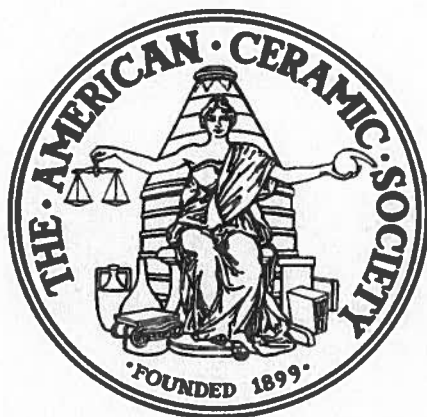


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# Kinetics of Carbon Transfer from Magnesia-Graphite Ladle Refractories to Ultra-Low Carbon Steel

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## ABSTRACT

Kinetic mechanisms of carbon transport to ultra-low carbon (ULC) steel from magnesia-graphite ladle refractories were investigated through laboratory dip tests with commercially available ladle refractories in a vacuum induction furnace. The effect of refractory carbon content on carbon transfer was investigated by using refractories with carbon contents between 4-12 wt%. The influence of slag was also investigated by using slag free and slag containing dip tests with varying MgO content. Carbon transfer is controlled by steel penetrating into the refractory and dissolving carbon when no slag is present. The rate controlling step of this mechanism is convective mass transfer of carbon into the bulk steel. The mass transfer coefficient for carbon transfer was found to be approximately  $1 \cdot 10^{-6}$  m/s. Corrosion of the refractory controlled the carbon transfer when slag was present. The mass transfer coefficient of MgO into slag was found to be  $8 \cdot 10^{-6}$  m/s for 10 wt%C bricks and  $12 \cdot 10^{-6}$  m/s for 4 wt%C bricks. The calculated carbon pickup based on these mechanisms was in good agreement with the measured carbon pickup which supports the proposed mechanisms.

## INTRODUCTION

Magnesia-graphite refractories are often employed in ladles to contain molten steel. The graphite in these refractories adds desirable properties such as resistance to molten slag attack, high temperature strength and wear resistance, low density, and thermal shock resistance.<sup>1,2,3,4,5,6</sup> However, the use of graphite has some drawbacks including refractory wear via decarburization, steel skull formation and steel bath temperature loss from graphite's high thermal conductivity, corrosion of the safely lining by reactions with CO, and pickup of carbon by the molten steel.<sup>1</sup> Ultra-low carbon (ULC) steels are particularly sensitive to carbon pickup because there is a greater driving force for carbon transport compared to higher carbon steels.<sup>7</sup> Interstitial carbon increases the strength of steel and decreases the ductility of steel.<sup>8</sup> Carbon pickup is detrimental to the processing of ULC steels because they are employed in forming and drawing operations

where ductility must be at a maximum. Thus, the final carbon concentration of ULC steel is specified as less than 50 ppm.<sup>9</sup> Carbon pickup from MgO-C ladle refractories must be controlled to meet this specification. When carbon transfer is out of control, carbon pickup as high as 30 ppm can occur on a ULC steel heat with an aim under 50 ppm carbon.<sup>9</sup>

The kinetics of carbon transfer from refractory to steel should be well understood to control carbon pickup in molten steel. Carbon transfer into molten steel can occur through direct dissolution of graphite.



Steel can come into contact with graphite in MgO-C refractories by contact at the surface of the refractory, by steel penetrating into the refractory, and by erosion or corrosion of MgO grains which exposes graphite to steel. The kinetics of MgO transfer into slag should also be well understood if slag corrosion is the controlling mechanism for carbon pickup.



Direct dissolution of carbon by steel is the most significant contribution of carbon pickup from ladle refractories.<sup>2,9,10</sup> Two steps have been observed in the direct dissolution of carbon into steel. First, carbon dissolves from its base structure into liquid steel at the interface between steel and carbon. Then, mass transfer of carbon from the steel-carbon interface to the bulk liquid steel occurs.<sup>4,11,12,13,14,15,16</sup> When the interfacial reaction controls the transport of carbon to steel, the dissolution rate can be described by the following equation where  $J_c$  is the dissolution rate of carbon in g/s,  $A$  is the contact area between steel and carbon in  $cm^2$ ,  $k_r$  is the apparent rate constant,  $C_{eq}$  is the carbon concentration of the liquid steel in equilibrium with the solid carbon, and  $C_\infty$  is the carbon concentration of the bulk steel.<sup>15</sup>

$$J_c = Ak_r(C_{eq} - C_\infty) \quad (3)$$

When convective mass transfer of carbon into the bulk steel controls the transport of carbon, carbon dissolution can be described by the following equation where  $C_{sat}$  is the saturation concentration of carbon in steel,  $C_\infty$  is the carbon concentration of the bulk steel at time  $t$ ,  $C_o$  is the initial carbon concentration of the steel,  $A$  is the area of contact between steel and carbon,  $V$  is the volume of steel, and  $\beta_c$  is the mass transfer coefficient.<sup>13,15</sup>

$$\ln \left( \frac{C_{sat} - C_\infty}{C_{sat} - C_o} \right) = -\frac{\beta_c A}{V} t \quad (4)$$

Many studies have concluded that mass transfer of carbon into the bulk steel is the rate limiting step for carbon dissolution.<sup>4,11,12,13,14,15,16</sup> However, Khanna *et al.* found evidence suggesting that the interfacial reaction may be rate controlling initially, and the interfacial reaction rate increases

quickly which changes rate control to mass transfer.<sup>11</sup>

The corrosion of MgO grains in refractory by slag exposes graphite to dissolution by liquid steel.<sup>17,18</sup> This process begins with slag wetting the refractory and dissolving the exposed oxides. Then, steel wets and dissolves the exposed graphite.<sup>7,17,19</sup> It has been found that dissolution of MgO into slag is the rate controlling step.<sup>7,10,17,20</sup> The dissolution rate of MgO into slag can be described by the following equation where  $[MgO]$  is the concentration of MgO in the slag,  $[MgO]_{sat}$  is the concentration of MgO that would saturate the slag, and  $\beta_{MgO}$  is the mass transport constant.<sup>10</sup>

$$\frac{d[MgO]}{dt} = \beta_{MgO}([MgO]_{sat} - [MgO]) \quad (5)$$

The dissolution of MgO can also be evaluated through the corrosion rate of the refractory. The corrosion rate can be described by the following equation where  $V_{corr}$  is the corrosion rate in mm/hr,  $\beta_{MgO}$  is the mass transfer coefficient in m/s,  $\rho_{slag}$  is the density of the slag,  $\rho_{ref}$  is the density of the refractory,  $[MgO]_{sat}$  is the saturation concentration of the MgO in the slag, and  $[MgO]_0$  is the initial concentration of the MgO in the slag.<sup>21</sup>

$$V_{corr} = 36000\beta_{MgO} \frac{\rho_{slag}}{\rho_{ref}} ([MgO]_{sat} - [MgO]_0) \quad (6)$$

The goal of this study is to define the controlling kinetic mechanisms and kinetic parameters for carbon pickup from ladle refractories in ULC steels by analyzing data from induction furnace dip tests that reflect the conditions present in a ladle of ULC steel. The effects of different refractories and slag conditions on the kinetic mechanism will also be observed.

## PROCEDURE

Refractory dip tests were performed in a vacuum induction furnace (VIF) under an Ar atmosphere. The refractory fingers used were cored from commercially available MgO-C refractories using a 1.27 cm ID coring bit. Four carbon contents were tested: 4 wt%C, 6 wt%C, 10 wt%C, and 12 wt%C. All dip tests utilized approximately 5.5 kg of ULC steel. The nominal starting chemistry of the steel as shown in Table I was determined by arc spectroscopy. Three different conditions were tested: steel without slag, steel with slag, and steel with MgO saturated slag. The nominal slag chemistries are shown in Table II. These slags were prepared by mixing commercially available oxide powders and pre-melting them in a graphite crucible at 1350 °C. To begin a dip test, the steel was melted and heated to an aim temperature of 1600 °C in an alumina crucible with a composition of 89 % alumina, 10 % silica, and 1 % other oxides. Then, slag was added for the experimental runs that required it. An initial pin sample was taken with an evacuated quartz tube. The refractory rod was then submerged approximately 3 cm into the melt. Pin samples were taken one minute after refractory immersion and every four minutes thereafter up to 30 minutes of

immersion. More details on the experiment and materials preparation are given in our previous paper.<sup>22</sup>

Table I. Nominal starting chemistry in ppm of ULC steel used in VIF dip tests.

C	Si	Al	Ti	Mn	Cu	Cr	Ni	Mo	Fe
34	237	710	492	737	370	365	407	94	Remainder

Table II. Nominal starting chemistries of slags used in VIF dip tests.

	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO
Unsaturated Slag (wt%)	7.7	34.7	9.9	47.7
MgO-saturated Slag (wt%)	13.6	32.4	9.3	44.7

The steel pin samples taken from the melt were analyzed using an arc spectrometer. Carbon and oxygen contents of the steel were found by LECO analysis. Post mortem refractory samples were sectioned, mounted in epoxy, and polished to 1  $\mu$ m finish using diamond paste. The polished refractory surfaces were captured with a digital camera and by optical microscopy. The polished refractory surfaces were coated by gold palladium for SEM imaging and EDS mapping. Post mortem slag samples were analyzed by XRF.

## RESULTS AND DISCUSSION

Results from our previous paper showed that carbon pickup was controlled by steel penetration into the refractory when no slag was present.<sup>22</sup> The 4 wt%C and 6 wt%C refractories did not show any carbon pickup when no slag was present because steel could not penetrate the closely packed MgO grains.<sup>22</sup> Carbon pickup was controlled by corrosion of the refractory at the slag line when slag was present in the dip tests.<sup>22</sup> These controlling mechanisms were further evidenced by the agreement between measured carbon pickup values and calculations of expected carbon pickup based on the assumed mechanism.<sup>22</sup>

In the absence of slag, carbon pickup from MgO-C refractories was controlled by the penetration of steel into the refractory. Carbon pickup from penetration of steel into refractory has three steps. First, carbon in front of the penetrating steel is dissolved. Then, carbon diffuses from the high carbon steel at the penetrating tip to the low carbon steel near the interface between the refractory surface and the bulk steel. Finally, mass transfer of carbon into the bulk steel occurs by convection. The carbon concentration profile in the penetrated steel would be different depending on which step was rate limiting as shown in Figure 1. If the carbon dissolution reaction were rate controlling, the penetrating steel and the bulk steel would have the same carbon content throughout because diffusion and convection transport would occur faster than carbon can be dissolved. By contrast, if diffusion through the penetrating steel were rate controlling, the carbon concentration would

steadily decrease from carbon saturation at the penetrating tip to the bulk carbon concentration at the refractory surface because convection would occur fast enough to keep the steel at the refractory surface at the bulk carbon concentration. If convection of carbon into the bulk steel were rate controlling, the penetrated steel would be carbon saturated and a boundary layer would exist between the refractory and bulk steel where the carbon concentration lowers from saturation to the concentration in the bulk. This would occur because the convection of carbon into the bulk would not be able to transport carbon from the refractory surface as fast as diffusion can resupply it.

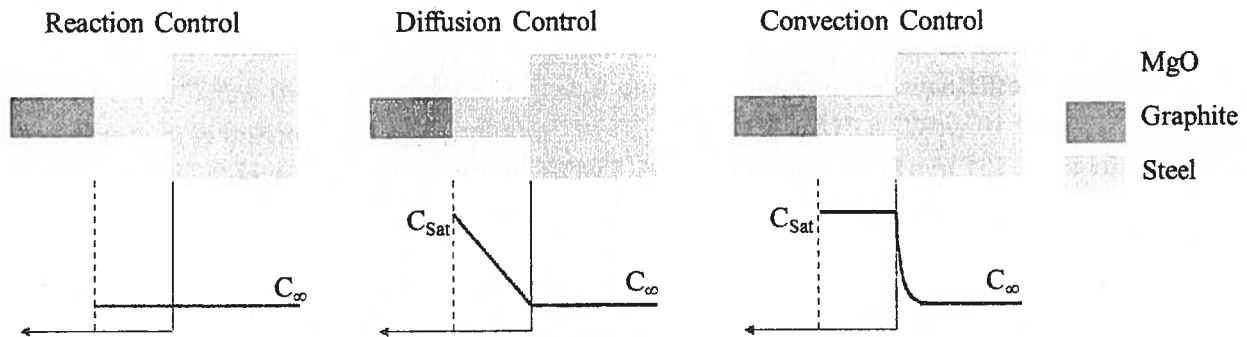


Figure 1. The carbon concentration gradients for three possible rate limiting steps for carbon transport.

A refractory sample from a 10 wt%C heat without slag was etched with 2% nitol solution for 15 seconds to observe the carbon profile of the penetrating steel. Figure 2 shows an optical micrograph of the etched steel. The steel contains massive carbides up to the refractory surface which suggests that the steel is carbon saturated. This observation suggests that convection is the rate limiting step for carbon pickup by steel penetration.

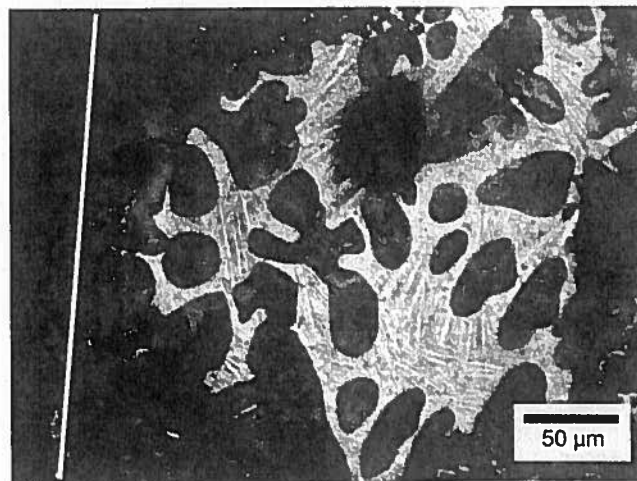


Figure 2. Etched sample of steel penetration in MgO-10 wt%C refractory. The white line is the steel-refractory interface.

The convective mass transfer of carbon into steel can be described by the following equation where  $C_{sat}$  is the saturation concentration of carbon in steel,  $C_{\infty}$  is the carbon concentration of the bulk steel at time  $t$ ,  $C_0$  is the initial carbon concentration of the steel,  $A$  is the area of contact between steel and carbon,  $V$  is the volume of steel, and  $\beta_C$  is the mass transfer coefficient.<sup>15</sup>

$$\ln\left(\frac{C_{sat}-C_{\infty}}{C_{sat}-C_0}\right) = -\frac{\beta_C A}{V} t \quad (4)$$

$\ln((C_{sat}-C_{\infty})/(C_{sat}-C_0))$  was plotted versus time for 10 wt%C and 12 wt%C no slag dip tests as shown in Figure 3. The plots of  $\ln((C_{sat}-C_{\infty})/(C_{sat}-C_0))$  versus time exhibit linear behavior, providing additional support for convective mass transport of carbon as the rate limiting step. The mass transfer coefficients calculated from Figure 3 were  $1.08 \cdot 10^{-6}$  m/s for 10 wt%C 0.017 SA/V,  $8.51 \cdot 10^{-7}$  m/s for 10 wt%C 0.018 SA/V, and  $1.20 \cdot 10^{-6}$  m/s for 12 wt%C. Jansson *et al.* calculated a coefficient of  $2 \cdot 10^{-6}$  m/s for dip tests of MgO-5.5 wt%C refractory in ULC steel.<sup>16</sup> The agreement is reasonable given the uncertainties in convection in the two experiments.

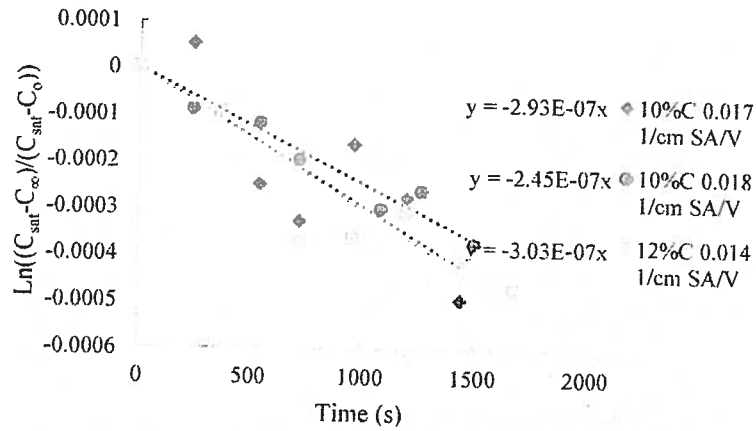


Figure 3. A plot of  $\ln((C_{sat}-C_{\infty})/(C_{sat}-C_0))$  versus time for dip tests without slag where penetration occurred.

In the presence of slag, refractory corrosion dominates the pickup of carbon. Potschke *et al.* found that refractory corrosion in an induction furnace containing both steel and slag in contact with refractory can be described by the following equation where  $V_{corr}$  is the corrosion rate in mm/hr,  $\beta_{MgO}$  is the mass transfer coefficient in m/s,  $\rho_{slag}$  is the density of the slag,  $\rho_{ref}$  is the density of the refractory,  $[MgO]_{sat}$  is the saturation concentration of MgO in the slag, and  $[MgO]_0$  is the initial concentration of MgO in the slag.<sup>21</sup>

$$V_{corr} = 36000 \beta_{MgO} \frac{\rho_{slag}}{\rho_{ref}} ([MgO]_{sat} - [MgO]_0) \quad (6)$$

Table III shows the initial MgO concentrations and the MgO saturation concentration for the slags used in the dip tests. MgO saturation concentrations were calculated from the final slag chemistries

using FactSage® version 7 and FToxid database. The conditions entered into FactSage were 1600 °C and an argon atmosphere with a partial pressure of oxygen of  $10^{-4}$ . The difference between initial slag MgO concentration and MgO saturation was plotted versus the corrosion rate of the refractory dip test fingers in Figure 4. The corrosion rate was calculated from the corrosion notch on post mortem refractory samples and the immersion time. The value of  $36000\beta_M(\rho_{\text{slag}}/\rho_{\text{ref}})$  is 0.2887 mm/hr for the 10 wt%C dip tests and 0.4797 mm/hr for the 4 wt%C dip tests. Potschke *et al.* calculated this value as 0.24 mm/hr for MgO-C bricks.<sup>21</sup> However, their data showed much scatter because they grouped a range of MgO-C bricks together that had between 5 and 12 wt%C.<sup>21</sup> Their value of 0.24 gives a mass transfer coefficient of  $8 \cdot 10^{-6}$  m/s.<sup>21</sup> The mass transfer coefficients calculated from Figure 4 were  $8 \cdot 10^{-6}$  m/s for 10 wt%C bricks and  $12 \cdot 10^{-6}$  m/s for 4 wt%C bricks. The density of slag was estimated as 2.8 g/cm<sup>3</sup> from collected values of slags similar in temperature and chemistry.<sup>23</sup> The density of the 10 wt%C and 4 wt%C refractories were 2.8 g/cm<sup>3</sup> and 3.1 g/cm<sup>3</sup> respectively.

Table III. Initial MgO content and calculated MgO saturation concentration for dip test slags.

MgO-C Refractory C (wt%)	4	4	10	10	10	10
Initial Slag MgO Content (wt%)	7.70	13.62	7.69	7.70	9.55	13.62
Calculated Slag MgO Saturation (wt%)	21	19	18	20	19	18

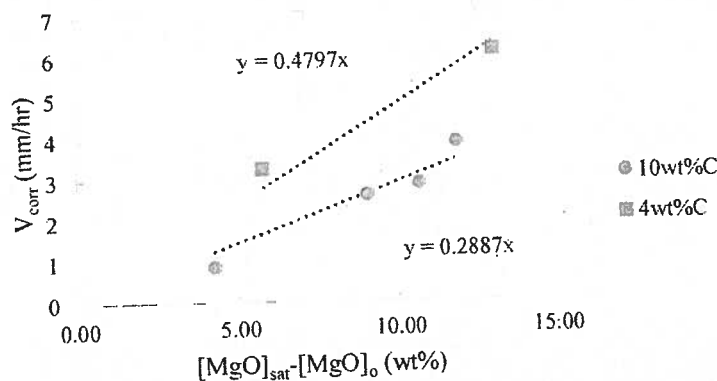


Figure 4. The corrosion rate of refractory dip test fingers versus the difference between MgO saturation and the initial MgO concentration of the slag.

The expected carbon pickup based on the pickup mechanisms revealed above was recalculated for the dip tests. The carbon pickup from penetration was found by analyzing SEM images as shown in Figure 5 of the refractory-steel interface. The images were processed with ImageJ software to measure the area of penetrated steel. This area was multiplied by the submerged length of the refractory rod to obtain a volume. This volume was multiplied by the volume fraction of carbon in the refractory. Then, the weight of carbon in that volume was found. The carbon pickup was calculated by assuming that the volume of steel in the refractory was saturated in carbon and that all the carbon replaced by steel went to either the penetrated steel or



the bulk steel.

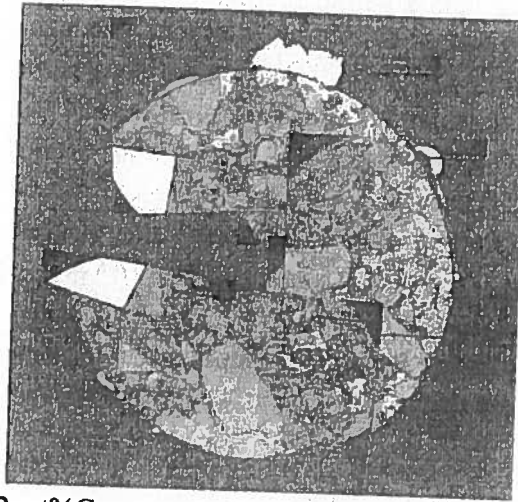


Figure 5. SEM images of 12 wt%C post mortem refractory. Copper tape was placed over an area without steel penetration to maintain conductivity.

Carbon pickup from slag corrosion was estimated by calculating the amount of carbon in the corroded volume at the slag line assuming that all of this carbon entered the steel bath. This volume was calculated by taking the area of the half-ellipse shaped notch at the slag line and multiplying by the circumference of the finger at the centroid of the notch. Figure 6 shows some of the corrosion notches. Table IV shows a comparison of the measured carbon pickup and the calculated carbon pickup for the refractory dip tests. Figure 7 shows that the calculated pickup based on the mechanisms generally agrees well with the measured carbon pickup when measurement error is taken into account.

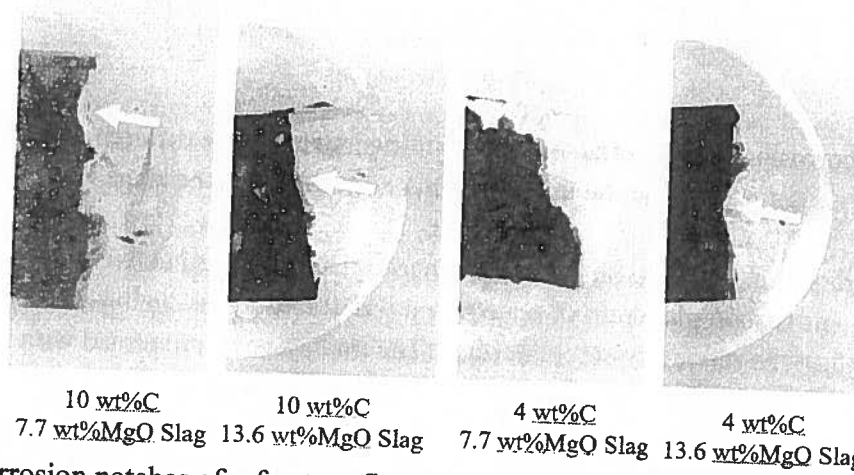


Figure 6. Corrosion notches of refractory fingers. Notches are indicated by white arrows. It can be seen that notch severity decreases with increased graphite in refractory and increased MgO in slag.

Table IV. Measured carbon pickup versus calculated carbon pickup from refractory dip tests.

Refractory	SA/V*100 θ (cm <sup>2</sup> /cm <sup>3</sup> )	Slag	Measured C Pickup (ppm)	Volume Corroded (cm <sup>3</sup> )	C Pickup from Corrosion (ppm)	C Pickup from Penetration (ppm)	Calc. C Pickup (ppm)
MgO-4 wt%C	28	7.7 wt%MgO	26 ± 5	0.87	19	0	19
MgO-4 wt%C	18	13.6 wt%MgO	23 ± 12	0.17	4	20*	24
MgO-10 wt%C	17	None	28 ± 15	0	0	44	44
MgO-10 wt%C	18	None	21 ± 13	0	0	31	31
MgO-10 wt%C	20	7.7 wt%MgO	29 ± 8	0.31	15	11	26
MgO-10 wt%C	16	7.7 wt%MgO	37 ± 12	0.24	12	17	29
MgO-10 wt%C	28	9.6 wt%MgO	32 ± 8	0.21	11	21	32
MgO-10 wt%C	15	13.6 wt%MgO	7 ± 5	0.032	2	8	10
MgO-12 wt%C	14	None	26 ± 8	0	0	31	31

\*Slag Penetration

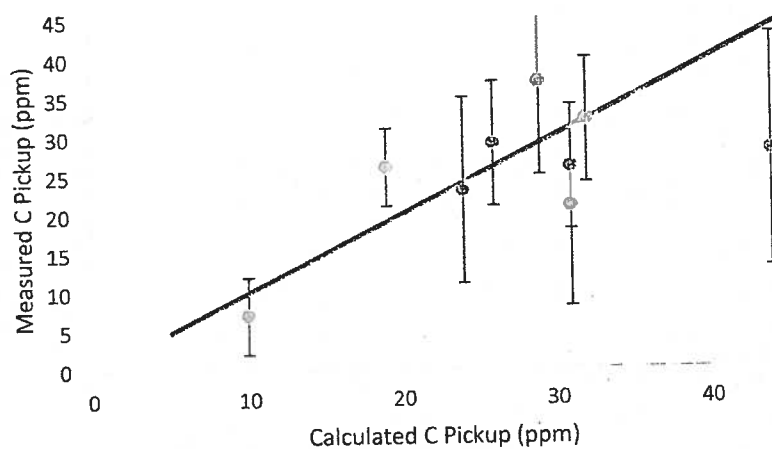


Figure 7. Comparison of the calculated carbon pickup and measured carbon pickup from refractory finger dip tests.

### CONCLUSION

Refractory finger dip tests have revealed the kinetic mechanisms for carbon pickup in ULC steel. Kinetic parameters have been calculated for these mechanisms and compared with literature values.

- Carbon pickup from 10 wt%C and 12 wt%C refractories is controlled by dissolution of carbon by steel penetrating into the refractory when no slag is present. The rate controlling step for carbon pickup from penetration is convection into the bulk liquid. The mass transfer coefficient for carbon into steel is about  $1 \cdot 10^{-6}$  m/s for static dip tests in an induction furnace with no slag.

- Carbon pickup is controlled by slag corrosion of refractory at the slag line for dip tests when slag was present. The controlling mechanism is convective mass transfer of MgO into slag. The mass transfer coefficient of MgO into slag is  $8 \cdot 10^{-6}$  m/s for 10 wt%C bricks and  $12 \cdot 10^{-6}$  m/s for 4 wt%C bricks for static dip tests in an induction furnace. The dissolution rate of MgO is slower for bricks with a higher carbon content.
- The measured carbon pickup has been shown to be in reasonable agreement with the carbon pickup calculated based upon the proposed mechanisms for carbon transport to steel.

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Steelmaking Refractories - 2030 Dream Scenario

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