3. Equilibrium time determination

Two possible rate-determining steps were considered – gas-phase mass transfer (of H_2O to or from the gas-slag interface) and mass transfer of $VO_{1.5}$ within the slag. To quantify the former, the correlation as used by Belton & Belton (1980) was employed to find the mass transfer constant of H_2O in the gas. No data on the diffusivity of vanadium cations in $CaO-Al_2O_3$ could be found, but data for transition metal cations (Fe^{2+}, Fe^{3+} and Mn^{2+}) were used to estimate the likely range of diffusivities (Verein Deutscher Eisenhüttenleute,1995). These data are given in Figure 44, with extrapolations to the equilibration temperature of 1700°C. From these data, the diffusivity is estimated to be at least 6×10^{-10} m^2/s.
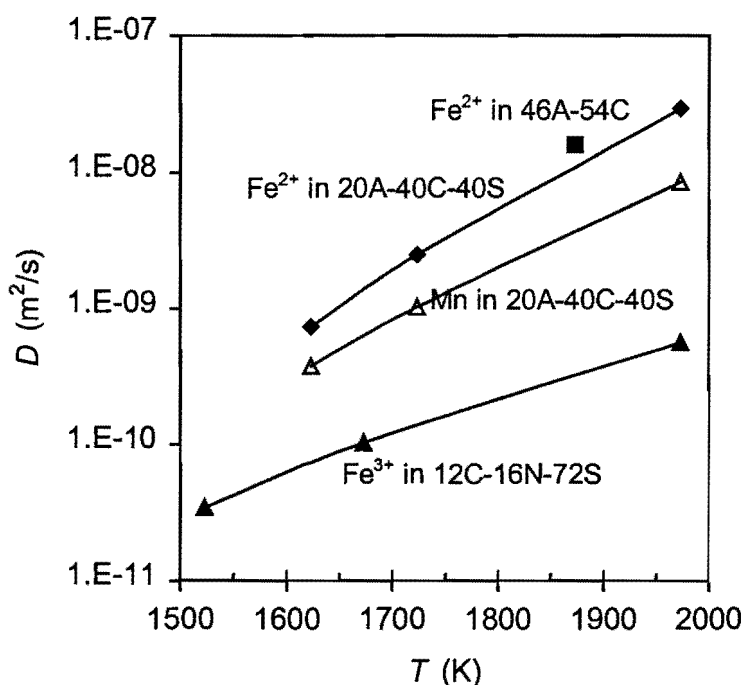

Figure 44. Literature data on diffusion coefficients of transition metal ions in slags similar to those used in this work. Slag compositions are given as mass percentages, where "A" refers to Al_2O_3, "C" is CaO, "S" is SiO_2, and "N" is Na_2O. The two data points at the lower temperatures give the temperature range for which the data are reported, and the line to 1973 K gives the extrapolation to the temperature used in this work.

Because of the low oxidizing capacity of the H_2O/H_2 ratios implemented in this work, care had to be taken that equilibrium could be obtained from both sides i.e. both from higher than equilibrium and lower than equilibrium vanadium oxide concentrations in the slags.

$VO_{1.5}$ mass transfer in the slag is possibly rate determining. Vanadium metal powder was charged in the initial mixtures to assist with the diffusion process by reducing the actual diffusion distance, which would have been 3mm if no powder was used (i.e. the radius of the pure vanadium crucible). Thorough mixing was ensured by grinding of the chunks of pellets with the vanadium or vanadium powder addition to a powder in a tungsten carbide grinding vessel. Another sample was loaded with vanadium oxide in the initial slag mixture to determine if the same final vanadium content, as in case of the sample containing pure vanadium metal, could be obtained. All these equilibration runs were conducted at a CaO: Al_2O_3 ratio of 1 and at 1700 °C (See experiment 1 and 3 in Table 16). The activity of oxygen was kept constant by using constant H_2O/H_2 ratios. The initial assumption that 6 hours should be sufficient if slag-mass transfer is the rate-determining step (for the lower band of the estimated diffusion) was confirmed by the two experiments.
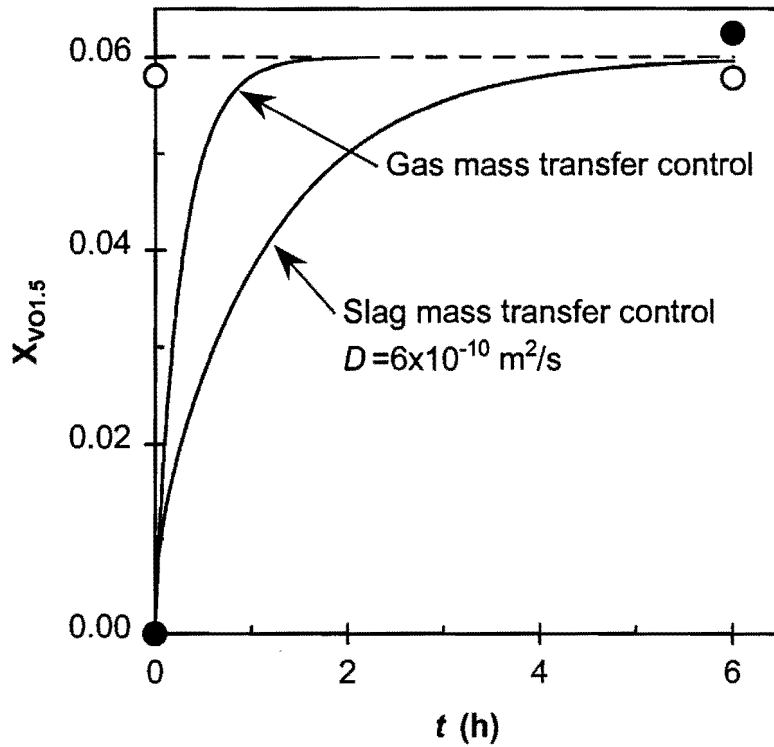
Figure 45. Calculated change in the average $VO_{1.5}$ content of the slag, for respectively gas phase mass transfer control and slag mass transfer control (lower-bound estimate of diffusivity). The data points give the actual change in vanadium content for a slag which contained no vanadium oxide to start with (filled circles), and one which contained a mole fraction of 0.058 of vanadium oxide at the start of the 6-hour equilibration period at 1700°C.

The same final vanadium oxide content in the synthetic slag was essentially reached, indicating that six hours should be sufficient to reach equilibrium. In this case, the standard amount of vanadium pentoxide, initially added to the synthetic slags, corresponding to a $VO_{1.5}$ mole fraction of about 0.06, happened to be very close to the equilibrium level.