



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

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Synopsis

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 report to the alloy. An equation has been developed that relates the recovery of various metals (such as Ni, Co, Cr, and PGMs) to the recovery of Fe. This recovery equation (for each metal) is characterized by a single parameter (K_f) 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 are 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 oxides of the various metallic elements reduce to different extents, at a given level of carbon addition. This allows some metallic elements to concentrate preferentially into an alloy phase, while others remain predominantly in the slag in oxidized form. This selective reduction behaviour allows a reasonable degree of separation (of one element from another) 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. This paper deals with the development of such an equation that relates the recovery of individual metals to the recovery of iron, in terms of a

single parameter that can be empirically fitted to experimental and plant data. This equation may be used for process design calculations over a range of feed material compositions.

Mintek is in the fortunate position of doing work in support of a great variety of industrial processes¹, 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 the well mixed nature of the melt in the 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 K_f recovery equation

In most of the ores and concentrates under consideration in this paper, iron is present as either the dominant or one of the most common reducible oxides. For this reason, and 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.

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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 work² that was specifically focused on cobalt recovery.

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



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.

$$K = \frac{a_{\text{Co}} \cdot a_{\text{FeO}}}{a_{\text{CoO}} \cdot a_{\text{Fe}}} \quad [2]$$

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

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

Although the standard states of each of the constituents of the reaction have not been listed explicitly (in the interests of keeping the equations as clear and simple as possible), it is important to note that the numerical values of the equilibrium constant and the activities and activity coefficients can vary according to the choice of standard states. It is obviously important that there is consistency in the choice of standard states, if individual values for K and γ are to be used.

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.

$$\text{Define } \gamma \equiv \frac{\gamma_{\text{CoO}} \cdot \gamma_{\text{Fe}}}{\gamma_{\text{Co}} \cdot \gamma_{\text{FeO}}} \quad [4]$$

In using γ , the ratio of the activity coefficients, rather than the individual activity coefficients themselves, we would like to make the assumption that γ , in a given system, is not a strong function of composition, so that 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. (This assumption is seen to be reasonable in at least some of the major systems of interest. For example, in the geological literature, Holzheid *et al.*³ found that the activity coefficients of FeO, NiO, and CoO in a high-temperature silicate melt were independent of oxygen fugacity and temperature over the range of 1300 to 1600°C, and were not affected by fairly wide variations in composition. In the case of iron being the major metal, its activity coefficient will be close to unity, and if the other non-ferrous metallic element is dilute the assumption of a constant activity coefficient is not unreasonable. In any case, the utility of the final equation will be tested by how well it fits actual data over a wide range of compositions.)

From Equations [3] and [4]:

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

The simple stoichiometric coefficients of Equation [1] (and more particularly the fact that the number of moles in the slag and alloy both remain constant) allows the equation above to be expressed simply in terms of numbers of moles:

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

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.

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

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.

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

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

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

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

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

Combining Equations [8] and [9]:

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

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

Substituting Equations [9] (rearranged) and [10] into [6] gives:

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

This can be simplified to:

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

This can be rearranged to give:

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

It is certainly possible to calculate a value for $K\gamma$ from published theoretical data (if this is available for the particular system and conditions of interest), but this would apply strictly only 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 shows a value of $K\gamma = 14$. (A comparison will be shown later in the paper between the model and experimental data.)

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

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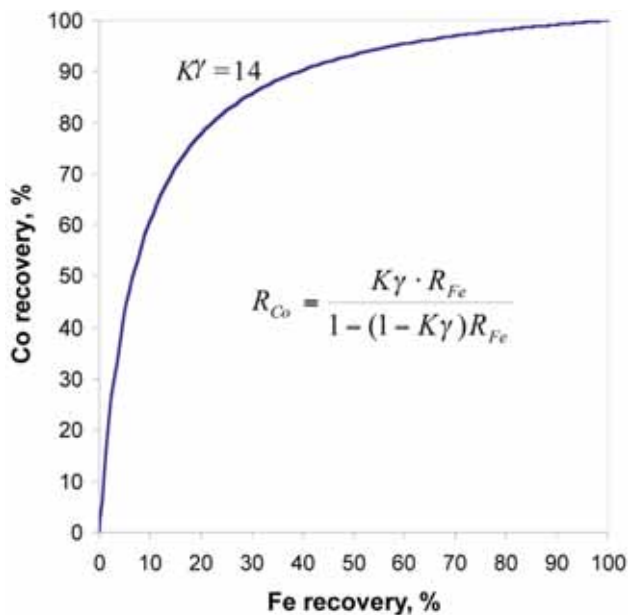


Figure 1—Illustrative relationship between Fe recovery and Co recovery to the alloy

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 (in particular, the mass balance expressions) 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 (i.e. the interchangeability of the two R terms in the same form of equation) 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 reflection across the ' $K\gamma = 1$ ' line.

Moderate values of $K\gamma$ result in curves having a moderate degree of curvature, and it can be expected that such curves may be usefully fitted to sets of experimental data. Curves having more extreme values of $K\gamma$ (say those above about 50, or those less than about $1/50$) will be subject to greater uncertainty as a result of experimental errors, as these will be accentuated in this area. Given that the activity coefficient ratio is unlikely to lie outside the range 10 to 0.1 (or maybe

100 to 0.01 at the most), then it is apparent that the K value cannot be either very large or very small if moderate values of $K\gamma$ are to be achieved. The result of this is that the two elements involved in the equilibrium (e.g. Co and Fe) must be chemically very similar. Therefore, this relationship might be expected to work well for elements close to iron in the periodic table, such as Cr, Mn, Co, and Ni.

Application to Co recovery by slag cleaning

Mineralogical studies have shown that cobalt is present largely as CoO in copper reverberatory furnace slag obtained from dumps in Zambia². Copper in this slag is mainly attributed to the presence of copper-rich sulphides. A slag-cleaning process involving reductive smelting of the dump slag, using carbon as a reductant, may be used to recover the valuable cobalt into an iron-rich alloy. 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.

The chemical reaction between Co and Fe that takes place in the molten slag may be shown as $\text{CoO(s)} + \text{Fe(l)} \rightleftharpoons \text{Co(l)} + \text{FeO(l)}$ which simply adds the appropriate standard states to Equation [1]. Liquid standard states have been used wherever possible. However, in the case of CoO, only solid data were available in the data-set used, but this will make little difference as the free energies of formation of solid and liquid phases become equal at the melting point anyway. 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.

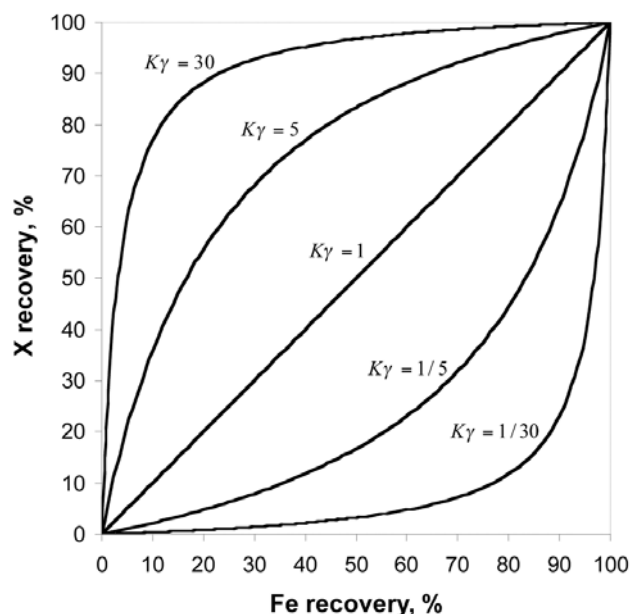


Figure 2—Recovery curves with different values of K

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For the calculation of γ , individual activity coefficients may, in principle, be obtained from the literature. However, in practice, in the case of multi-component industrially relevant systems, it is difficult to obtain consistent sets of activity coefficient data for the composition ranges and temperatures of interest. In this particular case, there is quite a spread of data between that obtained from the geological literature^{3,4} and the metallurgical literature^{5,6}, as well as there being large differences between the temperatures studied. Holzheid *et al.*³ worked with olivine-based silicate melts at temperatures up to 1600°C, in equilibrium with pure metals or alloys, and obtained values for γ_{FeO} of 1.70 ± 0.22 , and for γ_{CoO} of 1.51 ± 0.28 relative to the pure liquid oxide standard states, as well as recommending a method⁴ for the calculation of activity coefficients for the metallic species if sufficient interaction parameters are available. For this cobalt-recovery slag-cleaning process, it was difficult to obtain a good enough set of activity coefficient data to calculate K_γ on a theoretical basis, and it proved to be more useful to use pilot-plant data for the empirical fitting of a value for K_γ to be used in the recovery equation.

A set of experimental data from previously reported work on the recovery of cobalt from copper reverberatory furnace slag² shows a fair degree of scatter and covers mostly the high Co recovery area. These data points are shown (using the + symbol) in the upper portion of Figure 3. The scatter is to be expected as the data cover a wide range of experimental conditions, and are based on chemical analyses that have significant uncertainty associated with measurements of CoO in the slag at low concentration. However, some more recent work on the use of a DC arc furnace for cleaning flash furnace slags has provided further data in the low recovery area. These data points are 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. The best fit to the combined data is obtained with a value for K_γ of about 14.

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_γ recovery equation provides a useful tool for quantifying this effect.

The data shown in Figure 4 are derived from ferronickel smelting test work⁷ 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_γ

value of about 20.

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

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

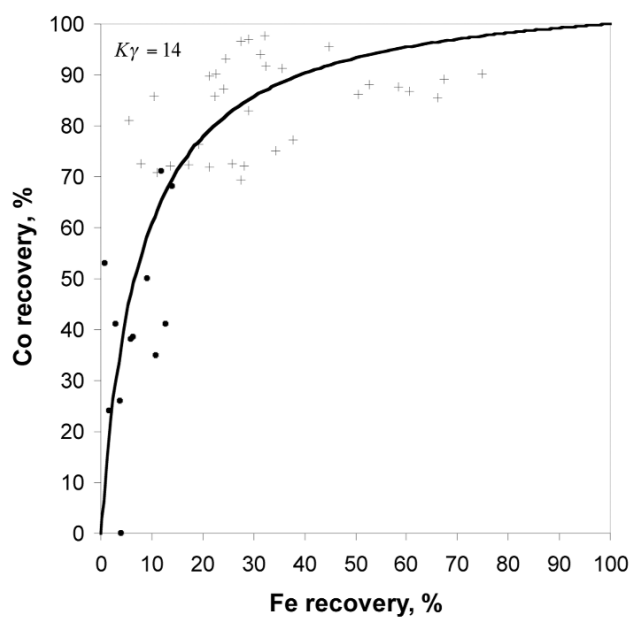


Figure 3—Recovery curve for Co ($K_\gamma = 14$) and two sets of data points

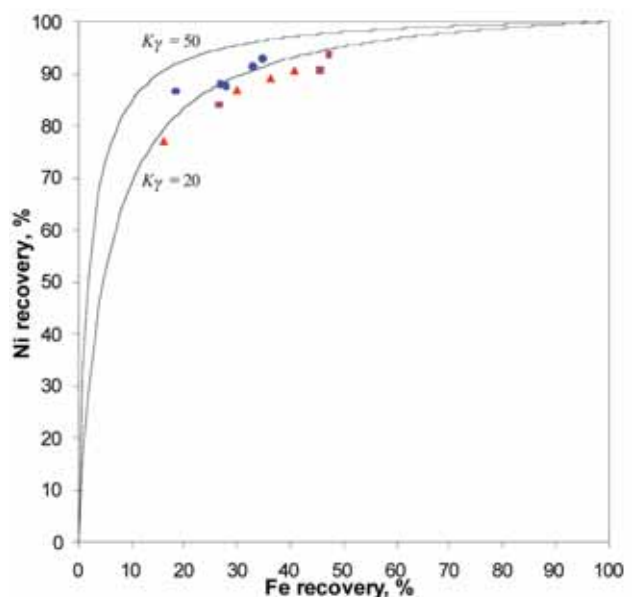


Figure 4—Recovery curve example for Ni ($K_\gamma = 20$ to 50) in ferronickel smelting

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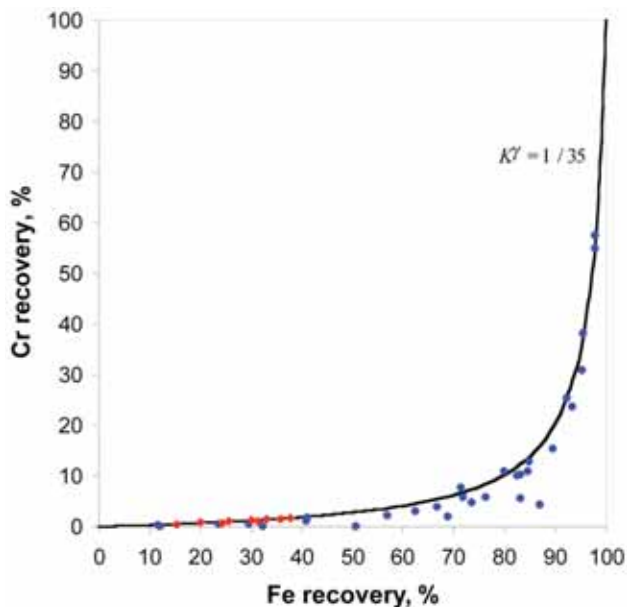


Figure 5—Recovery curve for Cr ($K_{\gamma} = 1/35$) in ferronickel smelting

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. It might seem surprising that the recovery curve fits the Cr data so well, given the earlier comments about the complexities of trying to model a system involving Cr_2O_3 . However, under reducing conditions, chromium is most likely to be present in the slag as CrO instead, in which case the recovery equation is most certainly applicable.

Application to PGM smelting

Mintek's ConRoast process⁸⁻¹⁰ 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) by keeping it dissolved in the slag, and away from the alloy product. 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 it has been found that PGM recovery can also be usefully

modelled using the K_{γ} recovery equation.

The values of K_{γ} obtained here for nickel and chromium are very similar to those used earlier, with a value of K_{γ} for Ni of 28 (compared to 20 earlier), and a value of K_{γ} for Cr of 1/40 (compared to 1/35 earlier).

Application to converting processes

The K_{γ} 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 elsewhere¹¹.

Conclusions

The K_{γ} 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 equation produces curves of the correct functional form that are applicable across the whole range of different extents of reduction. The value of K_{γ} to be used can be calculated theoretically, but it is often more effective to fit this value to experimental data. K_{γ} 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). Process design calculations can be carried out with confidence, knowing that there is good theoretical justification for the form of the equation, and that the single parameter K_{γ} is based on experimental work. The simplicity of the equation has made it straightforward to incorporate into spreadsheet models of various processes,

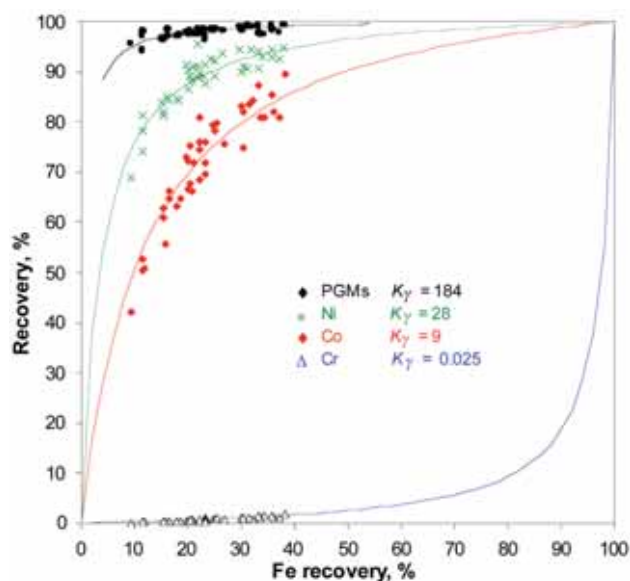


Figure 6—Recovery curves for PGMs ($K_{\gamma} = 184$), Ni ($K_{\gamma} = 28$), Co ($K_{\gamma} = 9$), and Cr ($K_{\gamma} = 0.025$)

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and this is now widely used. The equation clarifies the dependency of the recovery of the valuable metals on the recovery of iron in the furnace, and this allows a furnace operator to control the smelting process more easily and to target the correct degree of reduction.

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