CHAPTER 5

DISCUSSION OF THE EFFECT OF

VARIOUS PARAMETERS ON

Cr$_2$O$_3$ REDUCTION
CHAPTER 5

DISCUSSION OF THE EFFECT OF VARIOUS PARAMETERS ON Cr₂O₃ REDUCTION.

This chapter is concerned with a discussion of the effect of various parameters on the reduction of Cr₂O₃ 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 (Cr³⁺) is not affected by metal chromium contents up to 15 wt%. The reduction rate of (Cr²⁺) 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 $(\text{Cr}^{3+})$ and $(\text{Cr}^{2+})$ reduction.
\[ k_1 = 0.0190 \text{ cm.min}^{-1}, \quad k_2 = 0.0071 \text{ cm.min}^{-1}. \]
\[ k_3 = 0.0222 \text{ cm.min}^{-1}, \quad k_4 = 0.0011 \text{ cm.min}^{-1}. \]

Sums of squares of deviations are:
\[ \text{Cr}^{3+} = 0.160, \quad \text{Cr}^{2+} = 0.038, \quad \text{Cr}_{\text{Met.}} = 0.009. \]

Fig. 5.2 Time variation in concentration of (Cr$^{3+}$), (Cr$^{2+}$) and [Cr] for run AS7.
\[ k_1 = 0.0203 \text{ cm.min}^{-1}, \quad k_2 = 0.0163 \text{ cm.min}^{-1}, \]
\[ k_3 = 0.1496 \text{ cm.min}^{-1}, \quad k_4 = 0.0165 \text{ cm.min}^{-1}. \]

Sums of squares of deviations are:
\[ \text{Cr}^{3+} = 0.019, \quad \text{Cr}^{2+} = 0.068, \quad \text{Cr}_{\text{Met.}} = 0.003. \]

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.

<table>
<thead>
<tr>
<th>Initial [%Cr]</th>
<th>$k_1$</th>
<th>$k_2$ cm.min$^{-1}$</th>
<th>$k_3$</th>
<th>$k_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0239</td>
<td>0.0215</td>
<td>0.0609</td>
<td>0.0226</td>
</tr>
<tr>
<td>4</td>
<td>0.0203</td>
<td>0.0163</td>
<td>0.1496</td>
<td>0.0165</td>
</tr>
<tr>
<td>15</td>
<td>0.0190</td>
<td>0.0071</td>
<td>0.0222</td>
<td>0.0011</td>
</tr>
</tbody>
</table>

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$^\circ$C, respectively. In each case an initial concentration of 8 wt% Cr$_2$O$_3$ 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$_2$O$_3$ reduction increases with an increase in temperature. This is in good accord with the finding of other investigators into the reduction rate of Cr$_2$O$_3$ from slag$^{(31,69)}$.

Arrhenius plots for (Cr$^{3+}$), (Cr$^{2+}$) and Cr$_2$O$_3$ reduction were generated using the forward rate constants (Table 5.2) and are shown in Fig. 5.9. Activation energies of
$k_1 = 0.0098 \text{ cm.min}^{-1}.$ $k_2 = 0.0031 \text{ cm.min}^{-1}.$
$k_3 = 0.0483 \text{ cm.min}^{-1}.$ $k_4 = 0.0088 \text{ cm.min}^{-1}.$

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

Fig. 5.4 Time variation in concentration of (Cr$^{3+}$),
(Cr$^{2+}$) and [Cr] at $1400^\circ\text{C}$, data from Ref (37).
\( k_1 = 0.0148 \text{ cm.min}^{-1}. \quad k_2 = 0.0080 \text{ cm.min}^{-1}. \)
\( k_3 = 0.0815 \text{ cm.min}^{-1}. \quad k_4 = 0.0137 \text{ cm.min}^{-1}. \)

Sums of squares of deviations are:
\( \text{Cr}^{3+} = 0.069, \quad \text{Cr}^{2+} = 0.203, \quad \text{Cr}_{\text{Met.}} = 0.061. \)

Fig. 5.5 Time variation in concentration of (\text{Cr}^{3+}),
(\text{Cr}^{2+}) and [\text{Cr}] at 1450\degree C, data from Ref (37).
\[ k_1 = 0.0321 \text{ cm.min}^{-1}, \quad k_2 = 0.0223 \text{ cm.min}^{-1}, \]
\[ k_3 = 0.1086 \text{ cm.min}^{-1}, \quad k_4 = 0.0309 \text{ cm.min}^{-1}. \]

Sums of squares of deviations are:
\[ \text{Cr}^{3+} = 0.081, \quad \text{Cr}^{2+} = 0.204, \quad \text{Cr}_{\text{Met.}} = 0.048. \]

Fig. 5.6 Time variation in concentration of (Cr\(^{3+}\)), (Cr\(^{2+}\)) and [Cr] at 1500°C, data from Ref (37).
$k_1 = 0.0334 \text{ cm.min}^{-1}$. $k_2 = 0.0108 \text{ cm.min}^{-1}$. $k_3 = 0.0915 \text{ cm.min}^{-1}$. $k_4 = 0.0242 \text{ cm.min}^{-1}$.

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

Fig. 5.7 Time variation in concentration of $(Cr^{3+})$, $(Cr^{2+})$ and $[Cr]$ at $1550^\circ \text{C}$, 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$_2$O$_3$ reduction.
the reduction of the chromium species and $\text{Cr}_2\text{O}_3$ were determined according to equation (1.37). The activation energy for $\text{Cr}_2\text{O}_3$ 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 $\text{Cr}_2\text{O}_3$ to [Cr]. The activation energies obtained for $\text{Cr}^{3+}$, $\text{Cr}^{2+}$ and $\text{Cr}_2\text{O}_3$ 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 5.2: Variation of rate constants with temperature.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$k_1$ (cm.min$^{-1}$)</th>
<th>$k_2$ (cm.min$^{-1}$)</th>
<th>$k_3$ (cm.min$^{-1}$)</th>
<th>$k_4$ (cm.min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400</td>
<td>0.0098</td>
<td>0.0031</td>
<td>0.0483</td>
<td>0.0088</td>
</tr>
<tr>
<td>1450</td>
<td>0.0148</td>
<td>0.0080</td>
<td>0.0815</td>
<td>0.0137</td>
</tr>
<tr>
<td>1500</td>
<td>0.0321</td>
<td>0.0223</td>
<td>0.1086</td>
<td>0.0309</td>
</tr>
<tr>
<td>1550</td>
<td>0.0334</td>
<td>0.0108</td>
<td>0.0915</td>
<td>0.0242</td>
</tr>
</tbody>
</table>

### Table 5.3: Data for arrhenius plots of $\text{Cr}^{3+}$, $\text{Cr}^{2+}$ and $\text{Cr}_2\text{O}_3$ reduction.

<table>
<thead>
<tr>
<th>$T$ °K</th>
<th>$1/T$</th>
<th>$k_1$</th>
<th>Ln $k_1$</th>
<th>$k_3$</th>
<th>Ln $k_3$</th>
<th>Ln $k_1k_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1673</td>
<td>5.977</td>
<td>0.0098</td>
<td>-4.625</td>
<td>0.0483</td>
<td>-3.030</td>
<td>-7.656</td>
</tr>
<tr>
<td>1723</td>
<td>5.804</td>
<td>0.0148</td>
<td>-4.213</td>
<td>0.0815</td>
<td>-2.507</td>
<td>-6.720</td>
</tr>
<tr>
<td>1773</td>
<td>5.640</td>
<td>0.0321</td>
<td>-3.439</td>
<td>0.1086</td>
<td>-2.220</td>
<td>-5.659</td>
</tr>
<tr>
<td>1823</td>
<td>5.485</td>
<td>0.0334</td>
<td>-3.399</td>
<td>0.0915</td>
<td>-2.391</td>
<td>-5.791</td>
</tr>
</tbody>
</table>
A variation in the activation energy for the reduction of (Cr$^{3+}$), (Cr$^{2+}$) and Cr$_2$O$_3$ 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>
<thead>
<tr>
<th>Ref.</th>
<th>Temp. range $^\circ$C</th>
<th>System</th>
<th>Species reduced</th>
<th>Activation energy kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1710-1820</td>
<td>Fe-C</td>
<td>Cr$^{2+}$</td>
<td>106.75</td>
</tr>
<tr>
<td>29</td>
<td>1130-1490</td>
<td>H$_2$</td>
<td>Cr$_2$O$_3$</td>
<td>26.60</td>
</tr>
<tr>
<td>31</td>
<td>1550-1625</td>
<td>Fe-Si</td>
<td>Cr$^{3+}$</td>
<td>100.00 MTS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr$^{2+}$</td>
<td>130.00 ICR</td>
</tr>
<tr>
<td>36</td>
<td>1520-1720</td>
<td>C</td>
<td>Cr$_2$O$_3$</td>
<td>54.70</td>
</tr>
<tr>
<td>37</td>
<td>1400-1550</td>
<td>Fe-C</td>
<td>Cr$^{3+}$</td>
<td>52.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr$^{2+}$</td>
<td>80.00</td>
</tr>
<tr>
<td>40</td>
<td>1500-1680</td>
<td>Fe-C</td>
<td>Cr$_2$O$_3$</td>
<td>46.00</td>
</tr>
<tr>
<td>Present study</td>
<td>1400-1550</td>
<td>Fe-C</td>
<td>Cr$^{3+}$</td>
<td>54.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr$^{2+}$</td>
<td>27.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr$_2$O$_3$</td>
<td>81.33</td>
</tr>
</tbody>
</table>

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 experimental 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

- 236 -
$k_1 = 0.0478 \text{ cm.min}^{-1}$. $k_2 = 0.0318 \text{ cm.min}^{-1}$.

$k_3 = 0.1307 \text{ cm.min}^{-1}$. $k_4 = 0.0365 \text{ cm.min}^{-1}$.

Sums of squares of deviations are:

$Cr^{3+} = 0.120$, $Cr^{2+} = 0.101$, $Cr_{\text{Met.}} = 0.056$.

Fig. 5.10 Time variation in concentration of $(Cr^{3+})$, $(Cr^{2+})$ and [Cr] for run CRS24, Ref (37).
\[ k_1 = 0.0373 \text{ cm.min}^{-1}, \quad k_2 = 0.0245 \text{ cm.min}^{-1}, \]
\[ k_3 = 0.1330 \text{ cm.min}^{-1}, \quad k_4 = 0.0298 \text{ cm.min}^{-1}. \]

Sums of squares of deviations are:
\[ \text{Cr}^{3+} = 0.023, \quad \text{Cr}^{2+} = 0.281, \quad \text{Cr}_{\text{Met.}} = 0.013. \]

Fig. 5.11 Time variation in concentration of (\text{Cr}^{3+}),
(\text{Cr}^{2+}) \text{ and } [\text{Cr}] \text{ for run CRS25, Ref (37).}
\[ k_1 = 0.0339 \text{ cm.min}^{-1}, \quad k_2 = 0.0154 \text{ cm.min}^{-1}, \]
\[ k_3 = 0.1233 \text{ cm.min}^{-1}, \quad k_4 = 0.0289 \text{ cm.min}^{-1}. \]

Sums of squares of deviations are:
\[ \text{Cr}^{3+} = 0.189, \quad \text{Cr}^{2+} = 0.089, \quad \text{Cr}_{\text{Met.}} = 0.004. \]

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).

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Initial (wt%Cr₂O₃)</th>
<th>Metal wt. (g)</th>
<th>Slag wt. (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRS24</td>
<td>8</td>
<td>80</td>
<td>40</td>
</tr>
<tr>
<td>CRS25</td>
<td>8</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>CRS26</td>
<td>8</td>
<td>160</td>
<td>20</td>
</tr>
</tbody>
</table>

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 \((\text{Cr}^3+)\) 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.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>( k_1 ) cm.min(^{-1} )</th>
<th>( k_2 )</th>
<th>( k_3 )</th>
<th>( k_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRS24</td>
<td>0.0478</td>
<td>0.0318</td>
<td>0.1307</td>
<td>0.0365</td>
</tr>
<tr>
<td>CRS25</td>
<td>0.0373</td>
<td>0.0245</td>
<td>0.1330</td>
<td>0.0298</td>
</tr>
<tr>
<td>CRS26</td>
<td>0.0339</td>
<td>0.0154</td>
<td>0.1233</td>
<td>0.0289</td>
</tr>
</tbody>
</table>
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 \( \text{Cr}_2\text{O}_3 \) 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 \( \text{Cr}_2\text{O}_3 \) 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 \((\text{Cr}^{3+})\) and \((\text{Cr}^{2+})\) 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 \((\text{Cr}^{3+})\) increased as the metal sulphur content increased. The production rate of \((\text{Cr}^{2+})\) 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 transferred 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 \(\text{Cr}_2\text{O}_3\) 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 $\text{Fe}_t^{2+}$ content in slag.
place, leading to an increase in the rate of Cr$_2$O$_3$ 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$_2$O$_3$ in slag and because of their high residence time, the exposed iron then reacts with Cr$_2$O$_3$ by the reaction

\[(\text{Cr}_2\text{O}_3) + 3[\text{Fe}] = 2[\text{Cr}] + 3(\text{FeO}) \quad (5.1)\]

This reaction takes place simultaneously with that due to carbon oxidation

\[(\text{Cr}_2\text{O}_3) + 3[\text{C}] = 2[\text{Cr}] + 3\text{CO(g)} \quad (5.2)\]

The following reaction could also take place under these conditions

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

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$_2$O$_3$ reduction.
Reaction (5.4) is delayed probably because the presence

\[(\text{FeO}) + [\text{C}] = [\text{Fe}] + \text{CO(g)}\]  \hspace{1cm} (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 \((\text{Cr}^{3+})\) and \((\text{Cr}^{2+})\) 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 \(\text{Cr}_2\text{O}_3\) in the slag by equation (5.1). To clarify this point, graphs showing the variation of \(\text{Fe}^{2+}\), in form of \((\text{FeO})\) and that in form of \((\text{FeS})\) with time, were drawn for runs AS11 and AS12. The \(\text{Fe}^{2+}\) in form of \((\text{FeS})\) 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 Cr₂O₃ 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

\[ [S] + 2 e^- = (S^{2-}) \]  \hspace{1cm} (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

\[ [C] + (O^{2-}) = CO(g) + 2 e^- \]  \hspace{1cm} (5.6)

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

\[ [Fe] = (Fe^{2+}) + 2 e^- \]  \hspace{1cm} (5.7)
giving the overall molar solute transfer equivalent of

\[ 2n_S = 2n_{Fe} + 2n_C \]  (5.8)

and the overall sulphur transfer equation is

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

The Fe transferred 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 Cr₂O₃ presented in the preceding 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

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[wt% S]</th>
<th>Weight of metal droplets recovered (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 18</td>
<td>0.00</td>
<td>0.03</td>
</tr>
<tr>
<td>AS 19</td>
<td>0.10</td>
<td>0.36</td>
</tr>
</tbody>
</table>

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 Cr₂O₃ reduction. Comparison of the results for (Cr³⁺) reduction between runs AS18 and AS19 (Table 3.1) shows that the reduction in run AS19 is higher because of the low value of (Cr³⁺) realised after 25 minutes.
Anyakwo\textsuperscript{37}, in his investigation of the effect of sulphur addition to metal on the reduction rate of Cr\textsubscript{2}O\textsubscript{3} obtained similar results. The increase in the reduction rates of Cr\textsubscript{2}O\textsubscript{3} was attributed to metal emulsification.

\textbf{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\textsubscript{2}O\textsubscript{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\textsuperscript{3+}) and (Cr\textsuperscript{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\textsuperscript{3+}) and (Cr\textsuperscript{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\textsubscript{2}O\textsubscript{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 \( (\text{Cr}^{3+}) \) and \( (\text{Cr}^{2+}) \) reduction.
tension at metal sulphur contents higher than 0.10 wt%. The result is having rates of Cr₂O₃ 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 Cr₂O₃ 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.

<table>
<thead>
<tr>
<th>Wt% [S]</th>
<th>k_1</th>
<th>k_2</th>
<th>k_3</th>
<th>k_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.0248</td>
<td>0.0191</td>
<td>0.0434</td>
<td>0.0233</td>
</tr>
<tr>
<td>0.05</td>
<td>0.0460</td>
<td>0.0158</td>
<td>0.0386</td>
<td>0.0103</td>
</tr>
<tr>
<td>0.10</td>
<td>0.0869</td>
<td>0.0235</td>
<td>0.1127</td>
<td>0.0136</td>
</tr>
<tr>
<td>0.30</td>
<td>0.0800</td>
<td>0.0317</td>
<td>0.0965</td>
<td>0.0104</td>
</tr>
<tr>
<td>0.50</td>
<td>0.0941</td>
<td>0.0318</td>
<td>0.1033</td>
<td>0.0093</td>
</tr>
</tbody>
</table>

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
\[ k_1 = 0.0460 \text{ cm.min}^{-1}, \quad k_2 = 0.0158 \text{ cm.min}^{-1}. \]
\[ k_3 = 0.0386 \text{ cm.min}^{-1}, \quad k_4 = 0.0103 \text{ cm.min}^{-1}. \]

Sums of squares of deviations are:
\[ \text{Cr}^{3+} = 0.085, \quad \text{Cr}^{2+} = 0.071, \quad \text{Cr}_{\text{Met.}} = 0.024. \]

Fig. 5.19 Time variation in concentration of (\text{Cr}^{3+}), (\text{Cr}^{2+}) and [Cr] for run AS11.
\[ k_1 = 0.0869 \text{ cm.min}^{-1}, \quad k_2 = 0.0235 \text{ cm.min}^{-1}, \]
\[ k_3 = 0.1127 \text{ cm.min}^{-1}, \quad k_4 = 0.0136 \text{ cm.min}^{-1}. \]

Sums of squares of deviations are:

\[ \text{Cr}^{3+} = 0.024, \quad \text{Cr}^{2+} = 0.019, \quad \text{Cr}_{\text{Met.}} = 0.005. \]

Fig. 5.20 Time variation in concentration of (Cr\(^{3+}\)), (Cr\(^{2+}\)) and [Cr] for run AS12.
$k_1 = 0.0800 \text{ cm.min}^{-1}$, $k_2 = 0.0317 \text{ cm.min}^{-1}$.
$k_3 = 0.0965 \text{ cm.min}^{-1}$, $k_4 = 0.0104 \text{ cm.min}^{-1}$.

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

Fig. 5.21 Time variation in concentration of (Cr$^{3+}$),
(Cr$^{2+}$) and [Cr] for run AS13.
\[ k_1 = 0.0941 \text{ cm.min}^{-1}, \quad k_2 = 0.0318 \text{ cm.min}^{-1}, \]
\[ k_3 = 0.1033 \text{ cm.min}^{-1}, \quad k_4 = 0.0093 \text{ cm.min}^{-1}. \]

Sums of squares of deviations are:
\[ \text{Cr}^{3+} = 0.032, \quad \text{Cr}^{2+} = 0.025, \quad \text{Cr}_{\text{Met.}} = 0.007. \]

Fig. 5.22 Time variation in concentration of \((\text{Cr}^{3+})\), \((\text{Cr}^{2+})\) and [Cr] for run AS14.
Fig. 5.23 Effect of Sulphur addition to metal on the forward rate constants $k_1$ and $k_3$. 

- 262 -
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 \( \text{Cr}_2\text{O}_3 \) 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 mN\( \text{m}^{-1} \).

### 5.4.4 Effect of sulphur addition to slag.

To illustrate the effect of sulphur additions to slag on the rate of \( \text{Cr}_2\text{O}_3 \) 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 \( \text{Cr}^{3+} \) increases with sulphur addition to slag. The production rate of \( \text{Cr}^{2+} \) and its subsequent reduction also shows an
Fig. 5.24 Effect of Surface-tension on the forward rate constants $k_1$ and $k_3$. 

- 264 -
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$_2$O$_3$, 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$_2$O$_3$ 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$_2$O$_3$ 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>
<thead>
<tr>
<th>Run</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_3$</th>
<th>$k_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm.min$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AS5</td>
<td>0.0248</td>
<td>0.0191</td>
<td>0.0434</td>
<td>0.0233</td>
</tr>
<tr>
<td>AS15</td>
<td>0.1174</td>
<td>0.0205</td>
<td>0.0396</td>
<td>0.0136</td>
</tr>
<tr>
<td>AS16</td>
<td>0.1087</td>
<td>0.0058</td>
<td>0.0562</td>
<td>0.0171</td>
</tr>
</tbody>
</table>
Fig. 5.28  Effect of Sulphur addition to slag on \( Fe^{2+}_t \) content of slag.

Fig. 5.29  Variation of \( Fe^{2+} \) in slag in form of FeS and FeO for run AS16.
\[ k_1 = 0.1174 \text{ cm.min}^{-1}, \quad k_2 = 0.0205 \text{ cm.min}^{-1}, \]
\[ k_3 = 0.0396 \text{ cm.min}^{-1}, \quad k_4 = 0.0136 \text{ cm.min}^{-1}. \]

Sums of squares of deviations are:
\[ \text{Cr}^{3+} = 0.088, \quad \text{Cr}^{2+} = 0.144, \quad \text{Cr}_{\text{Met.}} = 0.037. \]

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

- 270 -
\[ k_1 = 0.1087 \text{ cm.min}^{-1}, \quad k_2 = 0.0058 \text{ cm.min}^{-1}, \]
\[ k_3 = 0.0562 \text{ cm.min}^{-1}, \quad k_4 = 0.0171 \text{ cm.min}^{-1}. \]

Sums of squares of deviations are:
\[ \text{Cr}^{3+} = 0.056, \quad \text{Cr}^{2+} = 0.300, \quad \text{Cr}_{\text{Met}} = 0.055. \]

Fig. 5.31 Time variation in concentration of \((\text{Cr}^{3+})\), \((\text{Cr}^{2+})\) and \([\text{Cr}]\) 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$_2$O$_3$ 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$_2$O$_3$. 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$_2$O$_3$ 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$_2$O$_3$ 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 earlier. An increase in \(k_2\) with selenium addition can also be seen from the table. This is due to the slow process of \((\text{Cr}^{2+})\) 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).
$k_1 = 0.0986 \text{ cm.min}^{-1}$, $k_2 = 0.0751 \text{ cm.min}^{-1}$, $k_3 = 0.0874 \text{ cm.min}^{-1}$, $k_4 = 0.0070 \text{ cm.min}^{-1}$.

Sums of squares of deviations are:

$\text{Cr}^{3+} = 0.067$, $\text{Cr}^{2+} = 0.063$, $\text{Cr}_{\text{Met.}} = 0.026$.

Fig. 5.37 Time variation in concentration of $\text{(Cr}^{3+})$, $\text{(Cr}^{2+})$ and $[\text{Cr}]$ for run AS20.
$k_1 = 0.1272 \text{ cm.min}^{-1}$. $k_2 = 0.0602 \text{ cm.min}^{-1}$.
$k_3 = 0.1042 \text{ cm.min}^{-1}$. $k_4 = 0.0084 \text{ cm.min}^{-1}$.

Sums of squares of deviations are:
Cr$^{3+} = 0.038$, Cr$^{2+} = 0.019$, Cr$_{\text{met.}} = 0.005$.

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

<table>
<thead>
<tr>
<th>Run</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_3$</th>
<th>$k_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm.min$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AS5</td>
<td>0.0248</td>
<td>0.0191</td>
<td>0.0434</td>
<td>0.0233</td>
</tr>
<tr>
<td>AS20</td>
<td>0.0986</td>
<td>0.0751</td>
<td>0.0874</td>
<td>0.0070</td>
</tr>
<tr>
<td>AS21</td>
<td>0.1272</td>
<td>0.0602</td>
<td>0.1042</td>
<td>0.0084</td>
</tr>
</tbody>
</table>

Anyakwo\(^{37}\) added antimony to metal in his investigation of the effect of surface-active elements on the rate of Cr$_2$O$_3$ 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.
\[ k_1 = 0.0631 \text{ cm.min}^{-1}, \quad k_2 = 0.0064 \text{ cm.min}^{-1}, \]
\[ k_3 = 0.0486 \text{ cm.min}^{-1}, \quad k_4 = 0.0151 \text{ cm.min}^{-1}. \]

Sums of squares of deviations are:
\[ \text{Cr}^{3+} = 0.092, \quad \text{Cr}^{2+} = 0.177, \quad \text{Cr}_{\text{Met.}} = 0.039. \]

Fig. 5.39 Time variation in concentration of \((\text{Cr}^{3+})\), \((\text{Cr}^{2+})\) and \([\text{Cr}]\) for 0.05 [wt% Sb] addition to metal, data from Ref (37).
\[ k_1 = 0.1220 \text{ cm.min}^{-1}, \quad k_2 = 0.0450 \text{ cm.min}^{-1}, \]
\[ k_3 = 0.2259 \text{ cm.min}^{-1}, \quad k_4 = 0.0115 \text{ cm.min}^{-1}. \]

Sums of squares of deviations are:
\[ \text{Cr}^{3+} = 0.049, \quad \text{Cr}^{2+} = 0.033, \quad \text{Cr}_{\text{met.}} = 0.055. \]

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).
Molecurally, 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

\[
\begin{array}{c}
\text{Si} - \text{O} - \text{Ca} - \text{O} - \text{Si} \\
\end{array}
\] (5.8)

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

\[
\begin{array}{c}
\text{Si} - \text{O} - \text{Ca} - \text{F} \\
\text{F} - \text{Ca} - \text{O} - \text{Si} \\
\end{array}
\] (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 \(\text{CaF}^+\) 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 \(\text{CaO-SiO}_2-\text{Al}_2\text{O}_3-\text{MgO}\) 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$_2$O$_3$, 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$_2$O$_3$. 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 $\text{Fe}^{2+}$ 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.

<table>
<thead>
<tr>
<th>Wt% CaF$_2$</th>
<th>$k_1$ cm.min$^{-1}$</th>
<th>$k_2$ cm.min$^{-1}$</th>
<th>$k_3$ cm.min$^{-1}$</th>
<th>$k_4$ cm.min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.0248</td>
<td>0.0191</td>
<td>0.0434</td>
<td>0.0233</td>
</tr>
<tr>
<td>2.00</td>
<td>0.0367</td>
<td>0.0386</td>
<td>0.0450</td>
<td>0.0186</td>
</tr>
<tr>
<td>3.50</td>
<td>0.0603</td>
<td>0.0344</td>
<td>0.0632</td>
<td>0.0101</td>
</tr>
<tr>
<td>5.00</td>
<td>0.1450</td>
<td>0.1156</td>
<td>0.1806</td>
<td>0.0116</td>
</tr>
</tbody>
</table>

To investigate the effect of CaF$_2$ addition to slag on the reduction rate of a high concentration of Cr$_2$O$_3$ in slag, run AS25 was carried out in which the initial
\[ k_1 = 0.0367 \text{ cm.min}^{-1} \quad k_2 = 0.0386 \text{ cm.min}^{-1} \]
\[ k_3 = 0.0450 \text{ cm.min}^{-1} \quad k_4 = 0.0189 \text{ cm.min}^{-1} \]

Sums of squares of deviations are:
\[ \text{Cr}^{3+} = 0.023, \quad \text{Cr}^{2+} = 0.018, \quad \text{Cr}_{\text{Met.}} = 0.006. \]

Fig. 5.44 Time variation in concentration of \((\text{Cr}^{3+})\), \((\text{Cr}^{2+})\) and \([\text{Cr}]\) for run AS22.
\[ k_1 = 0.0603 \text{ cm.min}^{-1}, \quad k_2 = 0.0344 \text{ cm.min}^{-1}, \]
\[ k_3 = 0.0632 \text{ cm.min}^{-1}, \quad k_4 = 0.0101 \text{ cm.min}^{-1}. \]

Sums of squares of deviations are:
\[ \text{Cr}^{3+} = 0.037, \quad \text{Cr}^{2+} = 0.028, \quad \text{Cr}_{\text{Met.}} = 0.028. \]

Fig. 5.45. Time variation in concentration of \((\text{Cr}^{3+})\), \((\text{Cr}^{2+})\) and [Cr] for run AS23.
\[ k_1 = 0.1450 \text{ cm.min}^{-1}, \quad k_2 = 0.1156 \text{ cm.min}^{-1}, \]
\[ k_3 = 0.1806 \text{ cm.min}^{-1}, \quad k_4 = 0.0116 \text{ cm.min}^{-1}. \]

Sums of squares of deviations are:
\[ \text{Cr}^{3+} = 0.044, \quad \text{Cr}^{2+} = 0.020, \quad \text{Cr}_{\text{Met.}} = 0.004. \]

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 $\text{Cr}_2\text{O}_3$ in slag was 10 wt% with a $\text{CaF}_2$ addition of 5 wt%. Fig. 5.48 shows concentration-time curves for the reduction of the chromium species for the cases where no $\text{CaF}_2$ (run AS3) and 5 wt% $\text{CaF}_2$ (run AS25) addition to slag were made. The increase in the reduction rates of ($\text{Cr}^{3+}$) and ($\text{Cr}^{2+}$) on addition of 5 wt% $\text{CaF}_2$ 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% $\text{CaF}_2$ to slag markedly increases the rate constant values an indication of the increase in the rate of $\text{Cr}_2\text{O}_3$ reduction.
Fig. 5.48 Effect of Calcium Fluoride on (Cr$^{3+}$) and (Cr$^{2+}$) reduction in slag containing 10 (wt% Cr$_2$O$_3$).
$k_1 = 0.2220 \text{ cm.min}^{-1}$. $k_2 = 0.0357 \text{ cm.min}^{-1}$.
$k_3 = 0.1719 \text{ cm.min}^{-1}$. $k_4 = 0.0125 \text{ cm.min}^{-1}$.

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

Fig. 5.49 Time variation in concentration of ($\text{Cr}^{3+}$),
($\text{Cr}^{2+}$) and [Cr] for run AS25.
CHAPTER 6

CONCLUSIONS

A first-order consecutive two-stage reaction model for the reduction of \( \text{Cr}_2\text{O}_3 \) 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 \( \text{Cr}_2\text{O}_3 \) under varying experimental conditions such as varying the furnace atmosphere, \( \text{Cr}_2\text{O}_3 \) concentration in slag, metal chromium content, employing surface-active elements, \( \text{S} \) and \( \text{Se} \), adding \( \text{FeO} \) 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 \( \text{Cr}_2\text{O}_3 \) 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 \((\text{Cr}^{3+})\) is not affected by the furnace atmosphere used. However, an argon atmosphere seems to increase the rate of \((\text{Cr}^{2+})\) reduction by a factor of about 1.4.

(3) Changes in the concentration of \(\text{Cr}_2\text{O}_3\) in slag show that the rate of \(\text{Cr}_2\text{O}_3\) 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 \(\text{Cr}_2\text{O}_3\) concentrations used.

(4) The reduction of \(\text{Cr}_2\text{O}_3\) from slag takes place in two stages. The first stage is the reduction of \((\text{Cr}^{3+})\) to \((\text{Cr}^{2+})\). 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 \((\text{Cr}^{2+})\) to [Cr] which is considered to be a slow process.

(5) It is established from the development of a model for \(\text{Cr}_2\text{O}_3\) 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 \((\text{Cr}^{2+})\) 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 \( \text{Cr}^{3+} \) directly reacts to form \([\text{Cr}]\), which takes place simultaneously with that through the intermediate, \( \text{Cr}^{2+} \), 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 \( \text{Cr}_2\text{O}_3 \) 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 \( \text{Cr}^{3+} \), i.e., the rate of the first-stage of the consecutive reaction is not affected. The reduction rate of \( \text{Cr}^{2+} \) decreases above 4 wt% chromium addition to metal. This is due to a reduction in the concentration gradient of \( \text{Cr}^{2+} \) 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 \((\text{Cr}^{3+})\) reduction the activation energy is 54.16 kcal/mol, for \((\text{Cr}^{2+})\) it is 27.15 kcal/mol and for \(\text{Cr}_2\text{O}_3\) reduction, it is 81.33 kcal/mol. \((\text{Cr}^{3+})\) is shown to be rate-limited by mass transport in the slag phase. \((\text{Cr}^{2+})\) is probably limited by an interfacial chemical reaction.

(10) Increasing the slag volume slightly increases the rate of \((\text{Cr}^{3+})\) reduction but has no effect on the rate of \((\text{Cr}^{2+})\) reduction. Increasing the metal volume has no effect on the rate of \((\text{Cr}^{3+})\) and \((\text{Cr}^{2+})\) reduction. This shows that the reduction of \((\text{Cr}^{3+})\) is controlled by mass transport of \((\text{Cr}^{3+})\) in the slag phase whereas \((\text{Cr}^{2+})\) 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$_2$O$_3$ 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.
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:

\[
\begin{align*}
(Cr^{3+}) \xrightleftharpoons[k_2]{k_1} (Cr^{2+}) \xrightleftharpoons[k_4]{k_3} [Cr]
\end{align*}
\]  \hspace{1cm} (A.1)

The differential equations are:

\[
\frac{d(Cr^{3+})}{dt} = \frac{k_2}{h} (Cr^{2+}) - \frac{k_1}{h} (Cr^{3+})
\]  \hspace{1cm} (A.2)

\[
\frac{d(Cr^{2+})}{dt} = \frac{k_1}{h} (Cr^{3+}) + \frac{k_4}{h} [Cr] - \frac{k_2}{h} (Cr^{2+})
\]  
\[ - \frac{k_3}{h} (Cr^{2+}) \]  \hspace{1cm} (A.3)
\[
\frac{d[Cr]}{dt} = \frac{k_3}{h} (Cr^{2+}) - \frac{k_4}{h} [Cr]
\]  
(A.4)

where \( h \) is the slag height in cm. The transformed functions for the boundary conditions; at \( t = 0 \), \( (Cr^{3+}) = (Cr^{3+})_0 \), \( (Cr^{2+}) = [Cr] = 0 \) for equations (A.2), (A.3) and (A.4) are:

\[
S (Cr^{3+}) - S (Cr^{3+})_0 = K_2 (Cr^{2+}) - K_1 (Cr^{3+}) 
\]  
(A.5)

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

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

where \( K_1 = k_1/h \) etc. Solving these equations in succession yields

\[
(Cr^{3+}) = \frac{(Cr^{3+})_0 \left\{ S^2 + S (K_2 + K_3 + K_4) + K_2 K_4 \right\}}{\left\{ S^2 + S (K_1 + K_2 + K_3 + K_4) + K_1 K_3 + K_2 K_4 + K_1 K_4 \right\}}
\]  
(A.8)

\[
(Cr^{2+}) = \frac{(Cr^{3+})_0 K_1 (S + K_4)}{\left\{ S^2 + S (K_1 + K_2 + K_3 + K_4) + K_1 K_3 + K_2 K_4 + K_1 K_4 \right\}}
\]  
(A.9)
\[
\frac{[\text{Cr}]}{[\text{Cr}^3+]_o K_1 K_3}
\left\{ \frac{S^2 + S(K_1 + K_2 + K_3 + K_4) + K_1 K_3 + K_2 K_4 + K_1 K_4}{S^2 + S(K_2 + K_3 + K_4) + K_2 K_4} \right\}
\]

(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

\[
S^2 + S(K_1 + K_2 + K_3 + K_4) + K_1 K_3 + K_2 K_4 + K_1 K_4 = 0
\]

(A.11)

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

\[
\frac{[\text{Cr}]}{[\text{Cr}^3+]_o K_1 K_3}
\left\{ \frac{S^2 + S(K_1 + K_2 + K_3 + K_4) + K_2 K_4}{S + m_1/(S + m_2)} \right\}
\]

(A.12)

\[
[\text{Cr}] = \frac{[\text{Cr}^3+]_o K_1 (S + K_4)}{(S + m_1)/(S + m_2)}
\]

(A.13)

\[
[\text{Cr}] = \frac{[\text{Cr}^3+]_o K_1 K_3}{(S + m_1)/(S + m_2)}
\]

(A.14)

Replacing the transforms with the appropriate originals yields the final solutions:
\[(\text{Cr}^{3+}) = (\text{Cr}^{3+})_0 \left\{ \frac{K_2 K_4}{m_1 m_2} + \frac{m_1^2 - m_1 (K_2 + K_3 + K_4) + K_2 K_4}{m_1 (m_1 - m_2)} \right. \]

\[\exp(-m_1 t) + \frac{m_2^2 - m_2 (K_2 + K_3 + K_4) + K_2 K_4}{m_2 (m_2 - m_1)} \exp(-m_2 t) \}\]

\[(A.15)\]

\[(\text{Cr}^{2+}) = K_1 (\text{Cr}^{3+})_0 \left\{ \frac{K_4}{m_1 m_2} - \frac{K_4 - m_1}{m_1 (m_2 - m_1)} \exp(-m_1 t) \right. \]

\[- \frac{K_4 - m_2}{m_2 (m_1 - m_2)} \exp(-m_2 t) \}\]

\[(A.16)\]

\[[\text{Cr}] = K_1 K_3 (\text{Cr}^{3+})_0 \left\{ \frac{1}{m_1 m_2} - \frac{1}{m_1 (m_2 - m_1)} \exp(-m_1 t) \right. \]

\[- \frac{1}{m_2 (m_1 - m_2)} \exp(-m_2 t) \}\]

\[(A.17)\]

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:
\[ m_1 = \frac{1}{2} \left\{ \frac{(K_1 + K_2 + K_3 + K_4)}{\sqrt{(K_1 + K_2 + K_3 + K_4)^2 - 4(K_1K_3 + K_2K_4 + K_1K_4)}} \right\} \]

(A.18)

\[ m_2 = \frac{1}{2} \left\{ \frac{(K_1 + K_2 + K_3 + K_4)}{-\sqrt{(K_1 + K_2 + K_3 + K_4)^2 - 4(K_1K_3 + K_2K_4 + K_1K_4)}} \right\} \]

(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.
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.

<table>
<thead>
<tr>
<th>Variable name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Slag height, cm.</td>
</tr>
<tr>
<td>M1, M2</td>
<td>Roots to equation (A.11)</td>
</tr>
<tr>
<td>CR3</td>
<td>Calculated (Cr$^{3+}$) concentration</td>
</tr>
<tr>
<td>CR2</td>
<td>Calculated (Cr$^{2+}$) concentration</td>
</tr>
<tr>
<td>CRFE</td>
<td>Calculated [Cr] concentration</td>
</tr>
<tr>
<td>CR</td>
<td>Calculated concentration of total chromium in slag</td>
</tr>
<tr>
<td>CRO</td>
<td>Initial concentration of total chromium in slag</td>
</tr>
<tr>
<td>T</td>
<td>Number of data points</td>
</tr>
<tr>
<td>K1, K2, K3, K4</td>
<td>Rate constants for consecutive reversible two-stage reactions</td>
</tr>
<tr>
<td>CRWT</td>
<td>Weight of chromium in slag</td>
</tr>
<tr>
<td>CR3D</td>
<td>Observed (Cr$^{3+}$) concentration</td>
</tr>
<tr>
<td>CR2D</td>
<td>Observed (Cr$^{2+}$) concentration</td>
</tr>
<tr>
<td>CRFED</td>
<td>Observed [Cr] concentration</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>LA</td>
<td>Sums of squares of deviations between observed and calculated (Cr$^{3+}$) concentrations</td>
</tr>
<tr>
<td>LB</td>
<td>Sums of squares of deviations between observed and calculated (Cr$^{2+}$) concentrations</td>
</tr>
<tr>
<td>LC</td>
<td>Sums of squares of deviations between observed and calculated [Cr] concentrations</td>
</tr>
<tr>
<td>L</td>
<td>Total sums of squares of deviations (SUMA + SUMB + SUMC)</td>
</tr>
<tr>
<td>K1MIN, K2MIN,</td>
<td>Rate constants giving minimum sums of squares of deviations</td>
</tr>
<tr>
<td>K3MIN, K4MIN</td>
<td></td>
</tr>
<tr>
<td>LMIN</td>
<td>Total minimum sums of squares of deviations</td>
</tr>
<tr>
<td>GO5CAF, GO5CBF</td>
<td>External subroutines for generating random numbers</td>
</tr>
<tr>
<td>SIMUMIN.OUT</td>
<td>Out put file for the rate constants</td>
</tr>
<tr>
<td>SIGMA</td>
<td>A factor for changing rate constants</td>
</tr>
<tr>
<td>ITER</td>
<td>Number of loops</td>
</tr>
</tbody>
</table>
PROGRAM SIMUMIN

C This program computes the rate constants for a
typical set of data from the reduction of Cr$_2$O$_3$ from
slag using an iteration method and expressions for
the variation of the concentrations of the chromium
species obtained for a consecutive reversible
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, GO5CAF
EXTERNAL GO5CAF, GO5CBF
CALL GO5CAF(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'

- 311 -
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, 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

- 313 -
The sums of squares of deviations for the chromium 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
```

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
```

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

```
X = GO5CAF(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)
```
CONTINUE
WRITE (6,20)
WRITE (6,21)
WRITE (6,25) K1MIN, K2MIN, K3MIN, K4MIN, LA, LB, LC

20 FORMAT (/,' RATE CONSTANTS ',/,$5X,',',/,$5X,'________________________________________')

21 FORMAT (/,' K1MIN K2MIN K3MIN K4MIN LA LB LC',/,$5X,'________________________________________')

25 FORMAT (/,3X,6(5X,F6.4))
WRITE (*,*) 'PROGRAM COMPLETED SUCCESSFULLY'
STOP
END

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

OUTPUT

<table>
<thead>
<tr>
<th>K1MIN</th>
<th>K2MIN</th>
<th>K3MIN</th>
<th>K4MIN</th>
<th>LA</th>
<th>LB</th>
<th>LC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0238</td>
<td>0.0198</td>
<td>0.0760</td>
<td>0.0313</td>
<td>0.004</td>
<td>0.042</td>
<td>0.006</td>
</tr>
</tbody>
</table>

- 315 -
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.

```plaintext
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,CR0,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 calculated in appendix B are read from their file and
```

- 316 -
C are used in the calculation below

OPEN(8,FILE='SIMULIN.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))

- 317 -
\[
CR(J) = C5 \times ((M1 \times M2)^{**-1} - ((M1 \times M2 \times M1)^{**-1}) \times \exp(-M2 \times J)) \\
\]  
\[
\$ \times \exp(-M1 \times J) - ((M2 \times (M1 - M2)^{**-1}) \times \exp(-M2 \times J))
\]  
\[
CRWT(J) = (CR(J) / 100) \times 20 \\
CRFE(J) = (CRWT(J) / (60 + CRWT(J))) \times 100
\]

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 SUCCESSFULLY '
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.
<table>
<thead>
<tr>
<th>K</th>
<th>CR3 (K)</th>
<th>CR2 (K)</th>
<th>CRFE (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.3305</td>
<td>0.0858</td>
<td>0.0012</td>
</tr>
<tr>
<td>2</td>
<td>3.2452</td>
<td>0.1608</td>
<td>0.0047</td>
</tr>
<tr>
<td>3</td>
<td>3.1636</td>
<td>0.2265</td>
<td>0.0100</td>
</tr>
<tr>
<td>4</td>
<td>3.0856</td>
<td>0.2840</td>
<td>0.0168</td>
</tr>
<tr>
<td>5</td>
<td>3.0108</td>
<td>0.3345</td>
<td>0.0249</td>
</tr>
<tr>
<td>6</td>
<td>2.9391</td>
<td>0.3788</td>
<td>0.0340</td>
</tr>
<tr>
<td>7</td>
<td>2.8701</td>
<td>0.4177</td>
<td>0.0440</td>
</tr>
<tr>
<td>8</td>
<td>2.8038</td>
<td>0.4520</td>
<td>0.0547</td>
</tr>
<tr>
<td>9</td>
<td>2.7399</td>
<td>0.4823</td>
<td>0.0659</td>
</tr>
<tr>
<td>10</td>
<td>2.6784</td>
<td>0.5089</td>
<td>0.0775</td>
</tr>
<tr>
<td>11</td>
<td>2.6190</td>
<td>0.5326</td>
<td>0.0894</td>
</tr>
<tr>
<td>12</td>
<td>2.5617</td>
<td>0.5535</td>
<td>0.1015</td>
</tr>
<tr>
<td>13</td>
<td>2.5063</td>
<td>0.5720</td>
<td>0.1137</td>
</tr>
<tr>
<td>14</td>
<td>2.4528</td>
<td>0.5886</td>
<td>0.1260</td>
</tr>
<tr>
<td>15</td>
<td>2.4011</td>
<td>0.6033</td>
<td>0.1384</td>
</tr>
<tr>
<td>K</td>
<td>CR3 (K)</td>
<td>CR2 (K)</td>
<td>CRFE (K)</td>
</tr>
<tr>
<td>----</td>
<td>----------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>16</td>
<td>2.3510</td>
<td>0.6165</td>
<td>0.1506</td>
</tr>
<tr>
<td>17</td>
<td>2.3025</td>
<td>0.6283</td>
<td>0.1628</td>
</tr>
<tr>
<td>18</td>
<td>2.2556</td>
<td>0.6389</td>
<td>0.1749</td>
</tr>
<tr>
<td>19</td>
<td>2.2101</td>
<td>0.6484</td>
<td>0.1868</td>
</tr>
<tr>
<td>20</td>
<td>2.1660</td>
<td>0.6571</td>
<td>0.1986</td>
</tr>
<tr>
<td>21</td>
<td>2.1233</td>
<td>0.6649</td>
<td>0.2102</td>
</tr>
<tr>
<td>22</td>
<td>2.0818</td>
<td>0.6720</td>
<td>0.2216</td>
</tr>
<tr>
<td>23</td>
<td>2.0416</td>
<td>0.6785</td>
<td>0.2328</td>
</tr>
<tr>
<td>24</td>
<td>2.0026</td>
<td>0.6844</td>
<td>0.2437</td>
</tr>
<tr>
<td>25</td>
<td>1.9648</td>
<td>0.6898</td>
<td>0.2545</td>
</tr>
<tr>
<td>26</td>
<td>1.9280</td>
<td>0.6948</td>
<td>0.2650</td>
</tr>
<tr>
<td>27</td>
<td>1.8924</td>
<td>0.6995</td>
<td>0.2753</td>
</tr>
<tr>
<td>28</td>
<td>1.8578</td>
<td>0.7038</td>
<td>0.2853</td>
</tr>
<tr>
<td>29</td>
<td>1.8242</td>
<td>0.7077</td>
<td>0.2952</td>
</tr>
<tr>
<td>30</td>
<td>1.7916</td>
<td>0.7115</td>
<td>0.3047</td>
</tr>
<tr>
<td>31</td>
<td>1.7599</td>
<td>0.7149</td>
<td>0.3141</td>
</tr>
<tr>
<td>32</td>
<td>1.7291</td>
<td>0.7182</td>
<td>0.3232</td>
</tr>
<tr>
<td>K</td>
<td>CR3 (K)</td>
<td>CR2 (K)</td>
<td>CRFE (K)</td>
</tr>
<tr>
<td>---</td>
<td>---------</td>
<td>---------</td>
<td>----------</td>
</tr>
<tr>
<td>33</td>
<td>1.6992</td>
<td>0.7212</td>
<td>0.3321</td>
</tr>
<tr>
<td>34</td>
<td>1.6702</td>
<td>0.7241</td>
<td>0.3407</td>
</tr>
<tr>
<td>35</td>
<td>1.6420</td>
<td>0.7268</td>
<td>0.3492</td>
</tr>
<tr>
<td>36</td>
<td>1.6146</td>
<td>0.7294</td>
<td>0.3574</td>
</tr>
<tr>
<td>37</td>
<td>1.5879</td>
<td>0.7319</td>
<td>0.3654</td>
</tr>
<tr>
<td>38</td>
<td>1.5621</td>
<td>0.7342</td>
<td>0.3732</td>
</tr>
<tr>
<td>39</td>
<td>1.5369</td>
<td>0.7364</td>
<td>0.3808</td>
</tr>
<tr>
<td>40</td>
<td>1.5125</td>
<td>0.7385</td>
<td>0.3881</td>
</tr>
<tr>
<td>41</td>
<td>1.4888</td>
<td>0.7405</td>
<td>0.3953</td>
</tr>
<tr>
<td>42</td>
<td>1.4657</td>
<td>0.7425</td>
<td>0.4023</td>
</tr>
<tr>
<td>43</td>
<td>1.4433</td>
<td>0.7443</td>
<td>0.4091</td>
</tr>
<tr>
<td>44</td>
<td>1.4215</td>
<td>0.7461</td>
<td>0.4157</td>
</tr>
<tr>
<td>45</td>
<td>1.4004</td>
<td>0.7478</td>
<td>0.4221</td>
</tr>
<tr>
<td>46</td>
<td>1.3798</td>
<td>0.7495</td>
<td>0.4284</td>
</tr>
<tr>
<td>47</td>
<td>1.3598</td>
<td>0.7511</td>
<td>0.4345</td>
</tr>
<tr>
<td>48</td>
<td>1.3404</td>
<td>0.7526</td>
<td>0.4404</td>
</tr>
<tr>
<td>49</td>
<td>1.3215</td>
<td>0.7541</td>
<td>0.4461</td>
</tr>
<tr>
<td>K</td>
<td>CR3 (K)</td>
<td>CR2 (K)</td>
<td>CRFE (K)</td>
</tr>
<tr>
<td>---</td>
<td>---------</td>
<td>---------</td>
<td>----------</td>
</tr>
<tr>
<td>50</td>
<td>1.3032</td>
<td>0.7555</td>
<td>0.4517</td>
</tr>
<tr>
<td>51</td>
<td>1.2854</td>
<td>0.7569</td>
<td>0.4571</td>
</tr>
<tr>
<td>52</td>
<td>1.2680</td>
<td>0.7582</td>
<td>0.4624</td>
</tr>
<tr>
<td>53</td>
<td>1.2512</td>
<td>0.7595</td>
<td>0.4676</td>
</tr>
<tr>
<td>54</td>
<td>1.2348</td>
<td>0.7608</td>
<td>0.4726</td>
</tr>
<tr>
<td>55</td>
<td>1.2189</td>
<td>0.7620</td>
<td>0.4774</td>
</tr>
<tr>
<td>56</td>
<td>1.2035</td>
<td>0.7631</td>
<td>0.4821</td>
</tr>
<tr>
<td>57</td>
<td>1.1885</td>
<td>0.7643</td>
<td>0.4867</td>
</tr>
<tr>
<td>58</td>
<td>1.1739</td>
<td>0.7654</td>
<td>0.4912</td>
</tr>
<tr>
<td>59</td>
<td>1.1597</td>
<td>0.7664</td>
<td>0.4955</td>
</tr>
<tr>
<td>60</td>
<td>1.1459</td>
<td>0.7675</td>
<td>0.4997</td>
</tr>
<tr>
<td>61</td>
<td>1.1325</td>
<td>0.7685</td>
<td>0.5038</td>
</tr>
<tr>
<td>62</td>
<td>1.1194</td>
<td>0.7695</td>
<td>0.5078</td>
</tr>
<tr>
<td>63</td>
<td>1.1068</td>
<td>0.7704</td>
<td>0.5116</td>
</tr>
<tr>
<td>64</td>
<td>1.0945</td>
<td>0.7713</td>
<td>0.5154</td>
</tr>
<tr>
<td>65</td>
<td>1.0825</td>
<td>0.7722</td>
<td>0.5191</td>
</tr>
<tr>
<td>66</td>
<td>1.0709</td>
<td>0.7731</td>
<td>0.5226</td>
</tr>
</tbody>
</table>

- 322 -
<table>
<thead>
<tr>
<th>K</th>
<th>CR3 (K)</th>
<th>CR2 (K)</th>
<th>CRFE (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>67</td>
<td>1.0596</td>
<td>0.7739</td>
<td>0.5261</td>
</tr>
<tr>
<td>68</td>
<td>1.0486</td>
<td>0.7747</td>
<td>0.5294</td>
</tr>
<tr>
<td>69</td>
<td>1.0379</td>
<td>0.7755</td>
<td>0.5327</td>
</tr>
<tr>
<td>70</td>
<td>1.0275</td>
<td>0.7763</td>
<td>0.5358</td>
</tr>
<tr>
<td>71</td>
<td>1.0174</td>
<td>0.7770</td>
<td>0.5389</td>
</tr>
<tr>
<td>72</td>
<td>1.0076</td>
<td>0.7778</td>
<td>0.5419</td>
</tr>
<tr>
<td>73</td>
<td>0.9981</td>
<td>0.7785</td>
<td>0.5448</td>
</tr>
<tr>
<td>74</td>
<td>0.9888</td>
<td>0.7792</td>
<td>0.5477</td>
</tr>
<tr>
<td>75</td>
<td>0.9798</td>
<td>0.7798</td>
<td>0.5504</td>
</tr>
<tr>
<td>76</td>
<td>0.9711</td>
<td>0.7805</td>
<td>0.5531</td>
</tr>
<tr>
<td>77</td>
<td>0.9626</td>
<td>0.7811</td>
<td>0.5557</td>
</tr>
<tr>
<td>78</td>
<td>0.9543</td>
<td>0.7817</td>
<td>0.5582</td>
</tr>
<tr>
<td>79</td>
<td>0.9463</td>
<td>0.7823</td>
<td>0.5606</td>
</tr>
<tr>
<td>80</td>
<td>0.9385</td>
<td>0.7829</td>
<td>0.5630</td>
</tr>
<tr>
<td>81</td>
<td>0.9309</td>
<td>0.7834</td>
<td>0.5653</td>
</tr>
<tr>
<td>82</td>
<td>0.9235</td>
<td>0.7840</td>
<td>0.5676</td>
</tr>
<tr>
<td>83</td>
<td>0.9164</td>
<td>0.7845</td>
<td>0.5698</td>
</tr>
</tbody>
</table>

- 323 -
<table>
<thead>
<tr>
<th>K</th>
<th>CR3 (K)</th>
<th>CR2 (K)</th>
<th>CRFE (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>84</td>
<td>0.9094</td>
<td>0.7850</td>
<td>0.5719</td>
</tr>
<tr>
<td>85</td>
<td>0.9026</td>
<td>0.7855</td>
<td>0.5740</td>
</tr>
<tr>
<td>86</td>
<td>0.8960</td>
<td>0.7860</td>
<td>0.5760</td>
</tr>
<tr>
<td>87</td>
<td>0.8896</td>
<td>0.7865</td>
<td>0.5779</td>
</tr>
<tr>
<td>88</td>
<td>0.8834</td>
<td>0.7869</td>
<td>0.5798</td>
</tr>
<tr>
<td>89</td>
<td>0.8774</td>
<td>0.7874</td>
<td>0.5817</td>
</tr>
<tr>
<td>90</td>
<td>0.8715</td>
<td>0.7878</td>
<td>0.5835</td>
</tr>
<tr>
<td>91</td>
<td>0.8658</td>
<td>0.7882</td>
<td>0.5852</td>
</tr>
<tr>
<td>92</td>
<td>0.8602</td>
<td>0.7886</td>
<td>0.5869</td>
</tr>
<tr>
<td>93</td>
<td>0.8548</td>
<td>0.7890</td>
<td>0.5886</td>
</tr>
<tr>
<td>94</td>
<td>0.8496</td>
<td>0.7894</td>
<td>0.5902</td>
</tr>
<tr>
<td>95</td>
<td>0.8445</td>
<td>0.7898</td>
<td>0.5917</td>
</tr>
<tr>
<td>96</td>
<td>0.8395</td>
<td>0.7902</td>
<td>0.5932</td>
</tr>
<tr>
<td>97</td>
<td>0.8347</td>
<td>0.7905</td>
<td>0.5947</td>
</tr>
<tr>
<td>98</td>
<td>0.8301</td>
<td>0.7909</td>
<td>0.5961</td>
</tr>
<tr>
<td>99</td>
<td>0.8255</td>
<td>0.7912</td>
<td>0.5975</td>
</tr>
<tr>
<td>100</td>
<td>0.8211</td>
<td>0.7915</td>
<td>0.5989</td>
</tr>
<tr>
<td>K</td>
<td>CR3 (K)</td>
<td>CR2 (K)</td>
<td>CRFE (K)</td>
</tr>
<tr>
<td>----</td>
<td>---------</td>
<td>---------</td>
<td>----------</td>
</tr>
<tr>
<td>101</td>
<td>0.8168</td>
<td>0.7918</td>
<td>0.6002</td>
</tr>
<tr>
<td>102</td>
<td>0.8126</td>
<td>0.7921</td>
<td>0.6014</td>
</tr>
<tr>
<td>103</td>
<td>0.8086</td>
<td>0.7924</td>
<td>0.6027</td>
</tr>
<tr>
<td>104</td>
<td>0.8046</td>
<td>0.7927</td>
<td>0.6039</td>
</tr>
<tr>
<td>105</td>
<td>0.8008</td>
<td>0.7930</td>
<td>0.6051</td>
</tr>
<tr>
<td>106</td>
<td>0.7971</td>
<td>0.7933</td>
<td>0.6062</td>
</tr>
<tr>
<td>107</td>
<td>0.7934</td>
<td>0.7936</td>
<td>0.6073</td>
</tr>
<tr>
<td>108</td>
<td>0.7899</td>
<td>0.7938</td>
<td>0.6084</td>
</tr>
<tr>
<td>109</td>
<td>0.7865</td>
<td>0.7941</td>
<td>0.6094</td>
</tr>
<tr>
<td>110</td>
<td>0.7832</td>
<td>0.7943</td>
<td>0.6104</td>
</tr>
<tr>
<td>111</td>
<td>0.7799</td>
<td>0.7946</td>
<td>0.6114</td>
</tr>
<tr>
<td>112</td>
<td>0.7768</td>
<td>0.7948</td>
<td>0.6124</td>
</tr>
<tr>
<td>113</td>
<td>0.7737</td>
<td>0.7950</td>
<td>0.6133</td>
</tr>
<tr>
<td>114</td>
<td>0.7708</td>
<td>0.7952</td>
<td>0.6142</td>
</tr>
<tr>
<td>115</td>
<td>0.7679</td>
<td>0.7954</td>
<td>0.6151</td>
</tr>
<tr>
<td>116</td>
<td>0.7651</td>
<td>0.7957</td>
<td>0.6159</td>
</tr>
<tr>
<td>117</td>
<td>0.7623</td>
<td>0.7959</td>
<td>0.6168</td>
</tr>
</tbody>
</table>

- 325 -
<table>
<thead>
<tr>
<th>K</th>
<th>CR3 (K)</th>
<th>CR2 (K)</th>
<th>CRFE (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>118</td>
<td>0.7597</td>
<td>0.7960</td>
<td>0.6176</td>
</tr>
<tr>
<td>119</td>
<td>0.7571</td>
<td>0.7962</td>
<td>0.6184</td>
</tr>
<tr>
<td>120</td>
<td>0.7546</td>
<td>0.7964</td>
<td>0.6191</td>
</tr>
</tbody>
</table>
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 different 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.

<table>
<thead>
<tr>
<th>Variable name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>B21, B22, B23, B31, B32, B33</td>
<td>The coefficients B from Frost and Pearson's treatment</td>
</tr>
<tr>
<td>DETB</td>
<td>The determinant of the matrix of the coefficients B</td>
</tr>
<tr>
<td>CR30, CR20, CRO</td>
<td>Initial concentrations of the chromium species</td>
</tr>
<tr>
<td>CRT</td>
<td>Total concentration of chromium in slag</td>
</tr>
<tr>
<td>WT</td>
<td>Weight of slag in each time</td>
</tr>
</tbody>
</table>
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,CR30,CR20,CR0,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),
$ CR30(20),CR20(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')
The guess rate constants and the initial 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
CR3TS = CR3OS + CR2OS
```

The number of experimental points and the file 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)
```

- 329 -
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) = CR0(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)) - 330 -
$ + B23*D3*EXP(-M2*TINV))
SS5(I) = CR20(I)*(B21*E1 + B22*E2*EXP(-M1*TINV)
$ + B23*E3*EXP(-M2*TINV))
SS6(I) = CRO(I)*(B21*F1 + B22*F2*EXP(-M1*TINV)
$ + B23*F3*EXP(-M2*TINV))
CR2(I) = (SS4(I) + SS5(I) + SS6(I)) / DETB
SS7(I) = CR30(I)*(B31*D1 + B32*D2*EXP(-M1*TINV)
$ + B33*D3*EXP(-M2*TINV))
SS8(I) = CR20(I)*(B31*E1 + B32*E2*EXP(-M1*TINV)
$ + B33*E3*EXP(-M2*TINV))
SS9(I) = CRO(I)*(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 assigned

CR30(I) = CR3(I)
CR20(I) = CR2(I)
CRO(I) = CR(I)
CRT(I) = 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

- 331 -
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 random number is generated by an external
C subroutine called GO5CAF. Multiplying the number
C generated by 4 determines which rate constant to
C change. A second generation of a random number gives
C value by which rate 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
  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

99 CONTINUE
WRITE(6,60)
WRITE(6,66)
WRITE(6,30) K1MIN, K2MIN, K3MIN, K4MIN, LA, LB, LC

- 332 -
FORMAT(/,, 'RATE CONSTANTS ,, $5X,'__________________________' )

FORMAT(/,, K1MIN K2MIN K3MIN K4MIN LA LB LC ,, $5X,'__________________________' )

FORMAT(/,, 3X,7(5X,F6.4))
WRITE (*,*) 'PROGRAM COMPILED SUCCESSFULLY'
STOP
END

SUBROUTINE CHANGE(K,X,SIGMA)
REAL K,SIGMA
DOUBLE PRECISION X

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,CR30,CR20,CRO,CR3,CR2,CR,CRT,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,WTD,CR,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),CR30(120),CR20(120),
         CRO(120),CRT(120),WTD(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
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

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

The number of experimental points and the file 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)
   ENDR
   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

   - 336 -
\[ D1 = B22 \cdot B33 - B23 \cdot B32 \]
\[ D2 = B31 \cdot B23 - B21 \cdot B33 \]
\[ D3 = B21 \cdot B32 - B31 \cdot B22 \]
\[ E1 = B32 - B33 \]
\[ E2 = B33 - B31 \]
\[ E3 = B31 - B32 \]
\[ F1 = B23 - B22 \]
\[ F2 = B21 - B23 \]
\[ F3 = B22 - B21 \]
\[ \text{DO 20 I = 1, TINV} \]
\[ SS1(I) = \text{CR30}(I) \cdot (D1 + D2 \cdot \text{EXP}(-M1*I)) \]
\[ SS2(I) = \text{CR20}(I) \cdot (E1 + E2 \cdot \text{EXP}(-M1*I)) \]
\[ SS3(I) = \text{CR0}(I) \cdot (F1 + F2 \cdot \text{EXP}(-M1*I) + F3 \cdot \text{EXP}(-M2*I)) \]
\[ \text{CR3}(I) = (SS1(I) + SS2(I) + SS3(I))/\text{DETB} \]
\[ SS4(I) = \text{CR30}(I) \cdot (B21 \cdot D1 + B22 \cdot D2 \cdot \text{EXP}(-M1*I)) \]
\[ SS5(I) = \text{CR20}(I) \cdot (B21 \cdot E1 + B22 \cdot E2 \cdot \text{EXP}(-M1*I)) \]
\[ SS6(I) = \text{CR0}(I) \cdot (B21 \cdot F1 + B22 \cdot F2 \cdot \text{EXP}(-M1*I)) \]
\[ \text{CR2}(I) = (SS4(I) + SS5(I) + SS6(I))/\text{DETB} \]
\[ SS7(I) = \text{CR30}(I) \cdot (B31 \cdot D1 + B32 \cdot D2 \cdot \text{EXP}(-M1*I)) \]
\[ SS8(I) = \text{CR20}(I) \cdot (B31 \cdot E1 + B32 \cdot E2 \cdot \text{EXP}(-M1*I)) \]
\[ SS9(I) = \text{CR0}(I) \cdot (B31 \cdot F1 + B32 \cdot F2 \cdot \text{EXP}(-M1*I)) \]
\[ \text{CR}(I) = (SS7(I) + SS8(I) + SS9(I))/\text{DETB} \]
\[ \text{CRT}(I) = \text{CR3}(I) + \text{CR2}(I) \]
\[ \text{CRWT}(I) = (\text{CRT}(I)/100) \cdot \text{WT}(J) \]
\[ \text{WTDF}(I) = \text{INC} - \text{CRWT}(I) + \text{SUM} \]
\[ \text{CRFE}(I) = (\text{WTDF}(I)/(60 + \text{WTDF}(I))) \cdot 100 \]

C The initial conditions for the next time interval are

- 337 -
C assigned

IF (I.EQ.TIMV) THEN
CR30(I) = CR3(I)
CR20(I) = CR2(I)
CRO(I) = CR(I)
CRT(I) = 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),CRF(K)
IF(K.EQ.TIMV) 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,DET,B,M2,
$ M3,CR30,CR20,CR0,CR3,CR2,CR,CRT,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),CR30(20),CR20(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,G05CAF
CHARACTER NAME*13
CALL G05CBF(0)
LMIN = 1000.0
OPEN (8,FILE='LAGMIN.OUT',STATUS='OLD')
The guessed rate constants and the number of 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
```

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

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

The number of experimental points and the file 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
```

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),
```
$\text{SCR2D(IL,J), Z, CRFED(IL,J)}$

998 CONTINUE
CLOSE(7)
WRITE(*,*), TIME(3,J), WT(3,J), CR3D(3,J), CR2D(3,J),
$\text{SCRFED(3,J)}$

80 CONTINUE

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

DO 777 ITER = 1, 10000
L = 0
DO 778 M = 1, D
CR30(1) = CR3OS(M)
CR20(1) = CR2OS(M)
CRO(1) = CROS(M)
CRT(1) = CRTS(M)
SUM = 0
DO 20 I = 2, T
TINV = TIME(I,M) - TIME(I-1,M)
INC = (CRT(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

- 342 -
ENDIF

DET_B = 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) = CR30(1)*(D1 + D2*EXP(-M2*TINV))

$ + D3*EXP(-M3*TINV))

SS2(I,M) = CR20(1)*(E1 + E2*EXP(-M2*TINV))

$ + E3*EXP(-M3*TINV))

SS3(I,M) = CR0(1)*(F1 + F2*EXP(-M2*TINV))

$ + F3*EXP(-M3*TINV))

CR3(I,M) = (SS1(I,M) + SS2(I,M) + SS3(I,M))/DET_B

SS4(I,M) = CR30(1)*(B21*D1 + B22*D2*EXP(-M2*TINV))

$ + B23*D3*EXP(-M3*TINV))

SS5(I,M) = CR20(1)*(B21*E1 + B22*E2*EXP(-M2*TINV))

$ + B23*E3*EXP(-M3*TINV))

SS6(I,M) = CR0(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))/DET_B

SS7(I,M) = CR30(1)*(B31*D1 + B32*D2*EXP(-M2*TINV))

$ + B33*D3*EXP(-M3*TINV))

SS8(I,M) = CR20(1)*(B31*E1 + B32*E2*EXP(-M2*TINV))

$ + B33*E3*EXP(-M3*TINV))

SS9(I,M) = CR0(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))/DET_B

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

- 343 -
\[ CRFE(I,M) = \frac{WTDF(I,M)}{60 + WTDF(I,M)} \times 100 \]

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

\[ CR30(1) = CR3(I,M) \]
\[ CR20(1) = CR2(I,M) \]
\[ CRO(1) = CR(I,M) \]
\[ CRT0(1) = CRT(I,M) \]
\[ SUM = WTDF(I,M) \]

20 CONTINUE

LA(M) = 0
LB(M) = 0
LC(M) = 0

C Sums of squares of deviations for the chromium 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), I TER
11   FORMAT(' L=', F6.3, ', LA=', 3(F5.3), ', LB=', 3(F5.3, 1X),
    $ LC=', 3(F5.3, 1X), I6)
ELSE

- 344 -
K1 = K1MIN
K2 = K2MIN
K3 = K3MIN
K4 = K4MIN
ENDIF

C A random number is generated by an external
C subroutine called G05CAF. Multiplying the number
C generated by 4 and scaling down determines which
C rate constant to change. A second generation of a
C random number gives a value by which the rate
C 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
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
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, \( \text{Cr}^{2+} \), a direct reduction of \( \text{Cr}^{3+} \) to \([\text{Cr}]\) 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,DET,B1,P1,P2,P3,P4,P5,P6,
 $       V1,V2,V3,CS1,CS2,CS3,CS4,CS5,CS6,CS7,CS8,CS9,
 $       Y1,Y2,Y3,Y4,CR30,CR20,CRO,L,LMIN,LA,LB,LC,
 $       CR3,CR2,CR,CRWT,CRFE,CRT,INC,SUM,WTDF,INCR,
 $       CR30S,CR20S,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),
 $       CR30(10),CR20(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(I)*(B11*P1 + B12*P2*EXP(-M1*TINV)

- 349 -
$ + B13*P3*EXP(-M2*TINV))
CS2(I) = CR20(I)*(B11*P4 + B12*P5*EXP(-M1*TINV))
$ + B13*P6*EXP(-M2*TINV))
CS3(I) = CR0(I)*(B11*V1 + B12*V2*EXP(-M1*TINV))
$ + B13*V3*EXP(-M2*TINV))
CR3(I) = (CS1(I) + CS2(I) + CS3(I))/DETB
CS4(I) = CR30(I)*(B21*P1 + B22*P2*EXP(-M1*TINV))
$ + B23*P3*EXP(-M2*TINV))
CS5(I) = CR20(I)*(B21*P4 + B22*P5*EXP(-M1*TINV))
$ + B23*P6*EXP(-M2*TINV))
CS6(I) = CR0(I)*(B21*V1 + B22*V2*EXP(-M1*TINV))
$ + B23*V3*EXP(-M2*TINV))
CR2(I) = (CS4(I) + CS5(I) + CS6(I))/DETB
CS7(I) = CR30(I)*(P1 + P2*EXP(-M1*TINV))
$ + P3*EXP(-M2*TINV))
CS8(I) = CR20(I)*(P4 + P5*EXP(-M1*TINV))
$ + P6*EXP(-M2*TINV))
CS9(I) = CR0(I)*(V1 + V2*EXP(-M1*TINV))
$ + V3*EXP(-M2*TINV))
CR(I) = (CS7(I) + CS8(I) + CS9(I))/DETB
CR(T) = 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
CR30(I) = CR3(I)
CR20(I) = CR2(I)
CR0(I) = CR(I)
CRT(I) = 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

- 350 -
\[ \text{LC} = \text{LC} + (\text{CRFE(J)} - \text{CRFED(J)})^2 \]

\begin{verbatim}
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
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)
CONTINUE
WRITE(6,60)
WRITE(6,66)
WRITE(6,30)K1MIN,K2MIN,K3MIN,K4MIN,K5MIN,K6MIN
FORMAT(''/,'RATE CONSTANTS','/'$5X,_______________________________________')
FORMAT(''/,'K1MIN K2MIN K3MIN K4MIN K5MIN

- 351 -
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,CR30,M11,M21,CR20,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),
      CR30(120),CR20(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)

  - 354 -
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))

- 355 -
\[\begin{align*}
CS3(I) & = CR0(I) \times (B11 \times V1 + B12 \times V2 \times \exp(-M1 \times I)) \\
& + B13 \times V3 \times \exp(-M2 \times I)) \\
CR3(I) & = (CS1(I) + CS2(I) + CS3(I)) / \text{DETB} \\
CS4(I) & = CR30(I) \times (B21 \times P1 + B22 \times P2 \times \exp(-M1 \times I)) \\
& + B23 \times P3 \times \exp(-M2 \times I)) \\
CS5(I) & = CR20(I) \times (B21 \times P4 + B22 \times P5 \times \exp(-M1 \times I)) \\
& + B23 \times P6 \times \exp(-M2 \times I)) \\
CS6(I) & = CR0(I) \times (B21 \times V1 + B22 \times V2 \times \exp(-M1 \times I)) \\
& + B23 \times V3 \times \exp(-M2 \times I)) \\
\text{CR2(I)} & = (CS4(I) + CS5(I) + CS6(I)) / \text{DETB} \\
\text{CS7(I)} & = CR30(I) \times (P1 + P2 \times \exp(-M1 \times I)) \\
& + P3 \times \exp(-M2 \times I)) \\
\text{CS8(I)} & = CR20(I) \times (P4 + P5 \times \exp(-M1 \times I)) \\
& + P6 \times \exp(-M2 \times I)) \\
\text{CS9(I)} & = CR0(I) \times (V1 + V2 \times \exp(-M1 \times I)) \\
& + V3 \times \exp(-M2 \times I)) \\
\text{CR(I)} & = (CS7(I) + CS8(I) + CS9(I)) / \text{DETB} \\
\text{CRT(I)} & = CR3(I) + CR2(I) \\
\text{CRWT(I)} & = (CRT(I) / 100) \times WT(J) \\
\text{WTDF(I)} & = \text{INC} - \text{CRWT(I)} + \text{SUM} \\
\text{CRFE(I)} & = (WTDF(I) / (60 + WTDF(I))) \times 100 \\
\text{IF}(I.\text{EQ.}\text{TINV})\text{THEN} \\
\text{CR30(I)} & = CR3(I) \\
\text{CR20(I)} & = CR2(I) \\
\text{CR0(I)} & = CR(I) \\
\text{CRT(I)} & = CRT(I) \\
\text{SUM} & = WTDF(I) \\
\text{ELSE} \\
\text{GO TO 20} \\
\text{ENDIF} \\
\text{20 CONTINUE} \\
\text{WRITE}(9,60) \\
\text{WRITE}(9,66) \\
\text{DO 40 K = 1,TINV} \\
\text{SUMB} = K + \text{SUMA} \\
\text{WRITE}(9,30) \text{SUMB,CR3(K)},\text{CR2(K)},\text{CRFE(K)}
\end{align*}\]
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


- 358 -


