Recovery of base metals and PGMs in a DC alloy-smelting furnace

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Abstract

Base metals and platinum group metals can be collected in metallic alloy form, via a wide variety of smelting processes. The recovery, or degree of collection, of the valuable metals is a function of the extent of reduction in the furnace, which, in turn, is indicated by the fraction of iron present in the feed materials that reports to the alloy. An equation has been developed that relates the recovery of various metals (such as Ni, Co, PGMs, and Cr) to the recovery of Fe. This recovery equation (for each metal) is characterised by a single parameter ($K\gamma$) that can either be empirically fitted to the data, or expressed in terms of the equilibrium constant and the ratios of the activity coefficients involved. Data from a number of varied DC arc furnace campaigns is presented to illustrate this behaviour.

Introduction

A number of pyrometallurgical processes involve reductive alloy smelting using a carbonaceous reducing agent. These processes include the smelting of chromite to produce ferrochromium, the smelting of nickel laterite ores to produce ferronickel, the recovery of base metals from slags, and the recovery of platinum group metals (PGMs) via collection in iron alloys. When carbon is added to the molten bath in a furnace, the various metallic elements reduce to different extents, at a given level of carbon addition. This behaviour allows a reasonable degree of separation to take place during smelting. It is well known that an increase in the amount of the reductant added to the furnace results in increased quantities of the various metallic elements that report to the alloy that is produced, but it would be very useful for the design of such smelting processes to have an equation that described this behaviour quantitatively.

Mintek is in the fortunate position of doing work in support of a great variety of industrial processes [1], and this provides a wider range of operating data than is readily available at a single operating plant elsewhere. In particular, Mintek has applied DC arc furnace technology to many alloy smelting processes, and it has been found that this type of furnace provides relatively consistent alloy and slag compositions, usually close to chemical equilibrium conditions, because of the largely uniform temperature and composition gradients in the well mixed furnace that is stirred effectively by the vigorous action of the open electric arc impinging on the surface of the slag. The stirring is sufficient to promote coalescence of small alloy droplets, but not so great that it keeps many droplets in suspension in the slag.

Theoretical development of the Kγ recovery equation

In deference to the dominant position of iron in the world of metallurgy (about ten times as much iron is produced as all other metals combined), the otherwise arbitrary decision is made to express the recoveries of the metals of interest in relation to the recovery of iron.

For the purposes of developing an equation that describes the recovery of metals, the simple relationship between Co and Fe is considered here. However, the same principles can be applied to other base metals too. The equation development below builds on and extends earlier work [2] that was specifically focused on cobalt recovery.

The interchange between Co and Fe can be seen by studying the liquid reaction between slag and alloy:

$$CoO + Fe \leftrightarrows Co + FeO \hspace{3cm} [1]$$
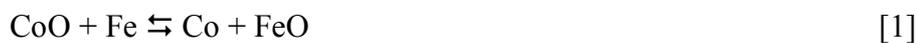
At equilibrium, the degree of separation between Co and Fe can be indicated by the equilibrium constant, K, which is strictly a function of temperature only.

$$K = \frac{a_{Co} \cdot a_{FeO}}{a_{CoO} \cdot a_{Fe}} \hspace{3cm} [2]$$

The activities a may be expressed in terms of activity coefficients γ and mole fractions x.

$$K = \frac{\gamma_{Co}\, x_{Co} \cdot \gamma_{FeO}\, x_{FeO}}{\gamma_{CoO}\, x_{CoO} \cdot \gamma_{Fe}\, x_{Fe}} \qquad \text{[3]}$$

In the interests of simplicity, we may lump together the ratio of the activity coefficients of these four chemical species in solution. Individual activity coefficients may be obtained from the literature.

Define $\gamma = \dfrac{\gamma_{CoO} \cdot \gamma_{Fe}}{\gamma_{Co} \cdot \gamma_{FeO}}$ \qquad [4]

If we make the reasonable assumption that γ is not a strong function of composition, then we may derive a simple expression to show the relationship between the recovery of Co to the alloy and the recovery of Fe to the alloy.

From Equations [3] and [4]:

$$K\gamma = \frac{x_{Co} \cdot x_{FeO}}{x_{CoO} \cdot x_{Fe}} \qquad \text{[5]}$$

The simple stoichiometry of Equation [1] allows the equation above to be expressed simply in terms of numbers of moles:

$$K\gamma = \frac{n_{Co} \cdot n_{FeO}}{n_{CoO} \cdot n_{Fe}} \qquad \text{[6]}$$

Note that the above equation may also be expressed in terms of mass percentages, simply by taking into account a conversion factor to allow for the ratios of the molecular masses.

$$K\gamma = 0.988 \left(\frac{\%Co \cdot \%FeO}{\%CoO \cdot \%Fe} \right) \qquad \text{[7]}$$

If the amounts of cobalt and iron initially present in the feed are denoted by a superscript zero, the following mass balance equations may be written.

$$n_{Co} = n_{Co}^{0} + n_{CoO}^{0} - n_{CoO} \qquad \text{[8a]}$$

$$n_{Fe} = n_{Fe}^{0} + n_{FeO}^{0} - n_{FeO} \qquad \text{[8b]}$$

Recoveries R_{Co} and R_{Fe} may be defined as follows:

$$R_{Co} \equiv \frac{n_{Co}}{n_{Co}^{0} + n_{CoO}^{0}} \qquad \text{[9a]}$$

$$R_{Fe} \equiv \frac{n_{Fe}}{n_{Fe}^{0} + n_{FeO}^{0}} \qquad \text{[9b]}$$

Combining Equations [8] and [9]:

$$n_{CoO} = (1 - R_{Co})(n^0_{Co} + n^0_{CoO}) \qquad [10a]$$

$$n_{FeO} = (1 - R_{Fe})(n^0_{Fe} + n^0_{FeO}) \qquad [10b]$$

Substituting Equations [9] (re-arranged) and [10] into [6] gives:

$$K\gamma = \frac{R_{Co}(n^0_{Co} + n^0_{CoO}) \cdot (1 - R_{Fe})(n^0_{Fe} + n^0_{FeO})}{(1 - R_{Co})(n^0_{Co} + n^0_{CoO}) \cdot R_{Fe}(n^0_{Fe} + n^0_{FeO})} \qquad [11]$$

This can be simplified to:

$$K\gamma = \frac{R_{Co}(1 - R_{Fe})}{R_{Fe}(1 - R_{Co})} \qquad [12]$$

This can be re-arranged to give:

$$R_{Co} = \frac{K\gamma \cdot R_{Fe}}{1 - (1 - K\gamma)R_{Fe}} \qquad [13]$$

It is certainly possible to calculate a value for $K\gamma$ from published theoretical data, but this would only apply strictly to a perfect equilibrium system. It may be more useful to use the form of the theoretically derived equation, and to fit the model to actual plant data. Values of $K\gamma$ may be found by fitting Equation [13] to experimental data. For illustrative purposes, the curve in Figure 1 below shows a value of $K\gamma = 7$.
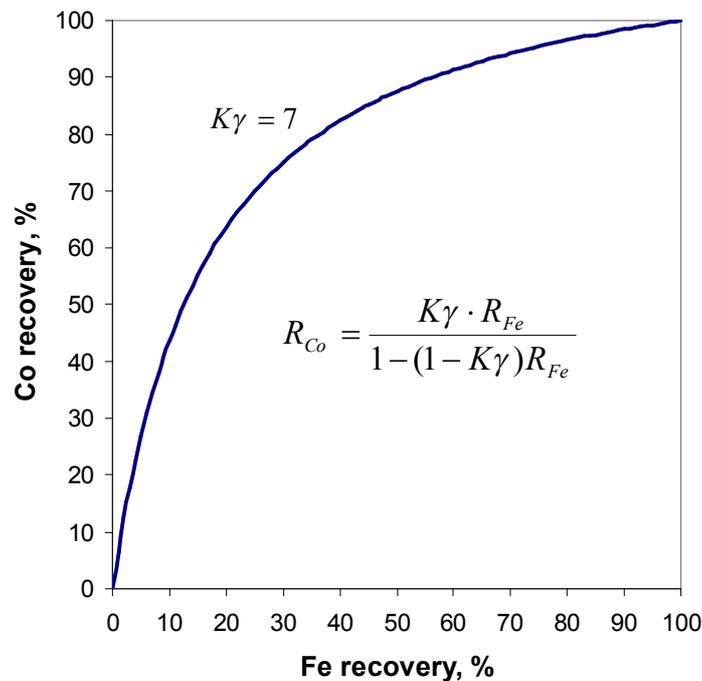

Figure 1: Illustrative relationship between Fe recovery and Co recovery to the alloy

The $K\gamma$ recovery equation presented here is based on the assumption of a 1:1 relationship in the stoichiometry of the exchange reaction exemplified by Equation [1]. This system has the great virtue of simplicity, in that it is possible to study the effect of the recovery of Fe on the recovery of another metallic element without having to take into account the other materials present. Additional work has been done to formulate similar equations for reactions of more complex stoichiometry (*e.g.* Cr_2O_3 and Fe). However, these relationships are inherently more complicated in that the recovery relationships depend on all the species present in the system. This dramatically decreases their utility, and they will not be discussed further here.

Effect of various values of $K\gamma$ on the shape of the recovery curve
The symmetrical nature of Equation [13] implies that it can be used to describe the recoveries of both elements that are more 'noble' (easier to reduce) than iron, and those that are less so. The more 'noble' the element, the higher the value of $K\gamma$. Figure 2 shows the effect of various values of $K\gamma$ on the shape of the recovery curve for a hypothetical element X. It can be seen from this set of curves that the higher the value of $K\gamma$, the closer the curve is to the top left. A value of 1 for $K\gamma$ yields a straight line, and can be seen as plotting the recovery of Fe against itself. Values of $K\gamma$ less than 1 generate curves closer to the bottom right. A pair of curves with reciprocal values of $K\gamma$ show a kind of symmetry involving both vertical and horizontal rotation.
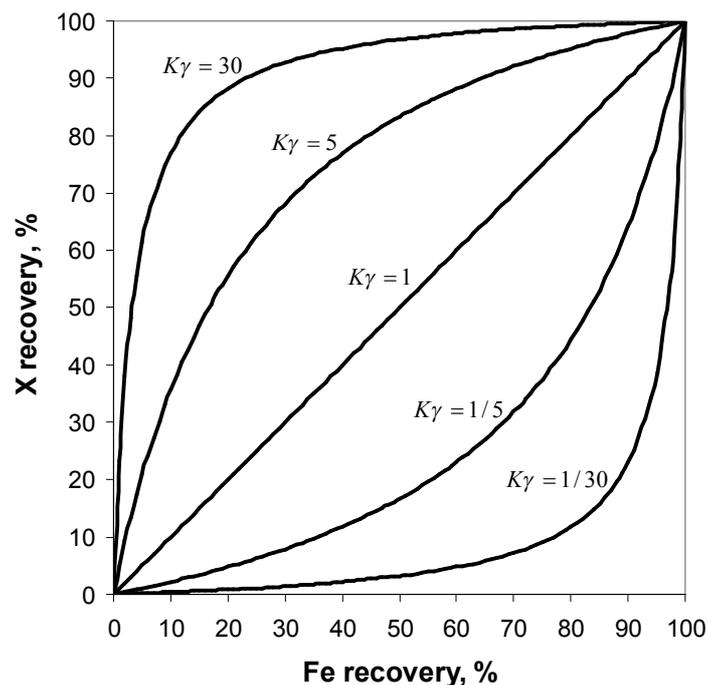

Figure 2: Recovery curves with different values of $K\gamma$

Application to Co recovery by slag cleaning
Mineralogical studies have shown that cobalt is present as CoO in copper reverberatory furnace slag. Copper in the slag is mainly attributed to the presence of copper-rich sulphides. The cobalt oxide, and, to a lesser extent, the copper oxide associated with the silicate/oxide phases, is reduced by Fe from the alloy to form metallic Co (and Cu), resulting in the formation of FeO in the slag. The CoO in the slag is associated primarily with Fe_2SiO_4, and

analysis by scanning electron microscopy showed some Fe_2SiO_4 particles with no detectable Co or Cu, thus demonstrating that it is, in principle, possible to remove all the Co and Cu from this phase.

For the chemical reaction between Co and Fe, shown in Equation [1], the equilibrium constant, K, is strictly a function of temperature only. Over the temperature range of interest (between 1500 and 1600°C), K has a value of approximately 30.

For the calculation of γ, individual activity coefficients may be obtained from the literature. Holzheid *et al.* [3] obtained values for γ_{FeO} of 1.70 ± 0.22, and for γ_{CoO} of 1.51 ± 0.28. Teague [4] indicates that the activity coefficient of Co in fayalitic slags is 0.92. The data reported [5] for the activity coefficient for Fe in fayalitic slags varies widely between 0.3 and 0.6.

A simple combination of the values of the equilibrium constant and the activity coefficients provides a theoretical value for $K\gamma$ of about 13.

A set of experimental data from previously reported work on the recovery of cobalt from copper reverberatory furnace slag [2] shows a fair degree of scatter and covers mostly the high Co recovery area. This data is shown (using the + symbol) in Figure 3. The scatter is to be expected as the data covers a wide range of experimental conditions, and is based on chemical analyses that have significant uncertainty associated with measurements at low concentration. However, some more recent work on flash furnace slags has provided further data in the low recovery area. This data is shown (using solid dots) in Figure 3. The combination of these two sets of data provides convincing evidence that the proposed recovery equation provides a curve of the correct shape to fit the data. Interestingly, the best fit to the data is obtained with a value for $K\gamma$ of about 14, which is very close to the theoretically derived number.
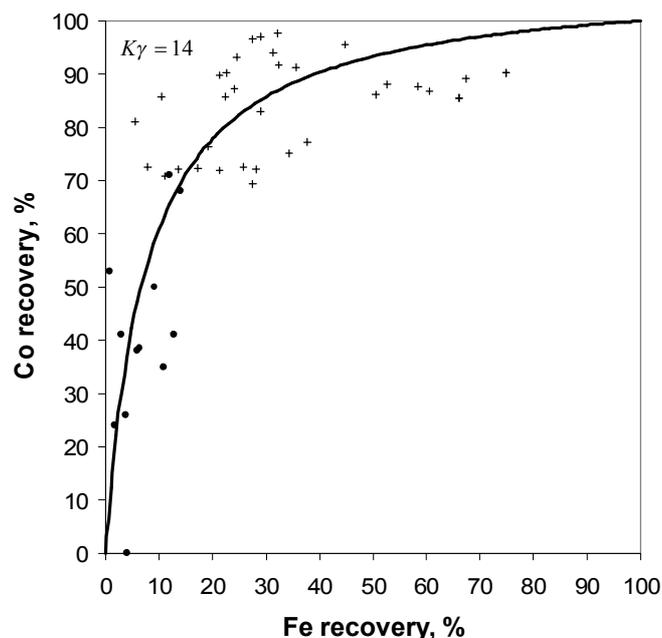

Figure 3: Recovery curve for Co ($K\gamma = 14$) and two sets of data points

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Application to ferronickel smelting (Ni and Cr)

The smelting of nickel laterite ores to produce ferronickel essentially involves a trade-off between recovery and grade. The greater the degree of reduction, the greater the recovery of nickel. However, as an increasing quantity of iron (and some more nickel) is reduced to the metallic state, so the nickel grade is diminished. The $K\gamma$ recovery equation provides a useful tool for quantifying this effect.

The data shown in Figure 4 is derived from ferronickel smelting testwork [6] carried out in a pilot-scale DC arc furnace with an operating diameter of 2 m. More than 190 tons of calcined nickel oxide ore was smelted over a period of about 19 days. Three different samples were smelted, each containing relatively low amounts of nickel and iron and relatively high amounts of silica. For two of the samples, dolime was added as flux. In the particular example shown here, there was evidence to suggest that slag-metal equilibrium was not fully attained because of a crusty layer that formed in the furnace, because of the particular experimental conditions employed. Even so, the recovery equation is shown to fit the data well, with a $K\gamma$ value of about 20.

As a point of comparison, another curve is shown, with a higher value of $K\gamma$ (from a different experimental campaign. This goes to show the importance of either testwork or wide experience in the selection of an appropriate value of $K\gamma$ to use for characterising the smelting of a particular ore. (The theoretical justification for this is that γ does depend to some extent on the slag and alloy composition.)
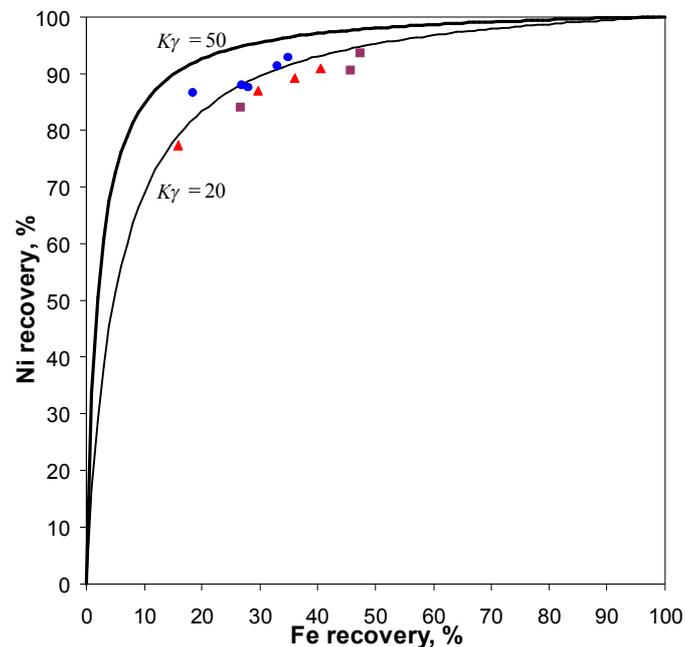

Figure 4: Recovery curve example for Ni ($K\gamma$ = 20 to 50) in ferronickel smelting

The recovery of Cr in base metal smelting shows interesting behaviour. Because Cr is 'less noble' than Fe, the curve is the other way around compared to Ni or Co. Figure 5 shows numerous data points from laboratory-scale smelting tests carried out on a typical nickel laterite. Tests were carried out on 200 g samples in MgO crucibles in an induction furnace.

Because so little metal is produced in these tests, it is quite easy to over-reduce the samples in order to obtain sufficient metal. In this case, the over-reduced tests produced a very nice wide range of data for plotting the Cr recovery as a function of Fe recovery. This data very nicely fitted a recovery curve with $K\gamma = 1 / 35$. As an additional comparison, a few points are shown (in red) to follow the same curve very closely. These results came from smelting PGM-containing revert tailings, and each point represents the monthly recovery figure for the period October 2007 to June 2008 at Mintek.
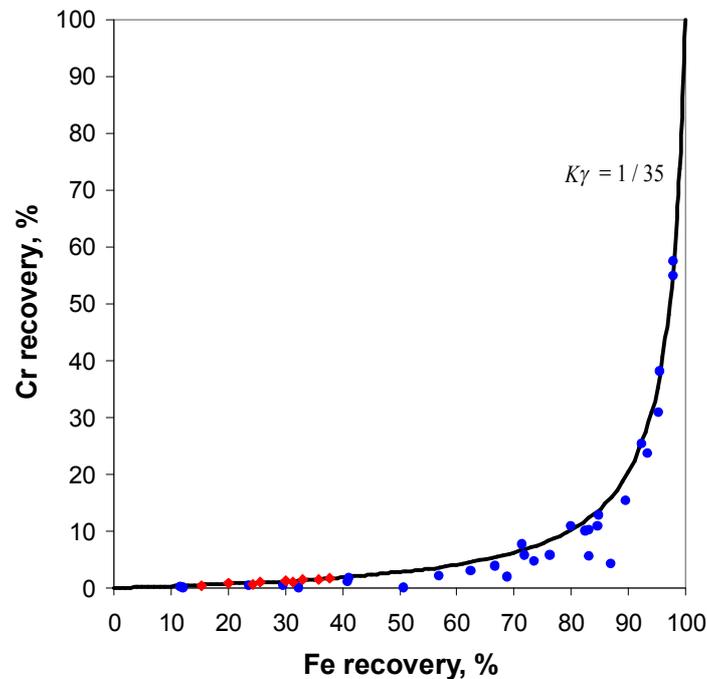

Figure 5: Recovery curve for Cr ($K\gamma = 1 / 35$) in ferronickel smelting

Application to PGM smelting
Mintek's ConRoast process [7,8,9] involves smelting low-sulphur concentrates in a DC arc furnace, and collecting the platinum group metals (PGMs) and valuable base metals in an iron alloy. The intention in this process is to separate the valuable metals from the iron and the gangue constituents present in the slag. The desirable area of operation is clearly somewhere in the region where the recovery of PGMs and valuable base metals is high, and the recovery of iron to the alloy is still reasonably low. This process is also effective at removing chromium (in this context, a deleterious contaminant) from the feed and keeping it from the alloy. Figure 6 shows the recovery of PGMs, Ni, Co, and Cr as a function of Fe recovery to the alloy. Under the conditions of interest, it is fair to model the Ni, Co, and Cr as interacting with NiO, CoO, and CrO in the slag. There is no apparent reason why the PGMs should behave in a similar fashion, but there are good indications that they do, and that PGM recovery can also be usefully modelled using the $K\gamma$ recovery equation.
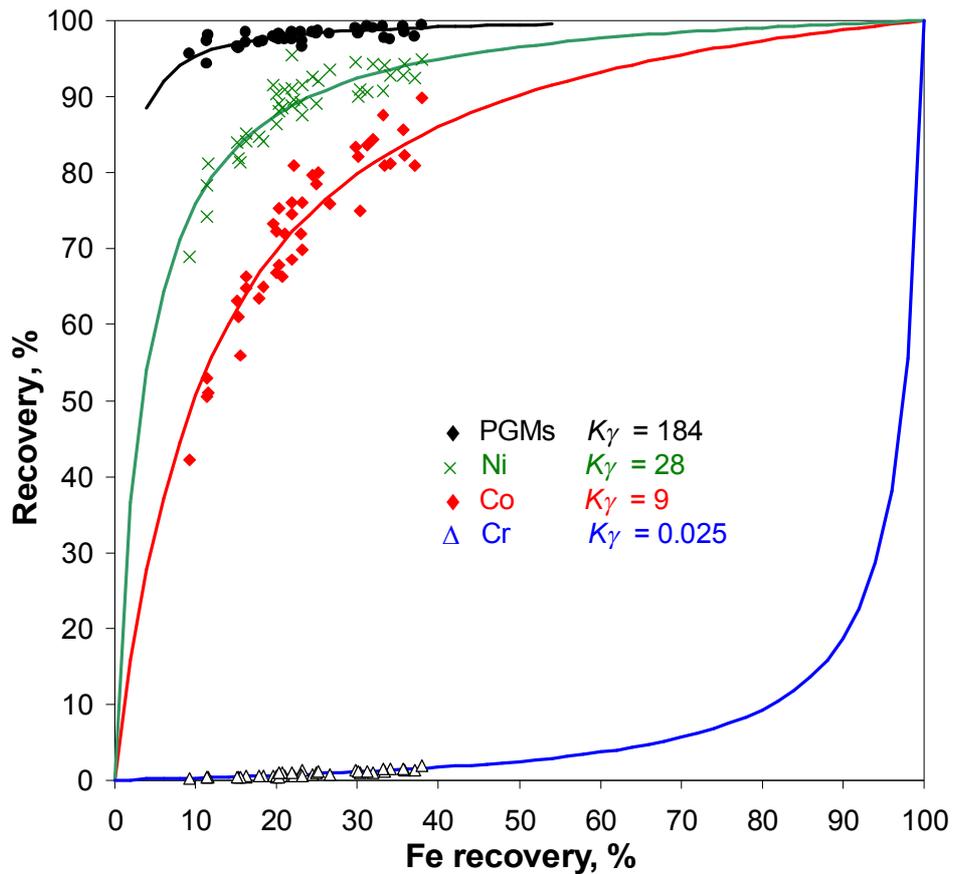
Figure 6: Recovery curves for PGMs ($K\gamma = 184$), Ni ($K\gamma = 28$), Co ($K\gamma = 9$), and Cr ($K\gamma = 0.025$)

Application to converting processes

The $K\gamma$ recovery equation applies also to oxidative converting processes as well as to reduction processes. These two very different types of process are governed by the same chemical reactions, albeit that the one is the reverse of the other. The recoveries of various elements can be plotted against the degree of iron removal from the alloy being converted. This has been well documented elsewhere [10].

Conclusions

The $K\gamma$ recovery equation has been found to provide a very useful basis for the design of processes involving the recovery of precious and base metals in DC arc furnaces. The value of $K\gamma$ to be used can be calculated theoretically, but it is often more effective to fit this value to experimental data. $K\gamma$ for a particular metal has a characteristic value that depends on the temperature of operation and to some degree on the composition of the slag and metal system under consideration (as this affects the individual activity coefficients).

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