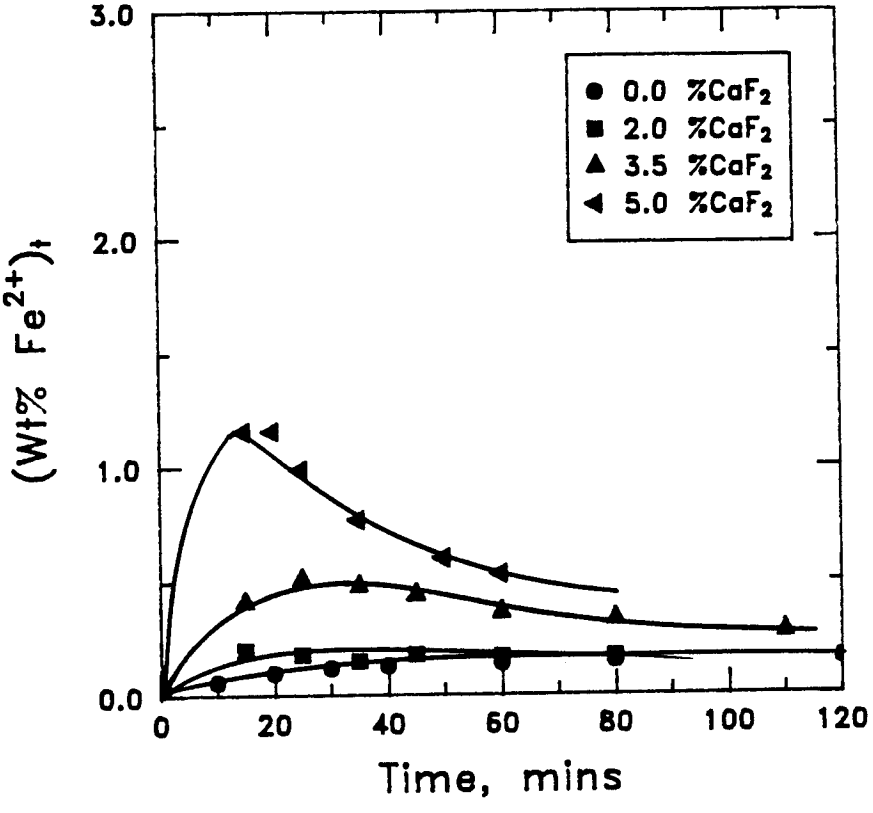


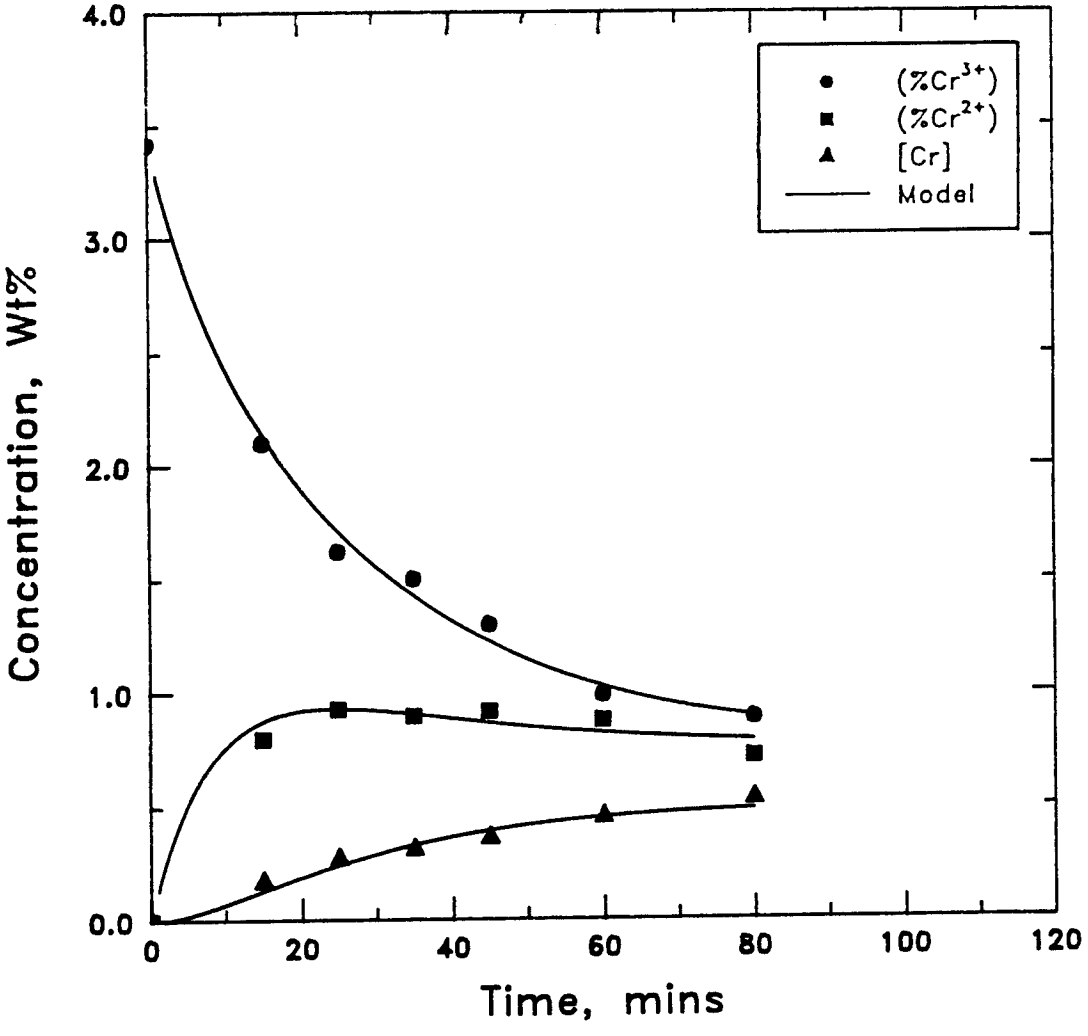
Fig. 5.43 Variation of Fe_t^{2+} in slag with calcium fluoride content.

Figs. 5.44, 5.45 and 5.46 show concentration-time curves for runs AS22, AS23 and AS24, respectively. The variation of the rate constants with calcium fluoride addition to slag is shown in Table 5.11 together with those of run AS5. The forward rate constants, k_1 and k_3, are shown in Fig. 5.47 as a function of CaF_2 contents of the slag. It is apparent from the figure that the forward rate constants increase with CaF_2 addition to slag up to 5 wt%. A drastic increase in k_2 on addition of 5 wt% CaF_2 is probably due to the slow nature of the reduction of (Cr^{2+}) relative to (Cr^{3+}) reduction and as such the reverse reaction increases leading to a high value of k_2.

Table 5.11: Variation of rate constants with slag calcium fluoride content.

Wt% CaF_2	k_1	k_2	k_3	k_4
	$cm.min^{-1}$			
0.00	0.0248	0.0191	0.0434	0.0233
2.00	0.0367	0.0386	0.0450	0.0186
3.50	0.0603	0.0344	0.0632	0.0101
5.00	0.1450	0.1156	0.1806	0.0116

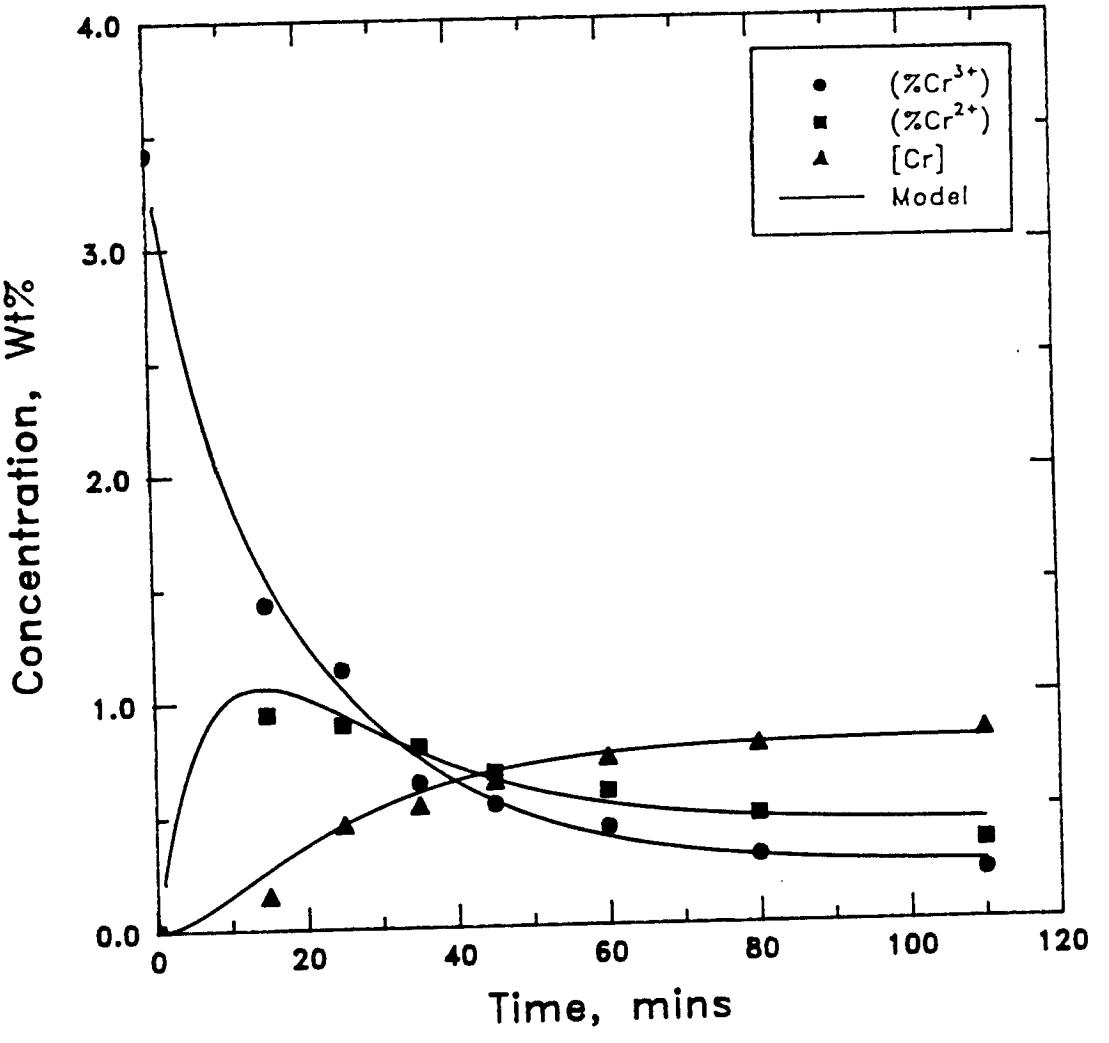
To investigate the effect of CaF_2 addition to slag on the reduction rate of a high concentration of Cr_2O_3 in slag, run AS25 was carried out in which the initial



$k_1 = 0.0367\ cm.min^{-1}$. $k_2 = 0.0386\ cm.min^{-1}$.
$k_3 = 0.0450\ cm.min^{-1}$. $k_4 = 0.0189\ cm.min^{-1}$.

Sums of squares of deviations are:
$Cr^{3+} = 0.023$, $Cr^{2+} = 0.018$, $Cr_{Met.} = 0.006$.

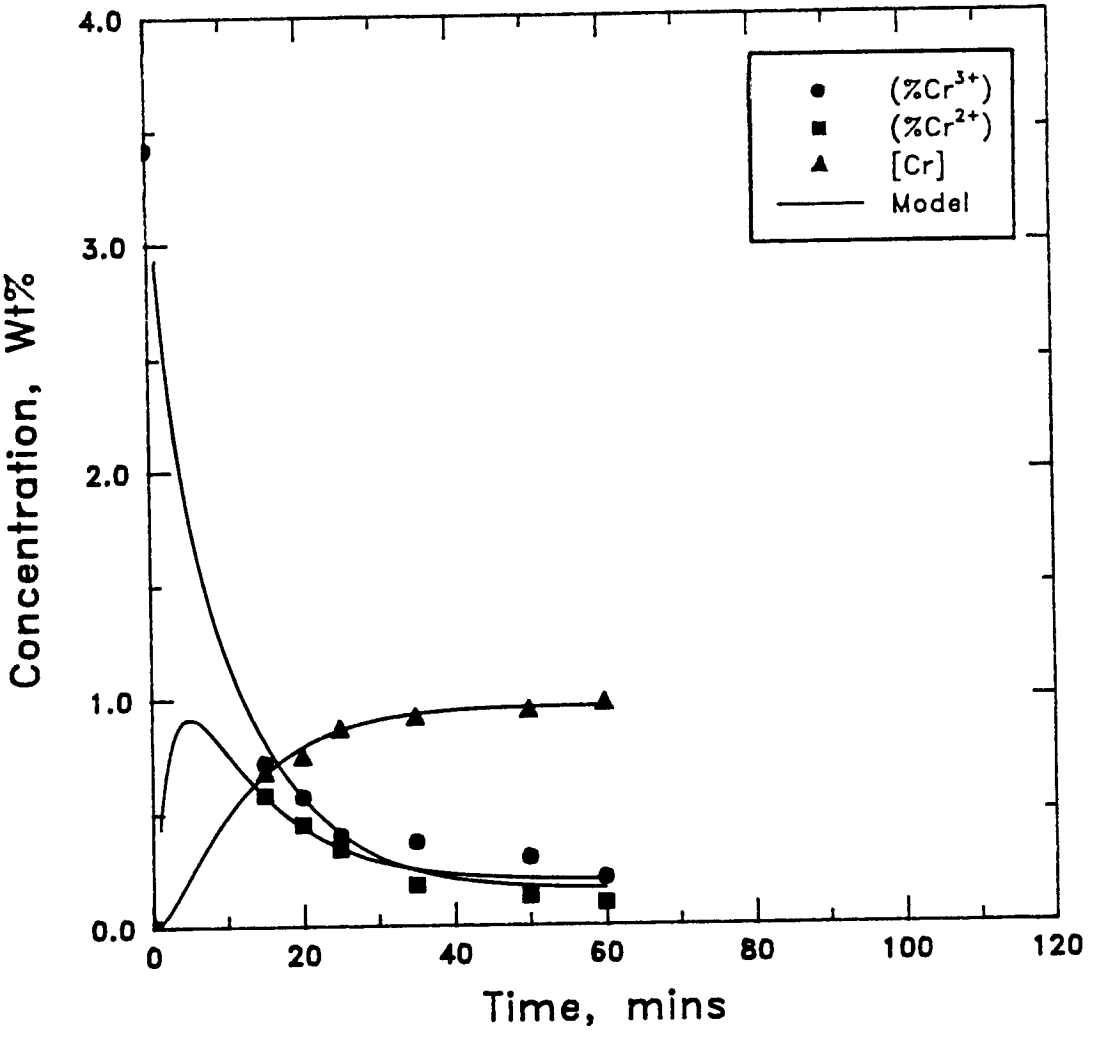
Fig. 5.44 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run AS22.



$k_1 = 0.0603\ cm.min^{-1}$. $k_2 = 0.0344\ cm.min^{-1}$.
$k_3 = 0.0632\ cm.min^{-1}$. $k_4 = 0.0101\ cm.min^{-1}$.

Sums of squares of deviations are:
$Cr^{3+} = 0.037$, $Cr^{2+} = 0.028$, $Cr_{Met.} = 0.028$.

Fig. 5.45. Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run AS23.



k_1 = 0.1450 cm.min^{-1}. k_2 = 0.1156 cm.min^{-1}.
k_3 = 0.1806 cm.min^{-1}. k_4 = 0.0116 cm.min^{-1}.

Sums of squares of deviations are:
Cr^{3+} = 0.044, Cr^{2+} = 0.020, $Cr_{Met.}$ = 0.004.

Fig. 5.46 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run AS24.

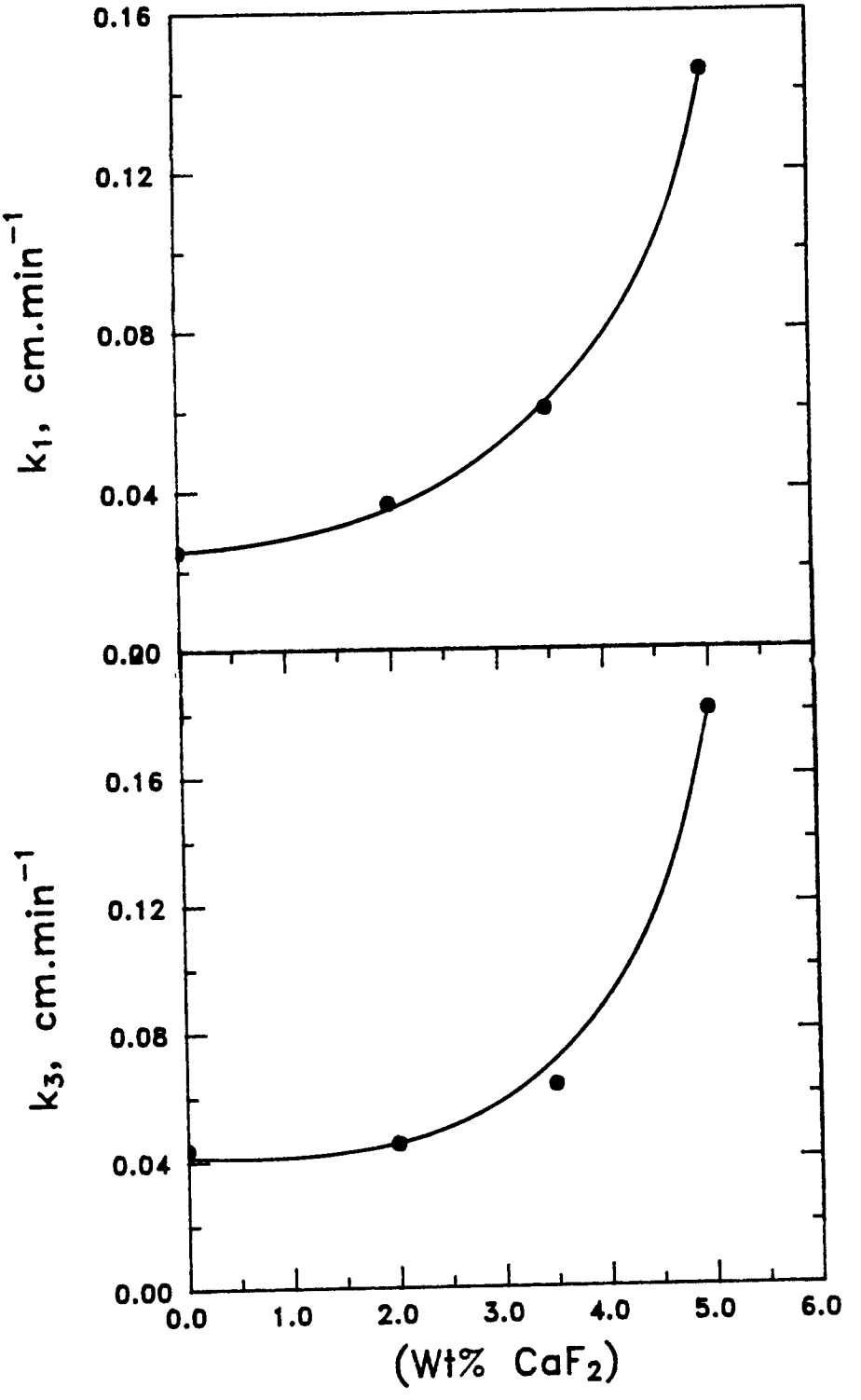


Fig. 5.47 Effect of Calcium Fluoride on the forward rate constants k_1 and k_3.

concentration of Cr_2O_3 in slag was 10 wt% with a CaF_2 addition of 5 wt%. Fig. 5.48 shows concentration-time curves for the reduction of the chromium species for the cases where no CaF_2 (run AS3) and 5 wt% CaF_2 (run AS25) addition to slag were made. The increase in the reduction rates of (Cr^{3+}) and (Cr^{2+}) on addition of 5 wt% CaF_2 is clearly shown in the figure. Fig. 5.49 shows concentration-time curves of the chromium species for run AS25. Comparison of the forward rate constants with those from run AS5 (Fig. 4.16) shows that addition of 5 wt% CaF_2 to slag markedly increases the rate constant values an indication of the increase in the rate of Cr_2O_3 reduction.

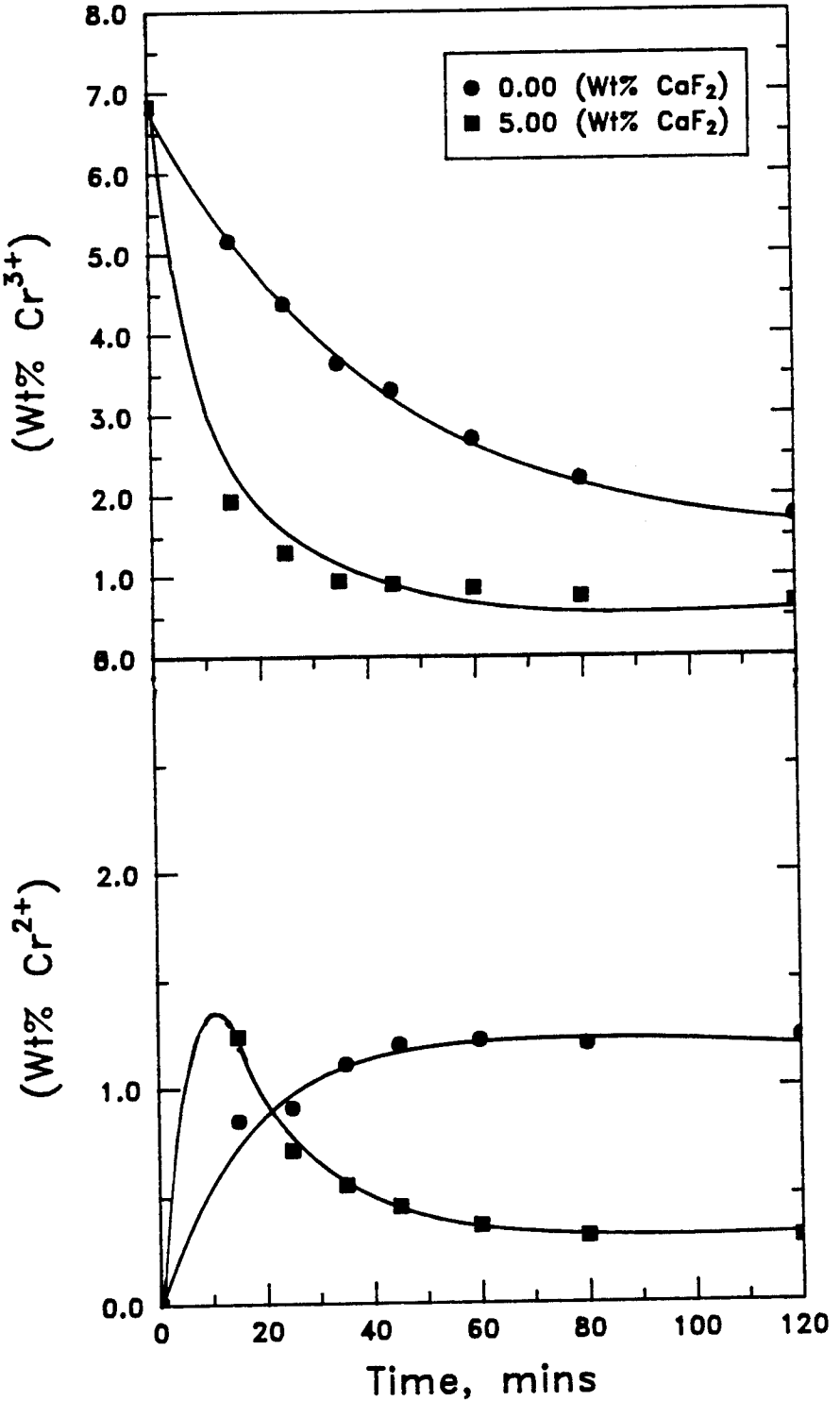
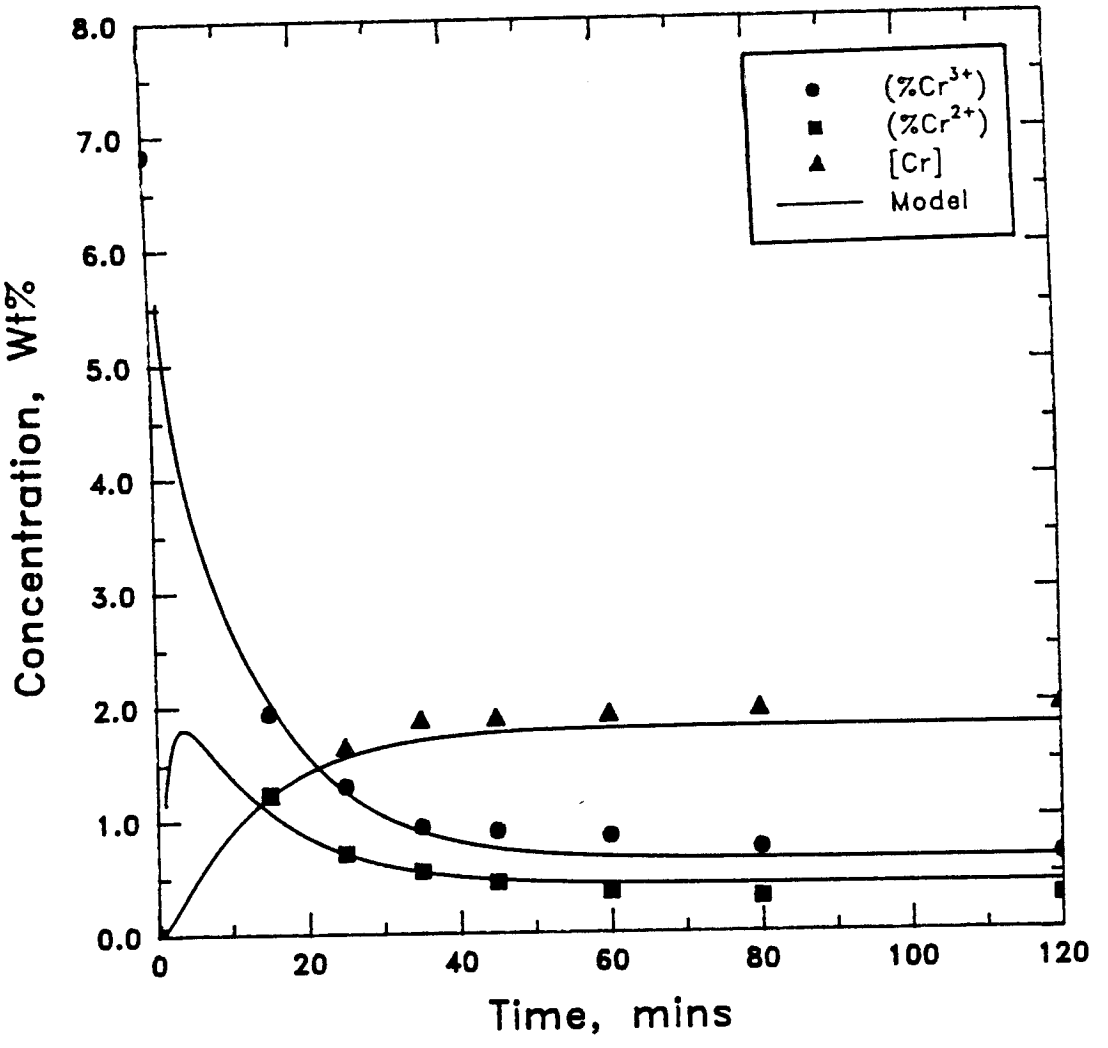


Fig. 5.48 Effect of Calcium Fluoride on (Cr^{3+}) and (Cr^{2+}) reduction in slag containing 10 (wt% Cr_2O_3).



$k_1 = 0.2220\ cm.min^{-1}.\ k_2 = 0.0357\ cm.min^{-1}.$
$k_3 = 0.1719\ cm.min^{-1}.\ k_4 = 0.0125\ cm.min^{-1}.$

Sums of squares of deviations are:
$Cr^{3+} = 0.087,\ Cr^{2+} = 0.060,\ Cr_{Met.} = 0.088.$

Fig. 5.49 Time variation in concentration of (Cr^{3+}), (Cr^{2+}) and [Cr] for run AS25.

CHAPTER 6

CONCLUSIONS

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A first-order consecutive two-stage reaction model for the reduction of Cr_2O_3 from slag by carbon dissolved in molten iron has been developed. The model has been applied to experimental data obtained by studying the kinetics of reduction of Cr_2O_3 under varying experimental conditions such as varying the furnace atmosphere, Cr_2O_3 concentration in slag, metal chromium content, employing surface-active elements, S and Se, adding FeO to slag and varying the slag calcium fluoride content. The model has also been applied to the results of Anyakwo[37] on the effect of temperature, melt geometry and antimony addition to metal. From the results obtained, the following conclusions are made.

(1) By carrying out experiments in the absence of a metal phase, it has been established that the reduction of Cr_2O_3 from slag takes place primarily at the slag/metal interface and that a metal surface is needed for the reduction to take place at all.

(2) From the runs carried out under an argon and carbon monoxide atmosphere, it is shown that the rate of

reduction of (Cr^{3+}) is not affected by the furnace atmosphere used. However, an argon atmosphere seems to increase the rate of (Cr^{2+}) reduction by a factor of about 1.4.

(3) Changes in the concentration of Cr_2O_3 in slag show that the rate of Cr_2O_3 reduction is proportional to its concentration as is expected from the law of mass action. This is substantiated by the similarity in the forward rate constants, k_1 and k_3, obtained for the different Cr_2O_3 concentrations used.

(4) The reduction of Cr_2O_3 from slag takes place in two stages. The first stage is the reduction of (Cr^{3+}) to (Cr^{2+}). This is a fast reaction and is associated with rapid gas evolution and colour change of slag from bright green to deep blue. The second stage is the reduction of (Cr^{2+}) to [Cr] which is considered to be a slow process.

(5) It is established from the development of a model for Cr_2O_3 reduction that its reduction from slag by carbon or silicon dissolved in molten iron follows a first-order consecutive reversible two-stage reaction scheme in which (Cr^{2+}) is the intermediary product.

(6) By modifying the model to take account of the variation in slag height due to sampling, it is

established that the sensitivity of the chromium species to changes in slag height is insignificant.

(7) A model (scheme 5) which takes account of the variation in slag height and includes a route where (Cr^{3+}) directly reacts to form [Cr], which takes place simultaneously with that through the intermediate, (Cr^{2+}), has been developed. This is found to give best fits but the rate constants obtained do not give any meaning as far as the metallurgy of the process is concerned. A model (scheme 4) which assumes the reduction of Cr_2O_3 to take place only through the intermediate is considered adequate and gives rate constants from which a sound metallurgical interpretation can be obtained, and as such it is used in the kinetic analysis of the results in this study.

(8) Addition of chromium to metal up to 15 wt% has no effect on the rate of reduction of (Cr^{3+}) i.e the rate of the first-stage of the consecutive reaction is not affected. The reduction rate of (Cr^{2+}) decreases above 4 wt% chromium addition to metal. This is due to a reduction in the concentration gradient of (Cr^{2+}) between the interface and bulk slag which slows down the rate of reduction.

(9) Raising the temperature of the process increases the reduction rates of the chromium species from slag. For (Cr^{3+}) reduction the activation energy is 54.16 kcal/mol, for (Cr^{2+}) it is 27.15 kcal/mol and for Cr_2O_3 reduction, it is 81.33 kcal/mol. (Cr^{3+}) is shown to be rate-limited by mass transport in the slag phase. (Cr^{2+}) is probably limited by an interfacial chemical reaction.

(10) Increasing the slag volume slightly increases the rate of (Cr^{3+}) reduction but has no effect on the rate of (Cr^{2+}) reduction. Increasing the metal volume has no effect on the rate of (Cr^{3+}) and (Cr^{2+}) reduction. This shows that the reduction of (Cr^{3+}) is controlled by mass transport of (Cr^{3+}) in the slag phase whereas (Cr^{2+}) reduction is not controlled by its mass transport in either the slag or metal phase, but probably by an interfacial chemical reaction.

(11) The rates of reduction of the chromium species increase on addition of sulphur to metal up to 0.1 wt%. The increase in the rates of reduction is due to enhanced metal emulsification as a result of the lowering of interfacial tension due to sulphur. Metal emulsification increases the slag/metal contact area for the reduction reactions to take place resulting in an increase in the rates of reduction.

(12) High sulphur additions to metal, above 0.1 wt%, do not increase the rates of reduction of the chromium species any further. This is substantiated by the nearly constant values of the forward rate constants, k_1 and k_3, obtained at 0.1, 0.3 and 0.5 wt% S additions to metal.

(13) The rates of reduction of the chromium species increase with sulphur addition to slag. The reduction rate of (Cr^{3+}) shows a drastic increase compared to that of (Cr^{2+}). The rate of (Cr^{2+}) reduction does not show any marked increase probably due to low levels of sulphur dissolved in the metal (about 0.03 %) which result in low emulsions and thus low slag/metal contact area. This ultimately leads to a low reduction rate of (Cr^{2+}) and an accumulation of (Cr^{2+}) in the slag phase.

(14) Addition of FeO to the slag decreases the reduction rates of the chromium species. This is due to competition of Cr_2O_3 and FeO for carbon which leads to reduced rates of reduction of the chromium species.

(15) Addition of other surface-active elements such as selenium and antimony to metal also increase the rates of reduction of the chromium species. Addition of selenium up to 0.02 wt% to metal increases the rate of reduction of the chromium species. The rate of the reverse reaction of the first-stage is increased due to the slow

process of (Cr^{2+}) reduction relative (Cr^{3+}) reduction. Addition of antimony to metal up to 0.2 wt% increases the reduction rates of the chromium species.

(16) Calcium fluoride additions to slag up to 5 wt% increases the rates of reduction of the chromium species. The increase in the reduction rates is due to the lowering of the slag viscosity which allows easy mixing of the slag and metal during CO bubbling. This leads to an increase in the contact area between slag and metal and consequently to an increase in the reduction rates.

APPENDICES

APPENDIX A

The method shown below of determining solutions to differential equations from consecutive reactions is derived from Capellos et al[62]. The method is known as 'the Operator method' in mathematical circles and makes use of Laplace Transforms. Differential equations from a first-order consecutive reversible two-stage reaction scheme are used in the following example to determine solutions by the method described above. The reactions for this scheme can be represented as:

$$(Cr^{3+}) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (Cr^{2+}) \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [Cr] \qquad (A.1)$$

The differential equations are:

$$\frac{d(Cr^{3+})}{dt} = \frac{k_2}{h}(Cr^{2+}) - \frac{k_1}{h}(Cr^{3+}) \qquad (A.2)$$

$$\frac{d(Cr^{2+})}{dt} = \frac{k_1}{h}(Cr^{3+}) + \frac{k_4}{h}[Cr] - \frac{k_2}{h}(Cr^{2+}) - \frac{k_3}{h}(Cr^{2+}) \qquad (A.3)$$

$$\frac{d[Cr]}{dt} = \frac{k_3}{h} (Cr^{2+}) - \frac{k_4}{h} [Cr] \qquad (A.4)$$

where h is the slag height in cm. The transformed functions for the boundary conditions; at t = 0, $(Cr^{3+}) = (Cr^{3+})_o$, $(Cr^{2+}) = [Cr] = 0$ for equations (A.2), (A.3) and (A.4) are:

$$S\ (Cr^{3+}) - S\ (Cr^{3+})_o = K_2\ (Cr^{2+}) - K_1\ (Cr^{3+}) \qquad (A.5)$$

$$S\ (Cr^{2+}) = K_1\ (Cr^{3+}) + K_4\ [Cr] - K_2\ (Cr^{2+}) - K_3\ (Cr^{2+}) \qquad (A.6)$$

$$S\ [Cr] = K_3\ (Cr^{2+}) - K_4\ [Cr] \qquad (A.7)$$

where $K_1 = k_1/h$ etc. Solving these equations in succession yields

$$(Cr^{3+}) = \frac{(Cr^{3+})_o \left\{ S^2 + S\ (K_2 + K_3 + K_4) + K_2K_4 \right\}}{\left\{ S^2 + S(K_1 + K_2 + K_3 + K_4) + K_1K_3 + K_2K_4 + K_1K_4 \right\}} \qquad (A.8)$$

$$(Cr^{2+}) = \frac{(Cr^{3+})_o\ K_1\ (S + K_4)}{\left\{ S^2 + S(K_1 + K_2 + K_3 + K_4) + K_1K_3 + K_2K_4 + K_1K_4 \right\}} \qquad (A.9)$$

$$[Cr] = \frac{(Cr^{3+})_o K_1 K_3}{\left\{ S^2 + S(K_1 + K_2 + K_3 + K_4) + K_1K_3 + K_2K_4 + K_1K_4 \right\}} \quad (A.10)$$

As can be seen equations (A.8), (A.9) and (A.10) have the same denominator. This can be converted by factoring to $(S + m_1)/(S + m_2)$, if one recognizes m_1 and m_2 as the negative roots of the quadratic equation

$$S^2 + S(K_1 + K_2 + K_3 + K_4) + K_1K_3 + K_2K_4 + K_1K_4 = 0 \quad (A.11)$$

Equations (A.8), (A.9) and (A.10) can then be written as

$$(Cr^{3+}) = \frac{(Cr^{3+})_o \left\{ S^2 + S(K_2 + K_3 + K_4) + K_2K_4 \right\}}{(S + m_1)(S + m_2)} \quad (A.12)$$

$$(Cr^{2+}) = \frac{(Cr^{3+})_o K_1 (S + K_4)}{(S + m_1)(S + m_2)} \quad (A.13)$$

$$[Cr] = \frac{(Cr^{3+})_o K_1K_3}{(S + m_1)(S + m_2)} \quad (A.14)$$

Replacing the transforms with the appropriate originals yields the final solutions:

$$(Cr^{3+}) = (Cr^{3+})_o \left\{ \frac{K_2K_4}{m_1m_2} + \frac{m_1^2 - m_1(K_2+ K_3+ K_4) + K_2K_4}{m_1(m_1 - m_2)} \right.$$

$$\left. \exp(-m_1t) + \frac{m_2^2 - m_2(K_2+ K_3+ K_4) + K_2K_4}{m_2(m_2 - m_1)} \exp(-m_2t) \right\}$$

(A.15)

$$(Cr^{2+}) = K_1 (Cr^{3+})_o \left\{ \frac{K_4}{m_1m_2} - \frac{K_4 - m_1}{m_1(m_2 - m_1)} \exp(-m_1t) \right.$$

$$\left. - \frac{K_4 - m_2}{m_2(m_1 - m_2)} \exp(-m_2t) \right\} \qquad \text{(A.16)}$$

$$[Cr] = K_1K_3 (Cr^{3+})_o \left\{ \frac{1}{m_1m_2} - \frac{1}{m_1(m_2 - m_1)} \exp(-m_1t) \right.$$

$$\left. - \frac{1}{m_2(m_1 - m_2)} \exp(-m_2t) \right\} \qquad \text{(A.17)}$$

The roots $-m_1$ and $-m_2$ can be obtained in terms of rate constants by solving the quadratic equation (A.11) as has been seen earlier. The derived values can be substituted in the equations above. The roots to the quadratic equation are:

$$m_1 = \frac{1}{2} \left\{ (K_1 + K_2 + K_3 + K_4) + \sqrt{(K_1 + K_2 + K_3 + K_4)^2 - 4(K_1K_3 + K_2K_4 + K_1K_4)} \right\} \quad \text{(A.18)}$$

$$m_2 = \frac{1}{2} \left\{ (K_1 + K_2 + K_3 + K_4) - \sqrt{(K_1 + K_2 + K_3 + K_4)^2 - 4(K_1K_3 + K_2K_4 + K_1K_4)} \right\} \quad \text{(A.19)}$$

Equations (A.15), (A.16) and (A.17) give expressions for the dependence of the concentrations of the chromium species on rate constants and time for a first-order consecutive reversible two-stage reaction scheme. These functions undergo a remarkable simplification when one or more of the velocity constants is reduced to zero. Thus, if the second stage is irreversible, $k_4 = 0$, we end up with Scheme 2, if the first stage is irreversible, $k_2 = 0$, we have Scheme 3 and if both stages are irreversible, $k_2 = k_4 = 0$, we have Scheme 1. This solution is thus a general solution for two-stage consecutive first-order reactions.

APPENDIX B

The program below computes rate constants for a typical set of data using a method which minimises the sums of squares of deviations between the observed and calculated concentrations. Ten thousand loops are performed to arrive at the rate constants giving the least sums of squares of deviations. This program and those that follow later are written in Fortran 77.

Variable name	Description
H	Slag height, cm.
M1, M2	Roots to equation (A.11)
CR3	Calculated (Cr^{3+}) concentration
CR2	Calculated (Cr^{2+}) concentration
CRFE	Calculated [Cr] concentration
CR	Calculated concentration of total chromium in slag
CRO	Initial concentration of total chromium in slag
T	Number of data points
K1, K2, K3, K4	Rate constants for consecutive reversible two-stage reactions
CRWT	Weight of chromium in slag
CR3D	Observed (Cr^{3+}) concentration
CR2D	Observed (Cr^{2+}) concentration

CRFED	Observed [Cr] concentration
LA	Sums of squares of deviations between observed and calculated (Cr^{3+}) concentrations
LB	Sums of squares of deviations between observed and calculated (Cr^{2+}) concentrations
LC	Sums of squares of deviations between observed and calculated [Cr] concentrations
L	Total sums of squares of deviations (SUMA + SUMB + SUMC)
K1MIN,K2MIN, K3MIN,K4MIN	Rate constants giving minimum sums of squares of deviations
LMIN	Total minimum sums of squares of deviations
G05CAF, G05CBF	External subroutines for generating random numbers
SIMUMIN.OUT	Out put file for the rate constants
SIGMA	A factor for changing rate constants
ITER	Number of loops

```
      PROGRAM SIMUMIN

C     This program computes the rate constants for a
C     typical set of data from the reduction of Cr2O3 from
C     slag using an iteration method and expressions for
C     the variation of the concentrations of the chromium
C     species obtained for a consecutive reversible
C     two-stage reaction scheme in appendix A.

      INTEGER  J, T, TIME
      REAL     H,A1,A2,A3,B1,B2,B3,B4,B5,C1,C2,C3,C4,C5,
     $         C6,C7,K1,K2,K3,K4,M1,M2,CR3,CR2,CR,CRO,L,
     $         CRWT,CRFE,CR3D,CR2D,CRFED,LMIN,K1MIN,
     $         K2MIN,K3MIN,K4MIN
      DIMENSION  CR3(20),CR2(20),CR(20),CRWT(20),
     $           CRFE(20),CR3D(20),CR2D(20),CRFED(20),
     $           TIME(20)
      CHARACTER NAME*13
      DOUBLE PRECISION X,G05CAF
      EXTERNAL G05CAF, G05CBF
      CALL G05CAF(0)
      LMIN = 1000.0
      OPEN (6,FILE='SIMUMIN.OUT',STATUS='OLD')

C     The height of slag is entered, calculated by
C     considering slag density to be 2.8 g/cc with slag
C     weight of 20 g and crucible diameter used of 3.2 cm.

      WRITE (*,*) 'ENTER SLAG HEIGHT'
      READ (*,'(F6.4)')H
      WRITE(*,'(1X,F6.4)')H

C     The number of data points and the name of the file
C     containing data are entered.

      WRITE (*,*) 'ENTER NUMBER OF DATA POINTS'
```

```
      READ (*,'(I3)')T
      WRITE (*,'(1X,I3)')T
      WRITE (*,*) 'ENTER DATA FILE NAME'
      READ (*,'(A13)')NAME
      OPEN(UNIT=7,FILE=NAME,STATUS='OLD',FORM=FORMATTED)

C     Input data from file above

      DO 999 IL = 1,16
        READ(7,*)
999   CONTINUE
      DO 998 IL = 1,8
        READ(7,*)TIME(IL),Z,Z,Z,CR3D(IL),CR2D(IL),Z,
     $  CRFED(IL)
998   CONTINUE
      CLOSE(7)
      WRITE(*,*)TIME(3),CR3D(3),CR2D(3),CRFED(3)

C     Input the initial total concentration of chromium in
C     slag and guess the rate constants to start the
C     iteration with. The rate constants have units of
C     cm.min^-1.

      WRITE (*,*) 'ENTER INITIAL CONCENTRATION'
      READ (*,'(F6.4)')CRO
      WRITE (*,'(1X,F6.4)')CRO
      WRITE (*,*) 'ENTER RATE CONSTANTS K1,K2,K3,K4'
      READ (*,'(4F6.4)')K1,K2,K3,K4
      WRITE (*,'(1X,F6.4)')K1,K2,K3,K4

C     Major loop. The expressions for variation of the
C     chromium species with time and rate constants are
C     broken down into variables which are later combined
C     to effect the calculation. Each loop goes
C     through all the data points.
```

```
      DO 777 ITER = 1,10000
      A1 = (K1 + K2 + K3 + K4)/H
      A2 = A1**2
      A3 = (K1*K3 + K2*K4 + K1*K4)/H**2
      M1 = 0.5*(A1 + SQRT(A2 - 4*A3))
      M2 = 0.5*(A1 - SQRT(A2 - 4*A3))
      B1 = (K2*K4)/(H**2*M1*M2)
      C1 = (K2 + K3 + K4)/H
      C2 = (K2*K4)/H**2
      B2 = (M1**2 - M1*C1 + C2)/(M1*(M1 - M2))
      B3 = (M2**2 - M2*C1 + C2)/(M2*(M2 - M1))
      C3 = (K4/H) - M1
      C4 = (K4/H) - M2
      B4 = C3/(M1*(M2 - M1))
      B5 = C4/(M2*(M1 - M2))
      C5 = (K1*K3/H**2)*CRO
      C6 = (K1/H)*CRO
      C7 = K4/(M1*M2*H)

C     Calculate the concentrations of the chromium  species
C     at different data points (times).

      DO 10 J = 1,T
      CR3(J) = CRO*(B1 + B2*EXP(-M1*TIME(J))
     $       + B3*EXP(-M2*TIME(J)))
      CR2(J) = C6*(C7 - B4*EXP(-M1*TIME(J))
     $       - B5*EXP(-M2*TIME(J)))
      CR(J) = C5*((M1*M2)**-1 - ((M1*(M2 - M1))**-1)
     $*EXP(-M1*TIME(J)) - ((M2*(M1 - M2))**-1
     $*EXP(-M2*TIME(J)))
      CRWT(J) = (CR(J)/100)*20
      CRFE(J) = (CRWT(J)/(60 + CRWT(J)))*100
10    CONTINUE
      LA = 0
      LB = 0
      LC = 0
```

```
C   The sums of squares of deviations for the chromium
C   species are computed.

      DO 888 J = 1,T
        LA = LA + (CR3(J) - CR3D(J))**2
        LB = LB + (CR2(J) - CR2D(J))**2
        LC = LC + (CRFE(J) - CRFED(J))**2
888   CONTINUE
      L = LA + LB + LC
      IF (L.LT.LMIN)THEN
        LMIN = L
        K1MIN = K1
        K2MIN = K2
        K3MIN = K3
        K4MIN = K4
      WRITE(*,*) 'L ',L,' LA ',LA,' LB ',LB,' LC ',LC
          ELSE
        K1 = K1MIN
        K2 = K2MIN
        K3 = K3MIN
        K4 = K4MIN
      ENDIF

C   A rundom number is generated which when multiplied
C   by 4 gives a number between 0 and 4. This determines
C   which rate constant to change. The amount by which
C   it changes is determined by the subroutine called
C   'change' in this case.

      X = G05CAF(X)
      ICHANGE = 4*X
      IF(ICHANGE.EQ.0)CALL CHANGE(K1,X,0.001)
      IF(ICHANGE.EQ.1)CALL CHANGE(K2,X,0.0001)
      IF(ICHANGE.EQ.2)CALL CHANGE(K3,X,0.001)
      IF(ICHANGE.EQ.3)CALL CHANGE(K4,X,0.0001)
```

```
777   CONTINUE
      WRITE (6,20)
      WRITE (6,21)
      WRITE(6,25)K1MIN,K2MIN,K3MIN,K4MIN,LA,LB,LC
20    FORMAT(/,'       RATE CONSTANTS       ',/,
     $5X,'_____________________________________________')
21    FORMAT(/,' K1MIN K2MIN K3MIN K4MIN LA LB LC',/,
     $5X,'_____________________________________________')
25    FORMAT(/,3X,6(5X,F6.4))
      WRITE (*,*) 'PROGRAM COMPLETED SUCCESFULLY'
      STOP
      END


      SUBROUTINE CHANGE(K,X,SIGMA)
      REAL  K,SIGMA
      DOUBLE PRECISION  X
      X = K + (X - 0.5)*SIGMA
      RETURN
      END
```

OUTPUT

K1MIN	K2MIN	K3MIN	K4MIN	LA	LB	LC
0.0238	0.0198	0.0760	0.0313	0.004	0.042	0.006

APPENDIX C

The computer program shown in this appendix calculates the concentrations of the chromium species with time using the expressions from appendix A, for a consecutive reversible two-stage reaction scheme, and the rate constants obtained in appendix B. The height of slag is assumed to be constant throughout an experimental run in this program The description of the variable names is the same as that in appendix B.

```
      PROGRAM SIMU
      INTEGER  J,K,T
      REAL  H,A1,A2,A3,B1,B2,B3,B4,B5,C1,C2,C3,C4,C5,
     $      C6,C7,K1,K2,K3,K4,M1,M2,CR3,CR2,CR,CRO,CRWT,
     $      CRFE
      DIMENSION  CR3(20),CR2(20),CR(20),CRWT(20),
     $           CRFE(20)
      OPEN(6,FILE='SIMU.OUT',STATUS='OLD')
      WRITE (*,*) 'ENTER SLAG HEIGHT'
      READ (*,'(F6.4)')H
      WRITE(*,'(1X,F6.4)')H

C     The period of a run is entered here in minutes

      WRITE(*,*) 'ENTER EXPERIMENTAL TIME'
      READ (*,'(I3)')T
      WRITE(*,'(1X,I3)')T

C     The rate constants for a particular set of data
C     calculated in appendix B are read from their file and
```

```
C   are used in the calculation below

      OPEN(8,FILE='SIMUMIN.OUT',STATUS='OLD',
     $FORM='FORMATTED')
      DO 666  IL = 1,7
        READ (8,*)
666   CONTINUE
      READ (8,*)K1,K2,K3,K4
      CLOSE (8)
      WRITE(*,*)K1,K2,K3,K4
      WRITE (*,*) 'ENTER INITIAL CONCENTRATION'
      READ (*,'(F6.4)')CRO
      WRITE (*,'(1X,F6.4)')CRO

C   Major loop

      A1 = (K1 + K2 + K3 + K4)/H
      A2 = A1**2
      A3 = (K1*K3 + K2*K4 + K1*K4)/H**2
      M1 = 0.5*(A1 + SQRT(A2 - 4*A3))
      M2 = 0.5*(A1 - SQRT(A2 - 4*A3))
      B1 = (K2*K4)/(H**2*M1*M2)
      C1 = (K2 + K3 + K4)/H
      C2 = (K2*K4)H**2
      B2 = (M1**2 - M1*C1 + C2)/(M1*(M1 - M2))
      B3 = (M2**2 - M2*C1 + C2)/(M2*(M2 - M1))
      C3 = (K4/H) - M1
      C4 = (K4/H) - M2
      B4 = C3/(M1*(M2 - M1))
      B5 = C4/(M2*(M1 - M2))
      C5 = (K1*K3/H**2)*CRO
      C6 = (K1/H)*CRO
      C7 = K4/(M1*M2*H)
      DO  10 J = 1,T
      CR3(J) = CRO*(B1 + B2*EXP(-M1*J) + B3*EXP(-M2*J))
      CR2(J) = C6*(C7 - B4*EXP(-M1*J) - B5*EXP(-M2*J))
```

```
      CR(J) = C5*((M1*M2)**-1 - ((M1*(M2 M1))**-1)
     $*EXP(-M1*J) - ((M2*(M1 - M2))**-1)*EXP(-M2*J))
      CRWT(J) = (CR(J)/100)*20
      CRFE(J) = (CRWT(J)/(60 + CRWT(J)))*100
10    CONTINUE
      WRITE (6,20)
      WRITE (6,21)
      DO  40 K = 1,T
      WRITE (6,25)K,CR3(K),CR2(K),CRFE(K)
40    CONTINUE
20    FORMAT (/,'     WEIGHT PERCENT AGAINST TIME',/,
     $5X,'_____________________________________________________')
21    FORMAT (/,'      K     CR3(K)    CR2(K)    CRFE(K)',/,
     $5X,'_____________________________________________________')
25    FORMAT (/,3X,I3,3(5X,F6.4))
      WRITE (*,*) ' PROGRAM COMPLETED SUCCESFULLY '
      STOP
      END
```

The output to this program is shown on the next page and the data is used to plot calculated curves of the chromium species which are superimposed on the observed results as shown in chapters 4 and 5.

WEIGHT PERCENTAGES AGAINST TIME

K	CR3(K)	CR2(K)	CRFE(K)
1	3.3305	0.0858	0.0012
2	3.2452	0.1608	0.0047
3	3.1636	0.2265	0.0100
4	3.0856	0.2840	0.0168
5	3.0108	0.3345	0.0249
6	2.9391	0.3788	0.0340
7	2.8701	0.4177	0.0440
8	2.8038	0.4520	0.0547
9	2.7399	0.4823	0.0659
10	2.6784	0.5089	0.0775
11	2.6190	0.5326	0.0894
12	2.5617	0.5535	0.1015
13	2.5063	0.5720	0.1137
14	2.4528	0.5886	0.1260
15	2.4011	0.6033	0.1384

K	CR3(K)	CR2(K)	CRFE(K)
16	2.3510	0.6165	0.1506
17	2.3025	0.6283	0.1628
18	2.2556	0.6389	0.1749
19	2.2101	0.6484	0.1868
20	2.1660	0.6571	0.1986
21	2.1233	0.6649	0.2102
22	2.0818	0.6720	0.2216
23	2.0416	0.6785	0.2328
24	2.0026	0.6844	0.2437
25	1.9648	0.6898	0.2545
26	1.9280	0.6948	0.2650
27	1.8924	0.6995	0.2753
28	1.8578	0.7038	0.2853
29	1.8242	0.7077	0.2952
30	1.7916	0.7115	0.3047
31	1.7599	0.7149	0.3141
32	1.7291	0.7182	0.3232

K	CR3 (K)	CR2 (K)	CRFE (K)
33	1.6992	0.7212	0.3321
34	1.6702	0.7241	0.3407
35	1.6420	0.7268	0.3492
36	1.6146	0.7294	0.3574
37	1.5879	0.7319	0.3654
38	1.5621	0.7342	0.3732
39	1.5369	0.7364	0.3808
40	1.5125	0.7385	0.3881
41	1.4888	0.7405	0.3953
42	1.4657	0.7425	0.4023
43	1.4433	0.7443	0.4091
44	1.4215	0.7461	0.4157
45	1.4004	0.7478	0.4221
46	1.3798	0.7495	0.4284
47	1.3598	0.7511	0.4345
48	1.3404	0.7526	0.4404
49	1.3215	0.7541	0.4461

K	CR3(K)	CR2(K)	CRFE(K)
50	1.3032	0.7555	0.4517
51	1.2854	0.7569	0.4571
52	1.2680	0.7582	0.4624
53	1.2512	0.7595	0.4676
54	1.2348	0.7608	0.4726
55	1.2189	0.7620	0.4774
56	1.2035	0.7631	0.4821
57	1.1885	0.7643	0.4867
58	1.1739	0.7654	0.4912
59	1.1597	0.7664	0.4955
60	1.1459	0.7675	0.4997
61	1.1325	0.7685	0.5038
62	1.1194	0.7695	0.5078
63	1.1068	0.7704	0.5116
64	1.0945	0.7713	0.5154
65	1.0825	0.7722	0.5191
66	1.0709	0.7731	0.5226

K	CR3(K)	CR2(K)	CRFE(K)
67	1.0596	0.7739	0.5261
68	1.0486	0.7747	0.5294
69	1.0379	0.7755	0.5327
70	1.0275	0.7763	0.5358
71	1.0174	0.7770	0.5389
72	1.0076	0.7778	0.5419
73	0.9981	0.7785	0.5448
74	0.9888	0.7792	0.5477
75	0.9798	0.7798	0.5504
76	0.9711	0.7805	0.5531
77	0.9626	0.7811	0.5557
78	0.9543	0.7817	0.5582
79	0.9463	0.7823	0.5606
80	0.9385	0.7829	0.5630
81	0.9309	0.7834	0.5653
82	0.9235	0.7840	0.5676
83	0.9164	0.7845	0.5698

K	CR3 (K)	CR2 (K)	CRFE (K)
84	0.9094	0.7850	0.5719
85	0.9026	0.7855	0.5740
86	0.8960	0.7860	0.5760
87	0.8896	0.7865	0.5779
88	0.8834	0.7869	0.5798
89	0.8774	0.7874	0.5817
90	0.8715	0.7878	0.5835
91	0.8658	0.7882	0.5852
92	0.8602	0.7886	0.5869
93	0.8548	0.7890	0.5886
94	0.8496	0.7894	0.5902
95	0.8445	0.7898	0.5917
96	0.8395	0.7902	0.5932
97	0.8347	0.7905	0.5947
98	0.8301	0.7909	0.5961
99	0.8255	0.7912	0.5975
100	0.8211	0.7915	0.5989

K	CR3 (K)	CR2 (K)	CRFE (K)
101	0.8168	0.7918	0.6002
102	0.8126	0.7921	0.6014
103	0.8086	0.7924	0.6027
104	0.8046	0.7927	0.6039
105	0.8008	0.7930	0.6051
106	0.7971	0.7933	0.6062
107	0.7934	0.7936	0.6073
108	0.7899	0.7938	0.6084
109	0.7865	0.7941	0.6094
110	0.7832	0.7943	0.6104
111	0.7799	0.7946	0.6114
112	0.7768	0.7948	0.6124
113	0.7737	0.7950	0.6133
114	0.7708	0.7952	0.6142
115	0.7679	0.7954	0.6151
116	0.7651	0.7957	0.6159
117	0.7623	0.7959	0.6168

K	CR3(K)	CR2(K)	CRFE(K)
118	0.7597	0.7960	0.6176
119	0.7571	0.7962	0.6184
120	0.7546	0.7964	0.6191

APPENDIX D

The program given below computes rate constants for a typical set of data by a method which minimises the sums of squares of deviations between the calculated and observed concentrations of the chromium species. The variation in slag height due to sampling is taken into account. Each time interval has a diiferent slag height and the final concentrations of the previous interval become the initial concentrations of the following interval. Some variable names used in the program and their description are given below. The variable names left out of this description are described in appendix B. The output is similar to appendix B.

Variable name	Description
B21, B22, B23, B31, B32, B33	The coefficients B from Frost and Pearson's[54] treatment
DETB	The determinant of the matrix of the coefficients B
CR3O, CR2O, CRO	Initial concentrations of the chromium species
CRT	Total concentration of chromium in slag
WT	Weight of slag in each time

	interval
INC	Initial weight of chromium in slag in each time interval
WTDF	Difference in the weight of chromium in slag between initial and final time in each interval
SLAGMIN.OUT	Output file for the rate constants
TINV	Time interval

```
      PROGRAM SLAGMIN
      INTEGER  I,K,C,T,TIME,TINV
      REAL  K1,K2,K3,K4,B21,B22,B23,B31,B32,B33,DETB,
     $      M1,M2,CR3O,CR2O,CRO,CR3,CR2,CR,CRWT,CRFE,
     $      A1,A2,A3,D1,D2,D3,E1,E2,E3,F1,F2,F3,SS1,
     $      SS2,SS3,SS4,SS5,SS6,SS7,SS8,SS9,WT,H,SUM,
     $      WTDF,CRT,INC,CR3D,CR2D,CRFED,L,LA,LB,LC,
     $      LMIN,K1MIN,K2MIN,K3MIN,K4MIN
      DIMENSION  SS1(20),SS2(20),SS3(20),SS4(20),SS5(20)
     $           SS6(20),SS7(20),SS8(20),SS9(20),CR3(20),
     $           CR2(20),CR(20),CRWT(20),CRFE(20),
     $           CR3O(20),CR2O(20),CRO(20),CRT(20),
     $           WTDF(20),CR3D(20),CR2D(20),CRFED(20),
     $           TIME(20),WT(20)
      DOUBLE PRECISION  X,GO5CAF
      CHARACTER NAME*13
      CALL GO5CAF (0)
      LMIN = 1000.0
      OPEN(6,FILE='SLAGMIN.OUT',STATUS='OLD')
```

```
C     The guess rate constants and the initial
C     concentrations of the chromium species are entered

      WRITE (*,*) 'ENTER RATE CONSTANTS K1,K2,K3,K4'
      READ (*,'(4F6.4)')K1,K2,K3,K4
      WRITE (*,(1X,4F6.4)')K1,K2,K3,K4
      WRITE (*,*) 'ENTER INITIAL CONCENTRATIONS'
      READ (*,(3F6.4)')CR3OS,CR2OS,CROS
      CRTS = CR3OS + CR2OS

C     The number of experimental points and the file
C     containing data are entered

      WRITE (*,*) 'ENTER NUMBER OF DATA POINTS'
      READ (*,'(I3)')T
      WRITE (*,'(1X,I3)')T
      WRITE(*,*) 'ENTER DATA FILE NAME'
      READ (*,'(A13)')NAME
      OPEN(7,FILE=NAME,STATUS='OLD',FORM='FORMATTED')
      DO  999  IL = 1,16
         READ (7,*)
999   CONTINUE
      DO  998  IL = 1,8
      READ (7,*)TIME(IL),Z,WT(IL),Z,CR3D(IL),CR2D(IL),
     $Z,CRFED(IL)
998   CONTINUE
      CLOSE (7)
      WRITE(*,*)TIME(3),WT(3),CR3D(3),CR2D(3),CRFED(3)
      DO  777  ITER = 1,10000
      CR3O(1) = CR3OS
      CR2O(1) = CR2OS
      CRO(1) = CROS
      CRT(1) = CRTS
      SUM = 0.0
      DO  20 I = 2,T
      TINV = TIME(I) - TIME(I-1)
```

```
 INC = (CRT(1)/100)*WT(I)
 H = 0.0444*WT(I)
 A1 = (K1 + K2 + K3 + K4)/H
 A2 = A1**2
 A3 = (K1*K3 + K2*K4 + K1*K4)/H**2
 M1 = 0.5*(A1 + SQRT(A2 - 4*A3))
 M2 = 0.5*(A1 - SQRT(A2 - 4*A3))
 B21 = K1/K2
 B22 = (K1 - M1*H)/K2
 B23 = (K1 - M2*H)/K2
 B31 = (K1*K3)/(K2*K4)
 B32 = (K3*(K1 - M1*H))/(K2*(K4 - M1*H))
 IF(ABS(K4-M2*H).GT.1.0E-3)THEN
   B33 = (K3*(K1 - M2*H))/(K2*(K4 - M2*H))
 ELSE
   B33 = K3/K2
 ENDIF
 DETB = B22*B33 + B23*B31 + B21*B32 - B31*B22
$       - B32*B23 - B33*B21
 D1 = B22*B33 - B23*B32
 D2 = B31*B23 - B21*B33
 D3 = B21*B32 - B31*B22
 E1 = B32 - B33
 E2 = B33 - B31
 E3 = B31 - B32
 F1 = B23 - B22
 F2 = B21 - B23
 F3 = B22 - B21
 SS1(I) = CR3O(1)*(D1 + D2*EXP(-M1*TINV) + D3*EXP
$ (-M2*TINV))
 SS2(I) = CR2O(1)*(E1 + E2*EXP(-M1*TINV) + E3*EXP
$ (-M2*TINV))
 SS3(I) = CRO(1)*(F1 + F2*EXP(-M1*TINV) + F3*EXP
$ (-M2*TINV))
 CR3(I) = (SS1(I) + SS2(I) + SS3(I))/DETB
 SS4(I) = CR3O(1)*(B21*D1 + B22*D2*EXP(-M1*TINV)
```

```
     $ + B23*D3*EXP(-M2*TINV))
      SS5(I) = CR2O(1)*(B21*E1 + B22*E2*EXP(-M1*TINV)
     $ + B23*E3*EXP(-M2*TINV))
      SS6(I) = CRO(1)*(B21*F1 + B22*F2*EXP(-M1*TINV)
     $ + B23*F3*EXP(-M2*TINV))
      CR2(I) = (SS4(I) + SS5(I) + SS6(I))/DETB
      SS7(I) = CR3O(1)*(B31*D1 + B32*D2*EXP(-M1*TINV)
     $ + B33*D3*EXP(-M2*TINV))
      SS8(I) = CR2O(1)*(B31*E1 + B32*E2*EXP(-M1*TINV)
     $ + B33*E3*EXP(-M2*TINV))
      SS9(I) = CRO(1)*(B31*F1 + B32*F2*EXP(-M1*TINV)
     $ + B33*F3*EXP(-M2*TINV))
      CR(I) = (SS7(I) + SS8(I) + SS9(I))/DETB
      CRT(I) = CR3(I) + CR2(I)
      CRWT(I) = (CRT(I)/100)*WT(I)
      WTDF(I) = INC - CRWT(I) + SUM
      CRFE(I) = (WTDT(I)/(60 + WTDT(I)))*100

C     The initial conditions for the next interval are
C     assigned

      CR3O(1) = CR3(I)
      CR2O(1) = CR2(I)
      CRO(1) = CR(I)
      CRT(1) = CRT(I)
      SUM = WTDT(I)
20    CONTINUE
      LA = 0.0
      LB = 0.0
      LC = 0.0
      DO  888 J = 2,T
        LA = LA + (CR3(J) - CR3D(J))**2
        LB = LB + (CR2(J) - CR2D(J))**2
        LC = LC + (CRFE(J) - CRFED(J))**2
888   CONTINUE
      L = LA + LB + LC
```

```
      IF(L.LT.LMIN)THEN
        LMIN = L
        K1MIN = K1
        K2MIN = K2
        K3MIN = K3
        K4MIN = K4
       WRITE (*,*) 'L ',L,' LA ',LA,' LB ',LB,' LC ',LC,
     $ 'ITER ',ITER
          ELSE
        K1 = K1MIN
        K2 = K2MIN
        K3 = K3MIN
        K4 = K4MIN
       ENDIF

C    A rundom number is generated by an external
C    subroutine called G05CAF.  Multiplying the number
C    generated by 4 determines which rate constant to
C    change.  A second generation of a rundom number gives
C    value by which rate constant is to change

       X = G05CAF(X)
       IF(INT(4*X).EQ.0)CALL CHANGE(K1,X,0.001)
       IF(INT(4*X).EQ.1)CALL CHANGE(K2,X,0.0001)
       IF(INT(4*X).EQ.2)CALL CHANGE(K3,X,0.001)
       IF(INT(4*X).EQ.3)THEN
99       CALL CHANGE(K4,X,0.0001)
         A1 = K1 + K2 + K3 + K4
         A3 = K1*K3 + K2*K4 + K1*K4
         M2 = (0.5*(A1 - SQRT(A1**2 - 4*A3)))/H
         IF(ABS(K4 - M2*H).LT.1.0E-8)GO TO 99
       ENDIF
777    CONTINUE
       WRITE(6,60)
       WRITE(6,66)
       WRITE(6,30) K1MIN, K2MIN, K3MIN, K4MIN, LA, LB, LC
```

```
60    FORMAT(/,'       RATE CONSTANTS  ',/,
     $5X,'_____________________________________________')
66    FORMAT(/, K1MIN K2MIN K3MIN K4MIN LA LB LC ',/,
     $5X,'_____________________________________________')
30    FORMAT (/,3X,7(5X,F6.4))
      WRITE (*,*) 'PROGRAM COMPLTED SUCCESSFULLY'
      STOP
      END



      SUBROUTINE  CHANGE(K,X,SIGMA)
      REAL  K,SIGMA
      DOUBLE PRECISION  X
99    X = GO5CAF(X)
      K = K + (X - 0.5)*SIGMA
      IF(K.LT.0.0)GO TO 99
      RETURN
      END
```

APPENDIX E

The program below calculates the concentrations of the chromium species using expressions for a consecutive reversible two-stage reaction scheme and consideration of the varying slag height due to sampling. The rate constants generated from appendix D are used in the calculation. The curves calculated are then compared with the observed concentrations for a particular run. Description of variable names is similar to that in appendices B and D. The output is similar to that in appendix C.

```
      PROGRAM SLAG
      INTEGER  I,K,J,C,T,SUMA,SUMB,TIME
      REAL  K1,K2,K3,K4,B21,B22,B23,B31,B32,B33,DETB,
     $      M1,M2,CR3O,CR2O,CRO,CR3,CR2,CR,CRWT,CRFE,
     $      A1,A2,A3,D1,D2,D3,E1,E2,E3,F1,F2,F3,SS1,
     $      SS2,SS3,SS4,SS5,SS6,SS7,SS8,SS9,WT,H,SUM,
     $      INCR,WTDF,CRT,INC
      DIMENSION  SS1(120),SS2(120),SS3(120),SS4(120),
     $           SS5(120),SS6(120),SS7(120),SS8(120),
     $           SS9(120),CR3(120),CR2(120),CR(120),
     $           CRWT(120),CRFE(120),CR3O(120),CR2O(120),
     $           CRO(120),CRT(120),WTDF(120),TIME(10),
     $           WT(10)
      CHARACTER NAME*13
      OPEN (7,FILE='SLAG.OUT',STATUS='OLD')

C     The rate constants are read from the output file of
```

```
C   the program in appendix D

      WRITE(*,*) 'ENTER RATE CONSTANTS K1,K2,K3,K4'
      OPEN(8,FILE='SLAGMIN.OUT',STATUS='OLD',
     $FORM=FORMATTED')
      DO  666  IL = 1,7
        READ(8,*)
666   CONTINUE
      READ (8,*)K1,K2,K3,K4,Z,Z
      CLOSE(8)
      WRITE(*,*)K1,K2,K3,K4

C   The initial concentrations of the chromium species
C   are entered. This program will take other initial
C   conditions where (Cr2+) and [Cr] are non-zero at time
C   zero

      WRITE (*,*) 'ENTER INITIAL CONCENTRATIONS CR3O(1)
     $CR2O(1),CRO(1)'
      READ (*,'3F6.4)')CR3O(1),CR2O(1),CRO(1)
      CRT(1) = CR3O(1) + CR2O(1)
      INCR = (CRT(1)/100)*20
      C = 0
      SUM = 0
      SUMA = 0
      SUMB = 0

C   The number of experimental points and the file
C   containing data are entered

      WRITE (*,*) 'ENTER NUMBER OF DATA POINTS'
      READ (*,'(I3)')T
      WRITE (*,'(1X,I3)')T
      WRITE (*,*) 'ENTER DATA FILE NAME'
      READ (*,'(A13)')NAME
      OPEN(5,FILE=NAME,STATUS='OLD',FORM=FORMATTED')
```

```
      DO  999  IL = 1,16
        READ (5,*)
999   CONTINUE
      DO  998  IL = 1,8
         READ(5,*)TIME(IL),Z,WT(IL),Z,Z,Z,Z,Z
998   CONTINUE
      CLOSE(5)
      WRITE(*,*)TIME(3),WT(3)

C   Top of major loop

      DO  90 J = 2,T
      TINV = TIME(J) - TIME(J-1)
      IF (CRT(1).EQ.3.42)THEN
      INC = INCR
        ELSE
          INC = (CRT(1)/100)*WT(J)
            ENDIF
      H = 0.0444*WT(J)
      A1 = (K1 + K2 + K3 + K4)/H
      A2 = A1**2
      A3 = (k1*K3 + K2*K4 + K1*K4)/H**2
      M1 = 0.5*(A1 + SQRT(A2 - 4*A3))
      M2 = 0.5*(A1 - SQRT(A2 - 4*A3))
      B21 = K1/K2
      B22 = (K1 - M1*H)K2
      B23 = (K1 - M2*H)/K2
      B31 = (K1*K3)/(K2*K4)
      B32 = (K3*(K1 - M1*H))/(K2*(K4 - M1*H))
      B33 = (K3*(K1 - M2*H))/(K2*(K4 - M2*H))

C     DETB is the determinant of the matrix of the
C     coefficients B_i j

      DETB = B22*B33 + B23*B31 + B21*B32 - B31*B22
     $     - B32*B23 - B33*B21
```

```
      D1 = B22*B33 - B23*B32
      D2 = B31*B23 - B21*B33
      D3 = B21*B32 - B31*B22
      E1 = B32 - B33
      E2 = B33 - B31
      E3 = B31 - B32
      F1 = B23 - B22
      F2 = B21 - B23
      F3 = B22 - B21
      DO  20 I = 1,TINV
      SS1(I) = CR3O(1)*(D1 + D2*EXP(-M1*I)
     $  + D3*EXP(-M2*I))
      SS2(I) = CR2O(1)*(E1 + E2*EXP(-M1*I)
     $  + E3*EXP(-M2*I))
      SS3(I)= CRO(1)*(F1 + F2*EXP(-M1*I) + F3*EXP(-M2*I))
      CR3(I) = (SS1(I) + SS2(I) + SS3(I))/DETB
      SS4(I)= CR3O(1)*(B21*D1 + B22*D2*EXP(-M1*I)
     $   + B23*D3*EXP(-M2*I))
      SS5(I)= CR2O(1)*(B21*E1 + B22*E2*EXP(-M1*I)
     $   + B23*E3*EXP(-M2*I))
      SS6(I)= CRO(1)*(B21*F1 + B22*F2*EXP(-M1*I)
     $   + B23*F3*EXP(-M2*I))
      CR2(I) = (SS4(I) + SS5(I) + SS6(I))/DETB
      SS7(I)= CR3O(1)*(B31*D1 + B32*D2*EXP(-M1*I)
     $   + B33*D3*EXP(-M2*I))
      SS8(I)= CR2O(1)*(B31*E1 + B32*E2*EXP(-M1*I)
     $   + B33*E3*EXP(-M2*I))
      SS9(I)= CRO(1)*(B31*F1 + B32*F2*EXP(-M1*I)
     $   + B33*F3*EXP(-M2*I))
      CR(I) = (SS7(I) + SS8(I) + SS9(I))/DETB
      CRT(I) = CR3(I) + CR2(I)
      CRWT(I) = (CRT(I)/100)*WT(J)
      WTDF(I) = INC - CRWT(I) + SUM
      CRFE(I) = (WTDF(I)/(60 + WTDF(I)))*100

C     The initial conditions for the next time interval are
```

```
C    assigned

       IF (I.EQ.TINV)THEN
       CR30(1) = CR3(I)
       CR20(1) = CR2(I)
       CRO(1) = CR(I)
       CRT(1) = CRT(I)
       SUM = WTDF(I)
         ELSE
           GO TO 20
             ENDIF
20     CONTINUE
       WRITE (7,60)
       WRITE (7,66)
       DO 40 K = 1,TINV
       SUMB = K + SUMA
       WRITE (7,30)SUMB,CR3(K),CR2(K),CRFE(K)
       IF(K.EQ.TINV)THEN
       SUMA = SUMB
         ELSE
          GO TO 40
            ENDIF
40     CONTINUE

C    The number of time intervals are counted

       C = C + 1
       IF (C.LE.7)THEN
         GO TO 90
           ELSE
             GO TO 45
              ENDIF
90     CONTINUE
45     CONTINUE
60     FORMAT (/,'     WEIGHT PERCENT AGAINST TIME    ',/,
      $5X,'_____________________________________________')
```

```
66    FORMAT (/,'  SUMB  CR3(K)  CR2(K)  CRFE(K) ',/,
     $5X,'_____________________________________________')
30    FORMAT (/,3X,I3,3(5X,F6.4))
      WRITE (*,*) 'PROGRAM COMPLETED SUCCESSFULLY'
      STOP
      END
```

APPENDIX F

The program below calculates average rate constants for three sets of data by minimisation of the sums of squares of deviations of the chromium species from the three sets of data at the same time using scheme 4. The iteration method used is similar to that in appendices B and D. The description of the variable names is as before.

```
      PROGRAM LAGMIN
      INTEGER I,K,C,T,SUMA,SUMB,TIME,D
      REAL K1,K4,K3,K4,B21,B22,B23,B31,B32,B33,DETB,M2,
     $     M3,CR3O,CR2O,CRO,CR3,CR2,CR,CRWT,CRFE,A1,A2,
     $     A3,D1,D2,D3,E1,E2,E3,F1,F2,F3,SS1,SS2,SS3,
     $     SS4,SS5,SS6,SS7,SS8,SS9,WT,H,SUM,INCR,WTDF,
     $     CRT,INC,CR3D,CR2D,CRFED,L,LA,CRTO,LB,LC,LMIN,
     $     K1MIN,K2MIN,K3MIN,K4MIN
      DIMENSION  SS1(20,5),SS2(20,5),SS3(20,5),SS4(20,5),
     $           SS5(20,5),SS6(20,5),SS7(20,5),SS8(20,5),
     $           SS9(20,5),CR3(20,5),CR2(20,5),CR(20,5),
     $           CRWT(20,5),CRFE(20,5),CR3O(20),CR2O(20),
     $           CRO(20),CRTO(20),CRT(20,5),WTDF(20,5),
     $           LA(5),LB(5),LC(5),CR3OS(5),CR2OS(5),
     $           CROS(5),CRTS(5),CR3D(10,5),CR2D(10,5),
     $           CRFED(10,5),TIME(10,5),WT(10,5)
      DOUBLE PRECISION X,GO5CAF
      CHARACTER NAME*13
      CALL GO5CBF(0)
      LMIN = 1000.0
      OPEN (8,FILE='LAGMIN.OUT',STATUS='OLD')
```

```
C     The guessed rate constants and the number of
C     data sets are entered

      WRITE (*,*) 'ENTER RATE CONSTANTS K1,K2,K3,K4'
      READ (*,'(4F6.4)')K1,K2,K3,K4
      WRITE (*,'(1X,4F6.4)')K1,K2,K3,K4
      WRITE(*,*) 'ENTER NUMBER OF DATA SETS'
      READ (*,'(I3)')D
      WRITE(*,'(1X,I3)')D

C     The initial concentrations of the chromium species
C     for each data set are entered

      DO 80 J = 1,D
      WRITE (*,*) 'ENTER INITIAL CONCENTRATIONS CR3O(1),
     $CR2O(1),CRO(1)'
      READ (*,'(3F6.4)')CR3OS(J),CR2OS(J),CROS(J)
      CRTS(J) = CR3OS(J) + CR2OS(J)

C     The number of experimental points and the file
C     containing data are entered

      WRITE (*,*) 'ENTER NUMBER OF DATA POINTS'
      READ (*,(I3)')T
      WRITE(*,'(1X,I3)')T
      WRITE (*,*) 'ENTER DATA FILE NAME'
      READ (*,'(A13)')NAME

C     The data from file is read

      OPEN(UNIT=7,FILE=NAME,STATUS='OLD',FORM=FORMATTED')
      DO 999 IL = 1,16
       READ(7,*)
999   CONTINUE
      DO 998 IL = 1,8
       READ(7,*)TIME(IL,J),Z,WT(IL,J),Z,CR3D(IL,J),
```

```
     $CR2D(IL,J),Z,CRFED(IL,J)
998   CONTINUE
      CLOSE(7)
      WRITE(*,*)TIME(3,J),WT(3,J),CR3D(3,J),CR2D(3,J),
     $CRFED(3,J)
80    CONTINUE

C     Iteration by minimisation on all the three sets of
C     data starts

      DO 777 ITER = 1,10000
      L = 0
      DO 778 M = 1,D
      CR3O(1) = CR3OS(M)
      CR2O(1) = CR2OS(M)
      CRO(1) = CROS(M)
      CRTO(1) = CRTS(M)
      SUM = 0
      DO 20 I = 2,T
      TINV = TIME(I,M) - TIME(I-1,M)
      INC = (CRTO(1)/100)*WT(I,M)
      H = 0.0444*WT(I,M)
      A1 = (K1 + K2 + K3 + K4)/H
      A2 = A1**2
      A3 = (K1*K3 + K2*K4 + K1*K4)/(H**2)
      M2 = 0.5*(A1 + SQRT(A2 - 4*A3))
      M3 = 0.5*(A1 - SQRT(A2 - 4*A3))
      B21 = K1/K2
      B22 = (K1 - M2*H)/K2
      B23 = (K1 - M3*H)/K2
      B31 = (K1*K3)/(K2*K4)
      B32 = (K3*(K1 - M2*H))/(K2*(K4 - M2*H))
      IF (ABS(K4 - M3*H).GT.1.0E-3)THEN
       B33 = (K3*(K1 - M3*H))/(K2*(K4 - M3*H))
      ELSE
       B33 = K3/K2
```

```
 ENDIF
 DETB = B22*B33 + B23*B31 + B21*B32 - B31*B22
$ - B32*B23 - B33*B21
 D1 = B22*B33 - B23*B32
 D2 = B31*B23 - B21*B33
 D3 = B21*B32 - B31*B22
 E1 = B32 - B33
 E2 = B33 - B31
 E3 = B31 - B32
 F1 = B23 - B22
 F2 = B21 - B23
 F3 = B22 - B21
 SS1(I,M) = CR3O(1)*(D1 + D2*EXP(-M2*TINV)
$ + D3*EXP(-M3*TINV))
 SS2(I,M) = CR2O(1)*(E1 + E2*EXP(-M2*TINV)
$ + E3*EXP(-M3*TINV))
 SS3(I,M) = CRO(1)*(F1 + F2*EXP(-M2*TINV)
$ + F3*EXP(-M3*TINV))
 CR3(I,M) = (SS1(I,M) + SS2(I,M) + SS3(I,M))/DETB
 SS4(I,M) = CR3O(1)*(B21*D1 + B22*D2*EXP(-M2*TINV)
$ + B23*D3*EXP(-M3*TINV))
 SS5(I,M) = CR2O(1)*(B21*E1 + B22*E2*EXP(-M2*TINV)
$ +B23*E3*EXP(-M3*TINV))
 SS6(I,M) = CRO(1)*(B21 * F1 + B22*F2*EXP(-M2*TINV)
$ + B23*F3*EXP(-M3*TINV))
 CR2(I,M) = (SS4(I,M) + SS5(I,M) + SS6(I,M))/DETB
 SS7(I,M) = CR3O(1)*(B31*D1 + B32*D2*EXP(-M2*TINV)
$ + B33*D3*EXP(-M3*TINV))
 SS8(I,M) = CR2O(1)*(B31*E1 + B32*E2*EXP(-M2*TINV)
$ + B33*E3*EXP(-M3*TINV))
 SS9(I,M) = CRO(1)*(B31*F1 + B32*F2*EXP(-M2*TINV)
$ + B33*F3*EXP(-M3*TINV))
 CR(I,M) = (SS7(I,M) + SS8(I,M) + SS9(I,M))/DETB
 CRT(I,M) = CR3(I,M) + CR2(I,M)
 CRWT(I,M) = (CRT(I,M)/100)*WT(I,M)
 WTDF(I,M) = INC - CRWT(I,M) + SUM
```

```
      CRFE(I,M) = (WTDF(I,M)/(60 + WTDF(I,M)))*100

C     The initial conditions for the next interval in each
C     data set are assigned

      CR3O(1) = CR3(I,M)
      CR2O(1) = CR2(I,M)
      CRO(1) = CR(I,M)
      CRTO(1) = CRT(I,M)
      SUM = WTDF(I,M)
20    CONTINUE
      LA(M) = 0
      LB(M) = 0
      LC(M) = 0

C     Sums of squares of deviations for the chromium
C     species in each data set are calculated

      DO 888 J = 2,J
       LA(M) = LA(M) + (CR3(J,M) - CR3D(J,M))**2
       LB(M) = LB(M) + (CR2(J,M) - CR2D(J,M))**2
       LC(M) = LC(M) + (CRFE(J,M) - CRFED(J,M))**2
888   CONTINUE
      L = LA(M) + LB(M) + LC(M)
778   CONTINUE
      IF(L.LT.LMIN)THEN
       LMIN = L
       K1MIN = K1
       K2MIN = K2
       K3MIN = K3
       K4MIN = K4
      WRITE(6,11)L,LA(1),LA(2),LA(3),LB(1),LB(2),LB(3),
     $LC(1),LC(2),LC(3),ITER
11     FORMAT(' L=',F6.3,' LA=',3(F5.3),' LB=',3(F5.3,1X),
     $' LC=',3(F5.3,1X),I6)
       ELSE
```

```
      K1 = K1MIN
      K2 = K2MIN
      K3 = K3MIN
      K4 = K4MIN
     ENDIF

C    A rundom number is generated by an external
C    subroutine called GO5CAF.  Multiplying the number
C    generated by 4 and scaling down determines which
C    rate constant to change.  A second generation of a
C    rundom number gives a value by which the rate
C    constant is to change

      X = GO5CAF(X)
      IF(INT(4*X).EQ.0)CALL CHANGE(K1,X,0.001)
      IF(INT(4*X).EQ.1)CALL CHANGE(K2,X,0.0001)
      IF(INT(4*X).EQ.2)CALL CHANGE(K3,X,0.001)
      IF(INT(4*X).EQ.3)THEN
99     CALL CHANGE(K4,X,0.0001)
       A1 = K1 + K2 + K3 + K4
       A3 = K1*K3 + K2*K4 + K1*K4
       M3 = (0.5*(A1 - SQRT(A1**2 - 4*A3)))/H
       IF(ABS(K4 - M3*H).LT.1.0E-8)GO TO 99
      ENDIF
777   CONTINUE
      WRITE(8,60)
      WRITE(8,66)
      WRITE(8,30)K1MIN,K2MIN,K3MIN,K4MIN,LA(3),LB(3),
     $LC(3)
60    FORMAT(/,'     CONSTANTS     ',/,
     $5X,'_____')
66    FORMAT(/,K1MIN K2MIN K3MIN K4MIN LA(3) LB(3)
     $LC(3) ',/,5X,'_____')
30    FORMAT (/,3X,9(3X,F6.4))
      WRITE (*,*) 'PROGRAM COMPLETED SUCCESSFULLY'
      STOP
```

```
      END



      SUBROUTINE CHANGE(K,X,SIGMA)
      REAL K,SIGMA
      DOUBLE PRECISION X
99    X = GO5CAF(X)
      K = K + (X - 0.5)*SIGMA
      IF(K.LT.0.0) GO TO 99
      RETURN
      END
```

APPENDIX G

The program below calculates rate constants for a particular set of data using the expressions from scheme 5 where in addition to reduction through the intermediate, (Cr^{2+}), a direct reduction of (Cr^{3+}) to [Cr] occurs. Six rate constants are calculated here. The method used is similar to that in appendices B and D. The varying slag height due to sampling is taken into account. The description of the variable names is as before.

```
      PROGRAM MODEMIN
      INTERGER  I,T,J
      REAL  K1,K2,K3,K4,K5,K6,A1,A2,A3,M1,M2,D,H,WT,B11,
     $      B12,B13,B21,B22,B23,DETB,P1,P2,P3,P4,P5,P6,
     $      V1,V2,V3,CS1,CS2,CS3,CS4,CS5,CS6,CS7,CS8,CS9,
     $      Y1,Y2,Y3,Y4,CR3O,CR2O,CRO,L,LMIN,LA,LB,LC,
     $      CR3,CR2,CR,CRWT,CRFE,CRT,INC,SUM,WTDF,INCR,
     $      CR3OS,CR2OS,CROS,M11,M21,K1MIN,K2MIN,K3MIN,
     $      K4MIN,K5MIN,K6MIN,Q1,Q2
      DIMENSION  CS1(10),CS2(10),CS3(10),CS4(10),CS5(10),
     $           CS6)10),CS7(10),CS8(10),CS9(10),CR3(10),
     $           CR2(10),CR(10),CRWT(10),CRFE(10),
     $           CR3O(10),CR2O(10),CRO(10),CRT(10),
     $           WTDF(10),CR3D(10),CR2D(10),CRFED(10),
     $           TIME(10),WT(10)
      DOUBLE PRECISION X,GO5CAF
      CHARACTER NAME*13
```

```
      CALL GO5CAF(0)
      LMIN = 1000.00
      OPEN(6,FILE= 'MODEMIN.OUT'STATUS='OLD')

C     Guessed rate constants and the concentrations at time
C     zero are entered

      WRITE(*,*)'ENTER RATE CONSTANTS K1,K2,K3,K4,K5,K6'
      READ (*,(6F6.4)')K1,K2,K3,K4,K5,K6
      WRITE(*,'(1X,6F6.4)')K1,K2,K3,K4,K5,K6
      WRITE(*,*)'ENTER INITIAL CONCENTRATIONS CR3O(1)
     $CR2O(1),CRO(1)'
      READ (*,'(3F6.4)')CR3OS,CR2OS,CROS
      CRTS = CR3OS + CR2OS
      WRITE(*,*) 'ENTER NUMBER OF DATA POINTS'
      READ (*,'(I3)')T
      WRITE(*,'(1X,I3)')T
      WRITE (*,*)'ENTER DATA FILE NAME'
      READ (*,'(A13)')NAME
      OPEN(7,FILE=NAME,STATUS='OLD',FORM=FORMATTED')
      DO 999 IL = 1,16
        READ (7,*)
999   CONTINUE
      DO 990 IL = 1,8
        READ(7,*)TIME(IL),Z,WT(IL),Z,CR3D(IL),CR2D(IL),
     $     Z,CRFED(IL)
990   CONTINUE
      CLOSE(7)
      WRITE(*,*)TIME(3),WT(3),CR3D(3),CR2D(3),CRFED(3)
      DO 777 ITER = 1,10000
      CR3O(1) = CR3OS
      CR2O(1) = CR2OS
      CRO(1) = CROS
      CRT(1) = CRTS
      SUM = 0.0
      A1 = K1 + K2 + K3 + K4 + K5 + K6
```

```
      A2 = A1**2
      A3 = K1*K3 + K2*K4 + K1*K4 + K3*K5 + K2*K5
     $   + K3*K6 + K2*K6 + K1*K6 + K4*K5
      IF (A2.LT.4*A3)GO TO 111
      DO 20 I = 2,T
      TINV = TIME(I) - TIME(I-1)
      INC = (CRT(1)/100)*WT(I)
      H = 0.0444*WT(I)
      M1 = (0.5*(A1 + SQRT(A2 - 4*A3)))/H
      M2 = (0.5*(A1 - SQRT(A2 - 4*A3)))/H
      M11 = 0.5*(A1 + SQRT(A2 - 4*A3))
      M21 = 0.5*(A1 - SQRT(A2 - 4*A3))
      Q1 = K2*K4 + K2*K6 + K3*K6
      Q2 = K2*K5 + K1*K3 + K3*K5
      Y1 = K4*(K1 + K5 - M11) + K1*K6
      Y2 = M11*(M11 - K1 - K5 - K6)
      Y3 = K4*(K1 + K5 - M21) + K1*K6
      Y4 = M21*(M21 - K1 - K5 - K6)
      B11 = Q1/Q2
      B12 = (Q1 - K2*M11)/(Q2 - K3*M11)
      B13 = (Q1 - K2*M21)/(Q2 - K3*M21)
      B21 = (K1*K4 + K4*K5 + K1*K6)/Q2
      B22 = (Y1 + Y2)/(Q2 - K3*M11)
      B23 = (Y3 + Y4)/(Q2 - K3*M21)
      DETB = B11*B22 + B12*B23 + B13*B21 - B22*B13
     $  - B23*B11 - B12*B21
      P1 = B22 - B23
      P2 = B23 - B21
      P3 = B21 - B22
      P4 = B13 - B12
      P5 = B11 - B13
      P6 = B12 - B11
      V1 = B12*B23 - B22*B13
      V2 = B21*B13 - B11*B23
      V3 = B11*B22 - B21*B12
      CS1(I) = CR30(1)*(B11*P1 + B12*P2*EXP(-M1*TINV)
```

```
     $ + B13*P3*EXP(-M2*TINV))
      CS2(I) = CR2O(1)*(B11*P4 + B12*P5*EXP(-M1*TINV)
     $ + B13*P6*EXP(-M2*TINV))
      CS3(I) = CRO(1)*(B11*V1 + B12*V2*EXP(-M1*TINV)
     $ + B13*V3*EXP(-M2*TINV))
      CR3(I) = (CS1(I) + CS2(I) + CS3(I))/DETB
      CS4(I) = CR3O(1)*(B21*P1 + B22*P2*EXP(-M1*TINV)
     $ + B23*P3*EXP(-M2*TINV))
      CS5(I) = CR2O(1)*(B21*P4 + B22*P5*EXP(-M1*TINV)
     $ + B23*P6*EXP(-M2*TINV))
      CS6(I) = CRO(1)*(B21*V1 + B22*V2*EXP(-M1*TINV)
     $ + B23*V3*EXP(-M2*TINV))
      CR2(I) = (CS4(I) + CS5(I) + CS6(I))/DETB
      CS7(I) = CR3O(1)*(P1 + P2*EXP(-M1*TINV)
     $ + P3*EXP(-M2*TINV))
      CS8(I) = CR2O(1)*(P4 + P5*EXP(-M1*TINV)
     $ + P6*EXP(-M2*TINV))
      CS9(I) = CRO(1)*(V1 + V2*EXP(-M1*TINV)
     $ + V3*EXP(-M2*TINV))
      CR(I) = (CS7(I) + CS8(I) + CS9(I))/DETB
      CRT(I) = CR3(I) + CR2(I)
      CRWT(I) = (CRT(I)/100)*WT(I)
      WTDF(I) = INC - CRWT(I) + SUM
      CRFE(I) = (WTDF(I)/(60 + WTDF(I)))*100
      CR3O(1) = CR3(I)
      CR2O(1) = CR2(I)
      CRO(1) = CR(I)
      CRT(1) = CRT(I)
      SUM = WTDF(I)
20    CONTINUE
      LA = 0.0
      LB = 0.0
      LC = 0.0
      DO 888  J = 2,T
        LA = LA + (CR3(J) - CR3D(J))**2
        LB = LB + (CR2(J) - CR2D(J))**2
```

```
        LC = LC + (CRFE(J) - CRFED(J))**2
888     CONTINUE
        L = LA + LB + LC
        IF(L.LT.LMIN)THEN
          LMIN = L
          K1MIN = K1
          K2MIN = K2
          K3MIN = K3
          K4MIN = K4
          K5MIN = K5
          K6MIN = K6
        WRITE(*,*)'L ',L,'LA ',LA,'LB ',LB,'LC ',LC,
       $ 'ITER ',ITER
            ELSE
          K1 = K1MIN
          K2 = K2MIN
          K3 = K3MIN
          K4 = K4MIN
          K5 = K5MIN
          K6 = K6MIN
        ENDIF
111     CONTINUE
        X = GO5CAF(X)
        IF(INT(6*X).EQ.0)CALL CHANGE(K1,X,0.001)
        IF(INT(6*X).EQ.1)CALL CHANGE(K2,X,0.001)
        IF(INT(6*X).EQ.2)CALL CHANGE(K3,X,0.0001)
        IF(INT(6*X).EQ.3)CALL CHANGE(K4,X,0.0001)
        IF(INT(6*X).EQ.4)CALL CHANGE(K5,X,0.001)
        IF(INT(6*X).EQ.5)CALL CHANGE(K6,X,0.0001)
777     CONTINUE
        WRITE(6,60)
        WRITE(6,66)
        WRITE(6,30)K1MIN,K2MIN,K3MIN,K4MIN,K5MIN,K6MIN
60      FORMAT (/,'    RATE CONSTANTS     ',/,
       $5X,'_____________________________________________')
66      FORMAT (/,' K1MIN   K2MIN   K3MIN   K4MIN   K5MIN
```

```
     $   K6MIN',/,
     $5X,'_____________________________________________________')
30    FORMAT (/,3X,6(4X,F6.4))
      WRITE (*,*)'PROGRAM COMPLETED SUCCESSFULLY'
      STOP
      END



      SUBROUTINE  CHANGE(K,X,SIGMA)
      REAL K,SIGMA
      DOUBLE PRECISION  X
10    X = GO5CAF(X)
      K = K + (X - 0.5)*SIGMA
      IF(K.LT.0.0)GO TO 10
      RETURN
      END
```

APPENDIX H

The program below calculates the concentrations of the chromium species using the expressions from scheme 5 and the six rate constants determined from the program in appendix G. The description of variable names is the same as before and the output is similar to appendix C.

```
      PROGRAM MODEL
      INTEGER  I,K,C,T,SUMA,SUMB,J,TIME
      REAL  K1,K2,K3,K4,K5,K6,A1,A2,A3,M1,M2,D,Q1,Q2,Q3,
     $      H,B11,B12,B13,B21,B22,B23,DETB,P1,P2,P3,P4,
     $      P5,P6,V1,V2,V3,CS1,CS2,CS3,CS4,CS5,CS6,CS7,
     $      CS8,CS9,Y1,Y2,Y3,Y4,CR3O,M11,M21,CR2O,CRO,WT,
     $      CR3,CR2,CR,CRWT,CRFE,CRT,INC,SUM,WTDF,INCR,
      DIMENSION  CS1(120),CS2(120),CS3(120),CS4(120),
     $      CS5(120),CS6(120),CS7(120),CS8(120),CS9(120),
     $     CR3(120),CR2(120),CR(120),CRWT(120),CRFE(120),
     $     CR3O(120),CR2O(120),CRO(120),CRT(120),
     $     WTDF(120),WT(10),TIME(10)
      CHARACTER NAME*13
      OPEN(9,FILE='MODE.OUT',STATUS='OLD')

C   Top of program loop

      WRITE(*,*) 'ENTER RATE CONSTANTS K1,K2,K3,K4,K5,K6'
      OPEN(7,FILE='MODEMIN.OUT',STATUS='OLD')
      DO 666 IL = 1,7
        READ(7,*)
666   CONTINUE
      READ(7,*)K1,K2,K3,K4,K5,K6
```

```
      CLOSE(7)
      WRITE(*,*)K1,K2,K3,K4,K5,K6
      WRITE(*,*) 'ENTER INITIAL CONCENTRATIONS CR3O(1),
     $CR2O(1),CRO(1)'
      READ (*,'(3F6.4)')CR3O(1),CR2O(1),CRO(1)
      CRT(1) = CR3O(1) + CR2O(1)
      INCR = (CRT(1)/100)*20
      C = 0
      SUM = 0.0
      SUMA = 0.0
      SUMB = 0.0
      WRITE (*,*) 'ENTER NUMBER OF EXPERIMENTAL POINTS'
      READ(*,'(I3)')T
      WRITE(*,'(1X,I3)')T
      WRITE (*,*) 'ENTER DATA FILE NAME'
      READ (*,'(A13)')NAME
      OPEN(8,FILE=NAME,STATUS='OLD',FORM=FORMATTED')
      DO  999 IL = 1,16
        READ(8,*)
999   CONTINUE
      DO 998 IL = 1,8
        READ(8,*)TIME(IL),Z,WT(IL),Z,Z,Z,Z,Z
998   CONTINUE
      CLOSE(8)
      WRITE(*,*)TIME(3),WT(3)

C  Top of major loop

      DO 120 J = 2,T
      TINV = TIME(J) - TIME(J-1)
      IF(CRT(1).EQ.3.42)THEN
      INC = INCR
       ELSE
        INC = (CRT(1)/100)*WT(J)
         ENDIF
      H = 0.0444*WT(J)
```

```
      A1 = K1 + K2 + K3 + K4 + K5 + K6
      A2 = A1**2
      A3 = K1*K3 + K2*K4 + K1*K4 + K3*K5 + K2*K5
     $   + K3*K6 + K2*K6 + K1*K6 + K4*K5
      M1 = (0.5*(A1 + SQRT(A2 - 4*A3)))/H
      M2 = (0.5*(A1 - SQRT(A2 - 4*A3)))/H
      M11 = 0.5*(A1 + SQRT(A2 - 4*A3))
      M21 = 0.5*(A1 - SQRT(A2 - 4*A3))
      Q1 = (K2*K4 + K2*K6 + K3*K6)/H**2
      Q2 = (K2*K5 + K1*K3 + K3*K5)/H**2
      Y1 = (K4*(K1 + K5 - M11) + K1*K6)/H**2
      Y2 = (M11*(M11 - K1 - K5 - K6))/H**2
      Y3 = (K4*(K1 + K5 - M21) + K1*K6)/H**2
      Y4 = (M21*(M21 - K1 - K5 - K6))/H**2
      B11 = Q1/Q2
      B12 = (Q1 - K2*M11)/(Q2 - K3*M11)
      B13 = (Q1 - K2*M21)/(Q2 - K3*M21)
      B21 = ((K1*K4 + K4*K5 + K1*K6)/H**2)/Q2
      B22 = (Y1 + Y2)/(Q2 - (K3*M11)/H**2)
      B23 = (Y3 + Y4)/(Q2 - (K3*M21)/H**2)
      DETB = B11*B22 + B12*B23 + B13*B21 - B22*B13
     $     - B23*B11 - B12*B21
      P1 = B22 - B23
      P2 = B23 - B21
      P3 = B21 - B22
      P4 = B13 - B12
      P5 = B11 - B13
      P6 = B12 - B11
      V1 = B12*B23 - B22*B13
      V2 = B21*B13 - B11*B23
      V3 = B11*B22 - B21*B12
      DO 20 I = 1,TINV
      CS1(I) = CR30(1)*(B11*P1 + B12*P2*EXP(-M1*I)
     $ + B13*P3*EXP(-M2*I))
      CS2(I) = CR20(1)*(B11*P4 + B12*P5*EXP(-M1*I)
     $ + B13*P6*EXP(-M2*I))
```

```
      CS3(I) = CRO(1)*(B11*V1 + B12*V2*EXP(-M1*I)
     $ + B13*V3*EXP(-M2*I))
      CR3(I) = (CS1(I) + CS2(I) + CS3(I))/DETB
      CS4(I) = CR3O(1)*(B21*P1 + B22*P2*EXP(-M1*I)
     $ + B23*P3*EXP(-M2*I))
      CS5(I) = CR2O(1)*(B21*P4 + B22*P5*EXP(-M1*I)
     $ + B23*P6*EXP(-M2*I))
      CS6(I) = CRO(1)*(B21*V1 + B22*V2*EXP(-M1*I)
     $ + B23*V3*EXP(-M2*I))
      CR2(I)  (CS4(I) + CS5(I) + CS6(I))/DETB
      CS7(I) = CR3O(1)*(P1 + P2*EXP(-M1*I)
     $ + P3*EXP(-M2*I))
      CS8(I) = CR2O(1)*(P4 + P5*EXP(-M1*I)
     $ + P6*EXP(-M2*I))
      CS9(I) = CRO(1)*(V1 + V2*EXP(-M1*I)
     $ + V3*EXP(-M2*I))
      CR(I) = (CS7(I) + CS8(I) + CS9(I))/DETB
      CRT(I) = CR3(I) + CR2(I)
      CRWT(I) = (CRT(I)/100)*WT(J)
      WTDF(I) = INC - CRWT(I) + SUM
      CRFE(I) = (WTDF(I)/(60 + WTDF(I)))*100
      IF(I.EQ.TINV)THEN
      CR3O(1) = CR3(I)
      CR2O(1) = CR2(I)
      CRO(1) = CR(I)
      CRT(1) = CRT(I)
      SUM = WTDF(I)
        ELSE
         GO TO 20
          ENDIF
20    CONTINUE
      WRITE (9,60)
      WRITE (9,66)
      DO 40 K = 1,TINV
      SUMB = K + SUMA
      WRITE(9,30)SUMB,CR3(K),CR2(K),CRFE(K)
```

```
      IF (K.EQ.TINV)THEN
      SUMA = SUMB
       ELSE
        GO TO 40
         ENDIF
40    CONTINUE
      C = C + 1
      IF(C.LE.7)THEN
       GO TO 120
        ELSE
         GO TO 45
          ENDIF
120   CONTINUE
45    CONTINUE
60    FORMAT (/,'   WEIGHT PERCENT AGAINST TIME  ',/,
     $5X,'_____________________________________________')
66    FORMAT (/,'  SUMB  CR3(K)  CR2(K)  CRFE(K)  ',/,
     $5X,'_____________________________________________')
30    FORMAT (/,3X,I3,3(5X,F6.4))
      WRITE(*,*) 'PROGRAM COMPLETED SUCCESSFULLY'
      STOP
      END
```

REFERENCES

REFERENCES

1. R.J. Fruehan: Ironmaking steelmaking,1976,vol.3, p153.

2. T. Watanabe and T. Tooge: tetsu-to-Hagane',1973, vol. 59,p1224.

3. K. Nakanishi, H. Ooi, N. Sumita and S. Suzuki: Tetsu-to-Hagane', 1973, vol. 59, p1523.

4. R.J. Fruehan: Met. Trans., 1977, vol. 88, p429.

5. R.G Ward: The Physical Chemistry of Iron and Steel-making, Arnold Publishers, 1962, pp136-149.

6. N.J. Grant, E.C. Roberts and J. Chipman: Trans. A.I.M.E., 1954, vol. 200, pp145-149.

7. R.V. Pathy and R.G. Ward: J. iron steel inst., 1964, vol. 202, pp995-1001.

8. F.P Glasser and E.F Osborn: J. Amer. Cer. Soc., 1958, vol. 41, No. 9, pp358-367.

9. C.W. McCoy and F.C. Langenberg: J. Metals, 1964, vol. 16, pp421-424.

10. K. Morita, A. Inoue, N. Takayama and N. Sano: J. iron steel Inst. Jpn., 1988, vol. 24, part 6, pp999-1005.

11. P. Herasymenko: Trans> Faraday Soc., 1938, vol.34, pp1254-1257.

12. H.M. Chen and J. Chipman: Trans. Amer. Soc. Metals, 1947, vol. 38, pp70-113.

13. M.L. Keith: J. Amer. Cer. Soc., 1954, vol. 37, No. 10, pp490-496.

14. R.E. Hook and A.M. Adair: Trans. A.I.M.E., 1964, vol. 230, pp1278-1283.

15. G.W. Healy and J.C. Schottmiller: Trans. A.I.M.E., 1964, vol. 230, pp420-425.

16. M. Meada and N. Sano: J. Iron steel Inst. Jpn., 1982, vol. 7, pp51-58.

17. W.J. Rankin and A.K. Biswas: Trans. Inst. Min. Metaal., 1978, vol. 87, ppC60-C70.

18. F. Korber and W. Oelsen: Mitt. K.-Wilh.-Inst. Eisenforsch., 1935, vol. 17, pp231-245.

19. T. Niimoni, Y. Matsushita and K. Kanamori: Tsetsu-to-Hagane', 1955, vol. 41, pp1075-1081.

20. C.W. McCoy and W.O. Philbrook: Trans. Amer. Inst. Min. (Metall.) Engrs., 1958, vol. 212, pp226-235.

21. H.G. Katayama, T. Tsao and N. Matsushima: Trans. Iron steel Inst. Jpn., 1988, vol. 28, pp186-191.

22. D.C. Hilty: Trans. A.I.M.E., 1949, vol. 185, pp91-95;Journal of Metals (Feb. 1949).

23. W.E Dennis and F.D. Richardson: J. Iron steel Inst., 1953, vol. 175, p264.

24. E.T. Turkdogan: Physical Chemistry of High Temperature Technology, 1980, Academic Press, pp365-367.

25. J.J. Moore: Chemical Metallurgy, 1981, Butterworths, London, pp97-128.

26. R.J. Pomfret and P. Grieveson: Canadian Metallurgical Quarterly, 1983, vol. 22, No. 3, pp287-299.

27. T.B. King: Electric Furnace Steelmaking, 1963, vol. 2, ch. 20, Interscience, NewYork, p233.

28. R.T. Grimley, R.P. Burns and M.G. Inghram: Journal of Chem. Phys., 1961, vol. 34, p664.

29. K. Strater and C.L. Mantell: Trans. TMS A.I.M.E., 1964, vol. 230, p1141.

30. V.N. Boronenkov, S.A. Lyamkin, M.A. Ryss, V.M. Getmanchuk and V.S. Volkov: Steel in USSR, 1971,p959

31. J.W. Robison Jr. and R.D. Pehlke: Met. Trans., 1974, vol. 5, p1041.

32. N. Sevinc and J.F. Elliot: Ironmaking and Steelmaking, 1976, No. 5, p268.

33. R.J. Fruehan: Met. Trans., 1977, vol. 8B, p429.

34. K. Suzuki and K. Mori: Trans. ISIJ, 1980, vol. 20, p607.

35. M. Hacioglu: Ph.D. Thesis, Division of Metallurgy and Engineering Materials, University of Strathclyde, 1982, Glasgow.

36. T. Shimoo, T. Isobe, S. Ando and H. Kimura: J. Jpn. Inst. Met., 1986, vol. 50, No. 2, p168.

37. C.N. Anyakwo: Ph.D. Thesis, Division of Metallurgy and Engineering Materials, University of Strathclyde, 1987, Glasgow.

38. J.W. Robison Jr.: Ph.D. Thesis, The University of Michigan, 1973, Michigan.

39. M. Kawakami, Y. Kitajima, K. Hashimoto and K. Ito: Trans. ISIJ, vol. 27, p176.

40. S. Fukagawa and T Shimoda: Trans. ISIJ, 1987, vol. 27, p609.

41. T. Shimoo, S. Ando and H. Kimura: J. Jpn. Inst. Met., 1987, vol. 51, no.5, pp439-445.

42. S. Kitamura, T. Arai, M. Matsuo, N. Sato, K. Okohira and H. Ishikawa: J. Iron steel Inst., Jpn., 1988, vol. 74, part 4, pp672-679.

43. Perkin-Elmer Instruction Manual of Analytical Methods for atomic absorption spectrophotometry, Norwak, Connecticut, U.S.A., 1971.

44. J.W. Robison Jr. and R.D. Pehlke: Analytical Chemistry, 1974, vol. 46, No. 7, p946.

45. J.J. Lingane and R.L. Pecsok: Analytical Chemistry, 1948, vol. 20, No. 5, pp425-428.

46. Methods for the Sampling and Analysis of iron, steel and other ferrous metals, 1970, BS Handbook No. 19.

47. C.J.B. Fincham and F.D. Richardson: J. Iron and Steel Inst., 1952, pp53-55.

48. R.F. Jones, P. Gale, P. Hopkins and L.N. Powell: J. Iron and Steel Inst., 1966, pp505-508.

49. W.O. Philbrook and L.D. Kirkbride: Trans. A.I.M.E., 1956, vol. 206, p351.

50. Y. Kawai, K. Mori and M. Iguchi: Trans. ISIJ., 1972, vol. 12, p138.

51. R.J. Pomfret, I.D. Sommerville and P. Grieveson: High Temperature Chemistry of Inorganic and Ceramic Materials, The Chemical Soc., 1976, pp21-40.

52. J.M. Los, L.B. Simpson and K. Wiesner: J. Am. Chem. Soc., 1956, vol. 78, p1564.

53. E.S. Lewis and M.D. Johnson: J. Am. Chem. Soc., 1960, vol. 5, pp5399-5407.

54. A. Frost and R.G. Pearson: Kinetics and Mechanism, 1961, John Wiley, NewYork, p166.

55. S.W. Benson: The Foundations of Chemical Kinetics, 1960, McGraw-Hill, NewYork, p33.

56. W. Esson: Phil. Trans. Roy. Soc., 1866, vol. 156, p220.

57. A. Rakowski: Z. Phys. Chem., 1906, vol. 57, p321.

58. T.M. Lowry and W.T. John: J. Chem. Soc., 1910, vol. 97, p2634.

59. A.E.R. Westman and D.B. DeLury: Can. J. Chem., 1956, vol. 34, p1134.

60. F.A. Matsen and J.L. Franklin: J. Am. Chem. Soc., 1950, vol. 72, p3337.

61. P.C. Jordan: Chemical Kinetics and Transport, 1980, Plenum Press, NewYork, pp113-153.

62. C. Capellos and B.H.J. Bielski: Kinetic systems-Mathematical Description of chemical kinetics in solutions, 1972, Wiley Interscience, NewYork.

63. S. Ramachandran, T.B. King and N.J. Grant: Trans. A.I.M.E., 1956, vol. 206, p1549.

64. P. Kozakevitch, G. Urbain and M. Sage: Revue de Metallurgie, 1955, vol. 52, No. 2, pp161-171.

65. H. Gaye and P.V. Riboud: Metall. Trans. B, 1977, B8, p409.

66. P. Kozakevitch, S. Chatel, G. Urbain and M. Sage: Revue de Metallurgie, 1955, vol. 52, No. 2, pp139-160.

67. P. Kozakevitch and G. Urbain: Mem. Sci. Rev. Metall., 1961, vol. 186, pp401-413.

68. P. Kozakevitch: Revue de Metallurgie, 1954, vol. 51, No. 8, pp570-587.

69. M. Meada and N. Sano: Abstracts of the 6th Process Technology Conference of the Iron and Steel Inst. A.I.M.E., April, 1986.