ELECTROCHEMICAL STUDIES OF FIRST ROW TRANSITION ELEMENTS IN CALCIUM MAGNESIUM SILICATES AT 1525°C

Ronald A. Rizzo

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 and Johnson Space Center, Code TN, Houston, Texas 77058

ABSTRACT

Electrochemical reactions of first row transition elements (Ti thru Zn) were investigated in molten CaO-MgO-2SiO2 at 1525°C using cyclic voltammetry and chronopotentiometry. The reductions of V(V), Co(II), Ni(II), and Zn(II) were found to proceed as simple reversible two electron transfers at platinum electrodes. A relative electrochemical reaction series was established for CaO-MgO-2SiO2 based on the voltammetric half-wave potentials: V(V) < Zn(II) < Co(II) < Ni(II). It was not possible to determine the charge transfer mechanisms for Ti, Cr, Mn, Fe, and Cu.

The electrochemical behavior of Ni(II) was studied as a function of melt composition at 1525°C and as a function of temperature in CaO-MgO-2SiO2. The diffusion coefficient of Ni(II) was dependent on the SiO2 content and the CaO:MgO ratio. The half-wave potential, however, was independent of composition: -0.26 V vs the platinum quasi-reference electrode, QRE (1). The constant half-wave potential implies the solvation sphere of the Ni(II) ion remains unchanged with melt composition. The diffusion coefficient of Ni(II) was characterized by an exponential rate law having an Arrhenius temperature dependence in CaO-MgO-2SiO2 with an activation energy of 25 kcal/mole for the temperature interval 1425-1575°C.

Cyclic voltammetry and chronopotentiometry can provide a great deal of information concerning the behavior of trace constituents in liquid systems. Fused salt mixtures such as the alkali halides have been studied extensively using both techniques (2,3). Liquid silicates, however, have received relatively little attention from the electrochemical community. This is presumably due to the high temperatures required to obtain the silicates in liquid form and because of the corrosive nature of the silicates once they are liquid.

Initial voltammetric studies using a silicate electrolyte were made at temperatures around 1000°C in alkali silicates (4-9). While the diffusion-limited current generally was proportional to the concentration of the electroactive species, the current-potential curves could not always be fit to an exact mathematical expression such as
the Kolthoff-Lingane or Heyrovsky-Ilkovic equations. These measurements also were complicated by substantial capacitance currents which were not easily compensated (10).

Recently, the $\text{SiO}_4^{4-}$, $\text{Si}_2\text{O}_7^{6-}$, and $\text{Si}_3\text{O}_10^{8-}$ polyanions were identified from chronopotentiometric measurements of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ glasses dissolved in a NaCl-KCl eutectic melt. (11,12). These species are called polyanions or polymers because they are formed by random condensation polymerization reactions such as the following:

$$\text{SiO}_4^{4-} + \text{SiO}_4^{4-} = \text{Si}_2\text{O}_7^{6-} + 2\text{O}^{2-}$$

The polymer theory for silicate liquids (13-15) predicts that the fraction of silicon found in the higher molecular weight polymers can be increased by increasing either the $\text{SiO}_2$ content of the liquid or its net cationic field strength. The field strength of a cation is defined as $Z/r^2$, where $Z$ is the cation charge and $r$ is the sum of the radii of the cation and oxygen.

This paper concerns an investigation to determine the effects of varying the polymer structure of calcium magnesium silicate liquids on the electrochemical behavior of a minor constituent, Ni(II). In addition, the electrochemical behavior of the first row transition elements Ti thru Zn was studied in a liquid of constant composition: CaO·MgO·2SiO$_2$.

**Experimental**

The silicate electrolytes were divided into two groups on the basis of chemical composition. Melts of the first group had compositions corresponding to the formula CaO·MgO·ZSiO$_2$, where Z was varied from 1.25 to 3. Melts of the second group had compositions corresponding to the formula XCaO·YMgO·2SiO$_2$, where X+Y=2 and X/(X+Y) was varied from 0.25 to 0.83. The composition CaO·MgO·2SiO$_2$ was common to both groups.

No purification procedures have been reported for the removal of electroactive contaminants from silicate liquids. Consequently, high purity oxide powders were used to synthesize the melts. The starting materials, purity (wt %), and commercial sources were as follows: $\text{V}_2\text{O}_5$ (99.5)-Baker; CoO (92.)-Fisher; MgO (99.97)-Materials Research Corporation; MnO (99.), $\text{NiO}$ (99.9 and 99.95)-Research Inorganic Chemicals; $\text{SiO}_2$ (99.9999)-Spex Industries; $\text{CaO}$ (99.95), TiO$_2$ (99.6), Cr$_2$O$_3$ (98.8), Fe$_2$O$_3$ (99.99), CuO (UP), ZnO (UP), where UP = ultrapure, 99.99 wt % minimum-Ventron. All materials except CaO, MgO, and SiO$_2$ were dried at 105-125°C and stored in desiccators over CaSO$_4$. CaO and MgO were dried at 900-1100°C and stored in desiccators. SiO$_2$ was used as received from the commercial supplier.
Pre-melt compositions were prepared by combining the appropriate amounts of CaO, MgO, and SiO$_2$ for one hour in a Spex Industries mixer mill. If the sample was to be a doped melt, the transition metal oxide was added after one-half hour of mixing. Plastic mixing balls and vials were used to minimize contamination by metallics. The mix was transferred to a 25 cc low profile, wide bottom platinum crucible having a reinforced top and bottom. The crucible was covered with a platinum lid and placed in a furnace at 1100°C for one-half to one hour. The temperature was then raised to 1525°C for five hours. On cooling to room temperature the surface of the silicate was inspected for small accumulations of platinum filings which were torn from the crucible walls during the melting process. All accumulations were removed using a diamond-coated drill bit.

A variety of platinum electrode configurations were tested. Small diameter wire and thin foil electrodes were unsuitable for work in the high temperature silicates. These electrodes would occasionally bend when inserted into the more viscous melts and tended to draw together once inside the liquid. The electrode assembly shown in Fig. 1 was not plagued with these problems. The reference and working electrodes were 0.145 cm in diameter and approximately 1.8 cm long. One end of each wire was reduced so the electrode fit snugly into the alumina protection tube. The alumina tube was 1 cm in diameter and approximately 56 cm long. The crucible containing the melt served as the counter electrode. Electrical contact was made to the potentiostatic instrumentation using 0.040 cm diameter platinum wires spot welded to the electrodes. A platinum vs 90% platinum-10% rhodium thermocouple was located between the reference and working electrodes. It was pulled flush to the base of the alumina tube and provided an accurate measure (±1 degree) of the melt temperature.

Crucibles containing the solidified melts were placed in a high temperature box furnace (16) for the electrochemical measurements. To minimize thermal gradients, a solid state SCR furnace controller was used instead of a conventional on/off unit. The platinum crucible and silicate glass were thermally equilibrated for one-half hour at 1000°C. The temperature was then raised to 1525°C over a period of one to two hours. This procedure was strictly followed to insure the crucible would not become deformed during the heat-up due to the different coefficients of expansion for the silicate glass and platinum. All electrochemical measurements were made with the melt exposed to the air atmosphere.

Cyclic voltammograms and chronopotentiograms were obtained using a Princeton Applied Research Model 170 Electrochemistry System. The current-potential and potential-time data were recorded photographically using a Tektronix R564B storage oscilloscope equipped with a Tektronix C-12 camera assembly. The voltammetric current data also were acquired digitally using a Biomation Model 802 Transient Recorder. The digital current information was stored on 9 track magnetic tape using a Kennedy 1708-9CR recorder which was interfaced to the
A substantial background current was observed in all silicates. Net cyclic voltammograms were obtained by subtracting the current recorded in the undoped melts from that recorded in the doped melts. Correction for different electrode areas was unnecessary since all measurements were made using the same electrode immersion depth (0.32 cm) which corresponded to an electrode area of 0.16 cm$^2$.

Biomation Model 802 thru a Datacap, Inc. Model B209 Data Coupler.

Results and Discussion

Electrochemical Studies of Ni(II) in Calcium Magnesium Silicates

Approximately the same cathodic and anodic potential limits were observed for the different silicates. The cathodic limit at about -0.85 V vs the platinum QRE is probably due to the reduction of a silicate species such as SiO$_4^{14-}$(11,12). The anodic limit at about +0.35 V vs the platinum QRE is attributed to the oxidation of the platinum electrode. Cyclic voltammograms were always recorded with the initial scan potential set at 0 V, the approximate zero current potential.

Several small, ill-defined waves were detected in the background voltammograms for the calcium magnesium silicates. The number of waves present and their location on the potential axis depended on the scan rate and composition. No attempt was made to deduce the exact nature of the reactions responsible for these waves. Their presence had little influence on the net electrolysis current since they were observed at precisely the same potentials in the doped and undoped melts for a given composition.

Figures 2 and 3 are computer reconstructions of digitally-acquired voltammograms for undoped and NiO-doped CaO*MgO*2SiO$_2$. The net voltammogram obtained by subtracting the current information of Fig. 2 from that of Fig. 3 is shown in Fig. 4. The well-defined, peak-shaped response of Fig. 4 was characteristic of net voltammograms obtained in the different silicates. Accurate measurement of the current-potential relations was facilitated using a digital smoothing routine. The smoothing process involved a fast Fourier transform technique analogous to an electronic low pass filter. Details of the method have been described elsewhere (16).

The exact nature of the electrochemical reaction mechanism was elucidated using the diagnostic criteria reported by Nicholson and Shain (17). The cathodic peak current function ($i_p/v^{1/2}$), cathodic half-peak potential ($E_p^{1/2}$), and anodic to cathodic peak current ratio ($i_a/i_p$) were determined as a function of voltage scan rate ($v$). Voltammograms recorded at scan rates below 0.1 v/sec were affected by convective stirring of the liquid. Scan rates greater than 50 to 100
v/sec were impractical because of the inability of the instrumentation to fully compensate the large ohmic potential losses. Consequently, the diagnostic criteria were evaluated at 8 to 10 different scan rates between 0.1 and 100 v/sec.

Plots of $i_p/v^{1/2}$ vs $v$ occasionally exhibited slightly increasing or decreasing trends with increasing scan rate before levelling off at constant value. For simple reversible charge transfer, $i_p/v^{1/2}$ is expected to be independent of scan rate (17). No significance is attached to these trends because of their small magnitude. They are the result of errors in measurement of the electrode immersion depth which may have produced larger or smaller electrode areas relative to the area for the standard immersion depth in the doped and/or undoped melts.

The anodic to cathodic peak current ratio was approximately 1 for all compositions studied. The peak current ratio and the cathodic half-peak potential were independent of scan rate. This behavior is indicative of simple reversible charge transfer (17). The mean and standard deviations of the peak current ratio and the individual potential measurements are compiled as a function of melt composition in Table 1. The anodic peak current was measured to a zero current baseline determined using the formulation of Polcyn and Shain (18). The half-wave potentials were measured at the potential corresponding to a current 0.85 $i_p$ (17). The precision for the potential measurements is reported to the nearest hundredth of a volt for values determined from photographic data and to the nearest millivolt for computer analyses of digitally-acquired data. The accuracy of the potential measurements is estimated to be ±20 to 30 mv.

Plots of log $[(i_p - i)]/i_p$ vs potential were linear over the approximate range of potentials corresponding to 0.35 - 0.70 $i_p$. Fig. 5 is an example of this type of plot for the reduction of Ni(II) in CaO·MgO·2SiO$_2$. For simple reversible charge transfer involving soluble reactants and products, the expected slope is 0.58 nF/RT (19). From the slopes of such plots, the number of electrons transferred was calculated to be 2.

The separations in the anodic to cathodic peak potential ($E_p^a - E_p^c$) and the half-peak to peak potential ($E_p^{1/2} - E_p^p$) are expected to be 2.22 RT/nF and 2.2 RT/nF (17) or 172 and 170 mv for $n = 2$ at 1525°C. The separations determined from the potentials listed in Table 1 indicate better agreement between theory and experiment for $E_p/2 - E_p^c$ than for $E_p^a - E_p^c$. This happens because the peaks have a broad, drawn out appearance which introduces a greater uncertainty in the measurement of the peak potentials than in the half-peak potential which is determined over the rising portion of the wave.

Considerable evidence exists in the literature to warrant the assumption that all the nickel is present as the divalent species in the silicates studied. Spectroscopic (20) and wet chemical (21)
analyses of sodium disilicate glasses containing NiO show less than a 2% conversion to the trivalent species for samples synthesized in air at 1085-1550°C. The Ni(III) content of the calcium magnesium silicates was determined using a Ce(IV) titration technique (22). In no instance was more than 1-2% of the total nickel found as the trivalent species.

The cathodic peak current was proportional to the Ni(II) concentration (at constant scan rate) over the range 4.6 x 10^-4 to 1.6 x 10^-2 M in CaO*MgO*2SiO2. If mass transport occurs via diffusion alone, the cathodic peak current should vary linearly with scan rate for any Ni(II) concentration in this range. Fig. 6 is a plot of ip vs v^1/2 for the reduction of Ni(II) in CaO*MgO*2SiO2. A linear relation which passed thru the origin was observed for scan rates up to a minimum of 5 v/sec for all compositions studied. Consequently, diffusion is the predominant means of mass transport at these scan rates and the Randles-Sevcik equation (17) is valid. At 1525°C this equation becomes

\[ i_p = 1.09 \times 10^5 n^{3/2} A D_{CV}^{1/2} c^* v^{1/2} \]  

The Ni(II) diffusion coefficient (D_{CV}) was calculated using Eq. 2 and the value of ip/v^1/2 determined from the slope of ip vs v^1/2 plots. The individual values and the estimated uncertainties in their measurement have been included in Table 1.

Chronopotentiograms for the reduction of Ni(II) to Ni were reasonably well-defined in all the silicates studied except one: CaO*MgO*3SiO2. Distortions resulting from large capacitance currents made it impossible to detect a transition in this melt. Voltammograms also were not as well-defined in melts of this composition as in the other systems.

Fig. 7 is a chronopotentiogram for Ni(II) reduction in CaO*MgO*2SiO2. Current densities (i0) were varied from 65-375 ma/cm² with corresponding transition times (T) of 600 - 3 msec. Transition times were measured using the technique of Laity and McIntyre (23). The quantity, i0T was invariant for the indicated current density range and plots of potential vs log ([T^2 - t^2]/t^2) were linear for times approaching the transition time. From the slopes of these plots (0.43 nF/RT), n was calculated to be 2.

The transition time constant, i0T^v/C^n, was measured from the slope of plots of i0T/C^n vs T^2. According to Bard (24,25), values of the constant obtained in this manner should be corrected for interferences due to charging current, electrode oxidation, and adsorption of the electroactive species. The diffusion coefficient (D_{CB}) of Ni(II) was determined using the Sand equation (26) and the transition time constant. The results of these calculations are included in Table 2.
Effect of Temperature on the Electrochemical Behavior of Ni(II) in CaO-MgO·2SiO₂

Net cyclic voltammograms were obtained for the reduction of Ni(II) in CaO-MgO·2SiO₂ at 50 degree intervals from 1425 to 1575°C. Except for a change in magnitude and a shift along the potential axis (\(E_{1/2}^c = -0.209 \pm 0.002 \text{ V at 1425°C and } -0.151 \pm 0.002 \text{ V at 1575°C} \)), voltammograms were unchanged in appearance for the different temperatures. The cathodic peak current function, half-peak potential, and peak current ratio were independent of scan rate indicating simple reversible charge transfer. Plots of \(i_p \text{ vs } v^2 \) were linear and passed thru the origin for scan rates up to \(10^4 \text{ v/sec} \) indicating that diffusion was the predominant means of mass transport at these scan rates.

The Ni(II) diffusion coefficient was obtained using the appropriate form of the Randles-Sevcik equation in the manner previously indicated. Fig. 8 is a plot of \(\ln D \text{ vs } 1/T \). The linearity of this plot suggests that the diffusion coefficient for Ni(II) in CaO-MgO·2SiO₂ can be described by an equation having Arrhenius temperature dependence such as the following:

\[
D = A \exp \left(-\frac{E_a}{RT}\right)
\]

where \(E_a\) is the activation energy for diffusion. The exact form of the pre-exponential factor \(A\) was derived by Glasstone et. al. (27) using absolute reaction rate theory. \(A\) is a function of the activation entropy, the distance between neighboring equilibrium positions for Ni(II) ions in the melt, and, to a lesser extent, temperature (28). \(A\) and \(E_a\) for Ni(II) diffusion in CaO-MgO·2SiO₂ were determined from the intercept and slope of Fig. 8 to be \(0.86 \times 10^{-5} \text{ cm}^2/\text{sec}\) and 25 kcal/mole, respectively.

Electrochemical Studies of First Row Transition Elements in CaO-MgO·2SiO₂

The electrochemical behavior of selected first row transition elements (Ti thru Zn) was investigated in CaO-MgO·2SiO₂ at 1525°C. It was impossible to determine the exact nature of the charge transfer reaction in melts containing TiO₂, Cr₂O₃, MnO, Fe₂O₃, and CuO. Voltammograms for the reduction of a Ti and Mn species were of limited value since the reduction peak potentials were more electronegative than the cathodic potential limit of the supporting electrolyte. The cathodic peak potentials for the reduction of V(V) and a Cr species were close to the cathodic potential limit. The resulting interference was considerable and in the case of Cr the only information obtained was that the charge transfer appeared to be reversible. Voltammograms recorded in CuO-doped melts were indecipherable. A substantial amount of the total Cu was removed from solution either
through adsorption or alloy formation with the platinum electrodes, in particular the crucible. Although a reasonably well-defined voltammetric response was recorded in melts containing Fe₅O₃, it was impossible to deduce the charge transfer mechanism on the basis of the variations in \( i_p/v^2 \), \( E_p \), and \( i_p/i_C \) with scan rate. A single well-defined, peak-shaped wave was observed for voltammograms in melts containing CoO, NiO, and ZnO. The reduction potentials for Co(II) and Ni(II) were sufficiently removed from the cathodic potential limit to enable detection of a transition for chronopotentiometric measurements.

Figures 9, 10, and 11 are net voltammograms for the reductions of V(V), Co(II), and Zn(II) in CaO-MgO-2SiO₂ at 1525°C. The anodic half of each voltammogram was distorted because of the small separation in the half-wave and switching potentials (17). For a given charge transfer, the anodic peak shifts to more positive values as this separation is decreased. The shift occurs because the electrode surface concentration of the reduced species over the anodic scan does not quite equal the surface concentration of the oxidized species at corresponding potentials for the cathodic scan.

The expected separation in the anodic to cathodic peak potentials was determined from voltammograms constructed using the theoretical current function-potential relations for simple reversible electron transfer. The experimentally-measured separation in the cathodic peak to switching potentials was used as a reference point for each construction with the theoretical cathodic peak current function normalized to the experimental cathodic peak current magnitude. The experimental and theoretical separations are listed in Table 2 for the different reactions. The mean and standard deviation for the potential measurements were determined for scan rates between 0.1 and 20 v/sec. The cathodic half-peak potential was constant for these scan rates indicating simple reversible charge transfer.

The anodic to cathodic peak current ratios were less than 1 when the anodic peak current was measured to a zero current baseline determined according to the method of Polcyn and Shain: 0.74 ± 0.04 for V(V)→V(III), 0.87 ± 0.01 for Zn(II)→Zn, and 0.91 ± 0.02 for Co(II)→Co. This was surprising in view of the agreement between the experimental and theoretical cyclic voltammograms for the different reactions. When the anodic peak current function was measured to an extension of the cathodic current function, however, the theoretical peak current ratio was found to be 1. The small separation in the half-wave and switching potentials has distorted the anodic half of each voltammogram to the extent that the approach of Polcyn and Shain is not valid. The phenomenon was not observed in the voltammograms for Ni(II) because of the greater separation in the cathodic peak and switching potentials. Consequently, the true ratio for the charge transfer reactions involving V(V), Zn(II), and Co(II) is approximately 1.
Plots of \( i_p \) vs \( v^3 \) were linear and passed thru the origin for the reduction of Co(II) and Zn(II) at scan rates between 0.1 and 10 v/sec. Although a linear response was observed for the reduction of V(V) at scan rates between 0.1 and 2 v/sec, the line did not pass thru the origin. The positive intercept was probably the result of incomplete compensation for interferences arising from the close proximity of the cathodic peak potential (-0.733 ± 0.010 V) to the melt decomposition potential (-0.85 V). Plots of \( \log \left( \frac{i_p - i}{i} \right) \) vs potential were linear over the approximate range 0.35 - 0.70 \( i_p \) with slopes corresponding to \( n = 2 \).

Electron paramagnetic resonance spectroscopy (16,29) and wet chemical analyses (16,21) indicated less than 1 % of the vanadium was present in an oxidation state other than the +5 and less than 2 % of the cobalt was present as the +3 species. Consequently, the V(V) and Co(II) concentrations were equated to the total vanadium and cobalt contents for diffusion coefficient calculations. The diffusion coefficients were determined using Eq. 2 and the values of \( i_p/v^3 \) measured from the slope of \( i_p \) vs \( v^3 \) plots. The estimated uncertainties in these measurements have been included with the individual values in Table 2.

Chronopotentiograms were obtained for the reduction of Co(II) in CaO-MgO-2SiO₂ at current densities of 60-435 ma/cm². Transition times were in the range 342-5 msec. The quantity \( i_{QT} \) was independent of current density and plots of potential vs \( \log \left( \frac{[T% - t]/T%}{t} \right) \) were linear with slopes corresponding to \( n = 2 \). This behavior is indicative of simple reversible charge transfer. The diffusion coefficient of Co(II) was calculated to be 1.88 ± 0.94 \( \times 10^{-6} \) cm²/sec using the Sand equation and the value of \( i_{QT}/c^k \) determined from the slope of plots of \( i_{QT}/c^k \) vs \( T% \). This agrees well with the value obtained from the voltammetric measurements.

Conclusions

The electrochemical behavior of Ni(II) can be interpreted in terms of the nature of the diffusing species and its mode of transport in the liquid silicates. Ni(II) exists predominantly in octahedral coordination with oxygen in silicate melts (20,30). The six oxygens can be of a variable nature such as free oxide ions, single bonded oxygens which are part of a silicate polyanion, or a combination thereof. The transport of Ni(II) ions is not the motion of any particular octahedrally-coordinated species, but the displacement of individual ions from one octahedral cavity in the liquid to another. Ni(II) ions arrive at the electrode surface by executing a series of random jumps. Electron transfer takes place to an ion that is surrounded by oxygens regardless of the polymer structure of the electrolyte.

The constant half-wave potential for the reduction of Ni(II) to Ni is consistent with this diffusion model. For simple reversible
electron transfer, the half-wave potential is approximately equal to
the standard electrode potential for the couple. Therefore, the half­
wave potentials are an indication of the thermodynamic stability of
Ni(II) with respect to Ni in the different electrolytes. The constant
half-wave potential implies the solvation sphere and stability of the
Ni(II) ions being reduced are unchanged with melt composition. The
Arrhenius temperature dependence of the Ni(II) diffusion coefficient
in CaO·MgO·2SiO2 also is consistent with a jump diffusion mode of mass
transport. The variation in the Ni(II) diffusion coefficient with
composition is most likely the result of changes in the A and Ea para­
meters defined in Eq. 3. In particular, the distance between neighboring
equilibrium positions and the activation energy for diffusion are
expected to be functions of the polymer structure of the electrolyte.

The reductions of V(V), Zn(II), Co(II), and Ni(II) were found to
proceed as simple reversible two electron transfers in CaO·MgO·2SiO2.
The half-wave potentials for the individual couples define a relative
electrochemical stability series (see Table 2) for this electrolyte.
It was not possible to arrive at a definite relation between field
strength (Z/r^2) of the electroactive species and half-wave potential.
Tetrahedrally-coordinated V(V) has the highest field strength, 1.7,
and the most electronegative half-wave potential, and octahedrally-
coordinated Ni(II) has the lowest field strength, 0.48, and the most
electropositive half-wave potential (20, 30-32). The correlation,
however, does not follow for tetrahedrally-coordinated Zn(II) and
Co(II) which have intermediate field strengths of 0.53 and 0.54,
respectively (30-32).

Low field strength ions such as Zn(II) and Co(II) do not polarize
the coordinating oxygens to as great an extent as high field strength
ions such as V(V) and Si(IV). Zn(II) and Co(II) undergo a jump dif­
fusion type of mass transport like Ni(II) whereas V(V) and Si(IV) dif­
fuse with the coordinating oxygens (33). Zn(II), Co(II), and Ni(II)
have approximately the same field strengths and very similar diffusion
coefficients. V(V), however, has an anomalously large diffusion co­
efficient for a high field strength ion which is considered to diffuse
as a complex species. Currently the best explanation for this obser­
vation concerns the errors present in determining the value of ip/v^2
used to calculate the diffusion coefficient. Plots of ip vs v^2 for
the reduction of V(V) were linear but had positive intercepts.
Apparently the slopes (ip/v^2) of these plots also have been affected
by the interferences responsible for the non-zero intercepts.

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Table 1. Cathodic peak potential, anodic peak potential, cathodic half-peak potential, half-wave potential, and anodic to cathodic peak current ratio for Ni(II) + 2e⁻ = Ni in calcium magnesium silicates at 1525°C. All potentials quoted WRT platinum ORE. Ni(II) diffusion coefficients from voltammetric and chronopotentiometric measurements.

| Composition         | [Ni(II)] M | E_p^c V  | E_p a V  | E_p/2 V  | E_1/2 V  | I_p/E p | D_ee *10^-6 cm²/sec | D_ch *10^-6 cm²/sec |
|---------------------|------------|----------|----------|----------|----------|---------|----------------------|----------------------|
| CaO·MgO·3SiO₂       | 0.073      | -0.370 ± 0.002 | -0.096 ± 0.010 | -0.159 ± 0.005 | -0.258 ± 0.008 | 0.90 ± 0.05 | 0.33 ± 0.17           | ---                  |
| CaO·MgO·2SiO₂       | 0.078      | -0.37 ± 0.02   | -0.16 ± 0.02   | -0.16 ± 0.01   | -0.26 ± 0.01   | 1.03 ± 0.03 | 0.92 ± 0.46           | 1.03 ± 0.52           |
| CaO·MgO·1.5SiO₂     | 0.071      | -0.38 ± 0.01   | -0.12 ± 0.01   | -0.17 ± 0.01   | -0.26 ± 0.01   | 1.01 ± 0.02 | 3.35 ± 1.18           | 3.02 ± 1.51           |
| CaO·MgO·1.25SiO₂    | 0.076      | -0.33 ± 0.02   | -0.09 ± 0.02   | -0.14 ± 0.01   | -0.23 ± 0.01   | 0.99 ± 0.05 | 4.24 ± 2.12           | 5.05 ± 2.53           |
| 1/2CaO·1/3MgO·2SiO₂ | 0.099      | -0.355 ± 0.011 | -0.166 ± 0.007 | -0.166 ± 0.006 | -0.258 ± 0.007 | 1.05 ± 0.04 | 1.53 ± 0.77           | 2.16 ± 1.08           |
| 1/2CaO·2/3MgO·2SiO₂ | 0.099      | -0.361 ± 0.016 | -0.143 ± 0.010 | -0.168 ± 0.010 | -0.261 ± 0.010 | 1.04 ± 0.06 | 1.16 ± 0.58           | 1.58 ± 0.79           |
| CaO·MgO·7SiO₂       | 0.117      | -0.352 ± 0.004 | -0.155 ± 0.005 | -0.169 ± 0.003 | -0.260 ± 0.002 | 1.03 ± 0.03 | 0.92 ± 0.46           | 1.03 ± 0.52           |
| 3/4CaO·1/2MgO·2SiO₂ | 0.100      | -0.359 ± 0.007 | -0.146 ± 0.006 | -0.166 ± 0.008 | -0.259 ± 0.009 | 1.00 ± 0.02 | 0.98 ± 0.49           | 1.49 ± 0.75           |
| 1/2CaO·1/2MgO·2SiO₂ | 0.094      | -0.364 ± 0.014 | -0.164 ± 0.013 | -0.171 ± 0.007 | -0.258 ± 0.007 | 1.10 ± 0.04 | 0.80 ± 0.40           | 1.40 ± 0.70           |
Table 2. Cathodic peak to switching potential (SP) separation, anodic to cathodic peak potential separation, half-peak to peak potential separation (theoretical values in parentheses), and half-wave potentials measured vs. platinum WE for reductions of V(V), Re(II), Co(II), and Ni(II) in CoO-NbO-25%O at 1325°C. Diffusion coefficients from volumetric measurements.

| Process | Concentration M | $E^P$ - SP mv | $E^R$ - $E^C$ mv | $E^P/2$ - $E^C$ mv | $E_{1/2}$ V | $D_{CV} \times 10^6$ cm$^2$ s$^{-1}$ |
|---------|-----------------|----------------|------------------|--------------------|--------------|-----------------------------------|
| V(V) + 2e$^-$ = V(III) | 0.144 | 69 | 219 ± 10 (198) | 171 ± 12 (170) | -0.647 ± 0.005 | 3.28 ± 1.64 |
| Re(II) = Re | 0.098 | 150 | 243 ± 19 (191) | 199 ± 11 (170) | -0.476 ± 0.008 | 1.45 ± 0.73 |
| Co(II) + 2e$^-$ = Co | 0.127 | 250 | 232 ± 16 (180) | 201 ± 7 (170) | -0.380 ± 0.007 | 1.46 ± 0.73 |
| Ni(II) + 2e$^-$ = Ni | 0.117 | 368 | 198 ± 8 (172) | 183 ± 5 (170) | -0.260 ± 0.002 | 0.92 ± 0.46 |
Fig. 1. Electrode assembly and enlargement of base showing thermocouple position.

Fig. 2. Cyclic voltammogram of CaO-MgO-2SiO$_2$.

Fig. 3. Cyclic voltammogram of CaO-MgO-2SiO$_2$ containing HNO. Ni(II) concentration: 0.117 M.

Fig. 4. Net cyclic voltammogram for the reduction of Ni(II) to Ni in CaO-MgO-2SiO$_2$. Ni(II) concentration: 0.117 M.
Fig. 5. Plot of \( \log \left( \frac{(i_p - 4)}{4} \right) \) vs potential for the reduction of Ni(II) to Ni in CuO-MgO-2SiO_2 at 1525°C. The dashed lines correspond to the approximate range 0.35 - 0.70 \( i_p \).

Fig. 6. Plot of \( i_p \) vs \( v^2 \) for reduction of Ni(II) to Ni in CuO-MgO-2SiO_2 at 1525°C. Ni(II) concentration: 0.078 M.

Fig. 7. Chronopotentiogram for the reduction of Ni(II) to Ni in CuO-MgO-2SiO_2 at 1525°C. Ni(II) concentration: 0.117 M; current density: 125 ma/cm².

Fig. 8. Variation in the Ni(II) diffusion coefficient with temperature in CuO-MgO-2SiO_2.
Fig. 9. Net cyclic voltammogram for the reduction of V(IV) to V(III) in CaO-MgO·2SiO₂. V(IV) concentration: 0.144 M.

Fig. 10. Net cyclic voltammogram for the reduction of Co(II) to Co in CaO-MgO·2SiO₂. Co(II) concentration: 0.127 M.

Fig. 11. Net cyclic voltammogram for the reduction of Zn(II) to Zn in CaO-MgO·2SiO₂. Zn(II) concentration: 0.098 M.