Reductive Smelting for the Recovery of Nickel in a DC Arc Furnace

Rodney T. Jones

Mintek
200 Malibongwe Drive
Randburg, South Africa

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Abstract

It is possible to recover nickel pyrometallurgically from a variety of secondary materials, such as slag, where the nickel is present either as entrained metallic particles or as dissolved oxides. If oxides are present, reductive smelting is used to get the nickel into the metallic form. One useful way of recovering the nickel is to collect it in an iron alloy. A DC arc furnace can be used very effectively for this purpose. Mintek has demonstrated this process on a number of furnaces, the largest of which is a 3 MW DC arc furnace. A water atomization demonstration plant has recently been commissioned, with the purpose of producing alloy particles of a size that is appropriate for further downstream processing.

1   Introduction

Many secondary raw materials contain valuable metals in oxide form. Reductive smelting is required for the recovery of these metals. DC arc furnaces are well suited to this type of process. For example, cobalt was recovered from non-ferrous smelter slags at Chambishi in Zambia [1]. Nickel can also be recovered from slags or other secondary sources in the same way. Furthermore, platinum group metals (PGMs) – occurring together with nickel – can be collected in iron alloys that are produced by means of reductive smelting [2, 3, 4]. There are many similarities between this process and that used commercially in the primary smelting of nickel laterite ores for the production of ferronickel [5, 6].

The essence of the reductive smelting processes described above involves the addition of carbon (typically anthracite or coke) to the molten material in a furnace. Sufficient carbon is required to reduce most of the oxides of the valuable metals, but care must be taken not to add more than is necessary for the reduction of a small part of the iron oxide that is usually present. In many of these processes, iron is essentially a waste material that needs to be separated from the more valuable constituents of the alloy that is produced in the furnace. Sufficient iron must be reduced to allow for

sufficiently reducing conditions in the furnace for valuable metals to be substantially reduced to the metallic state, but excessive iron reduction requires extra electrical energy and places a greater burden on the downstream refining of the alloy. This process of selective reduction needs a clear mathematical description in order to understand it sufficiently for design and control purposes.

2   Recovery Equation

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. In order for this to be done, it is useful to consider the simple exchange reaction shown, for the case of nickel and iron, in Equation (1).

$$NiO + Fe \leftrightarrows Ni + FeO \tag{1}$$

Previous work [4] has provided a description of the reductive smelting process in terms of the $K\gamma$ recovery equation. Equation (2) shows this relationship between the recovery of nickel (R_{Ni}) and the recovery of iron (R_{Fe}). K refers to the equilibrium constant (a function of temperature only) for the reaction above, and γ refers to the ratio of the activity coefficients for the same reaction. Further details may be found in reference [4].

$$R_{Ni} = \frac{K\gamma \cdot R_{Fe}}{1 - (1 - K\gamma)R_{Fe}} \tag{2}$$

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 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. Although the equilibrium constant K is independent of composition, the individual activity coefficients, and the ratio γ, are expected to vary to some degree with the composition of the slag and alloy. This emphasises the importance of practical test work for the selection of an appropriate value of $K\gamma$ to use for characterizing the smelting of a particular feed material. Values of $K\gamma$ may be found by fitting Equation (2) to experimental data.

3 Application to PGM Smelting

Mintek's ConRoast process [3] 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 1 illustrates the application of Equation (2) and 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. Typical slag and alloy compositions obtained from reductive smelting of PGM revert tailings are shown in Tables 1 and 2.
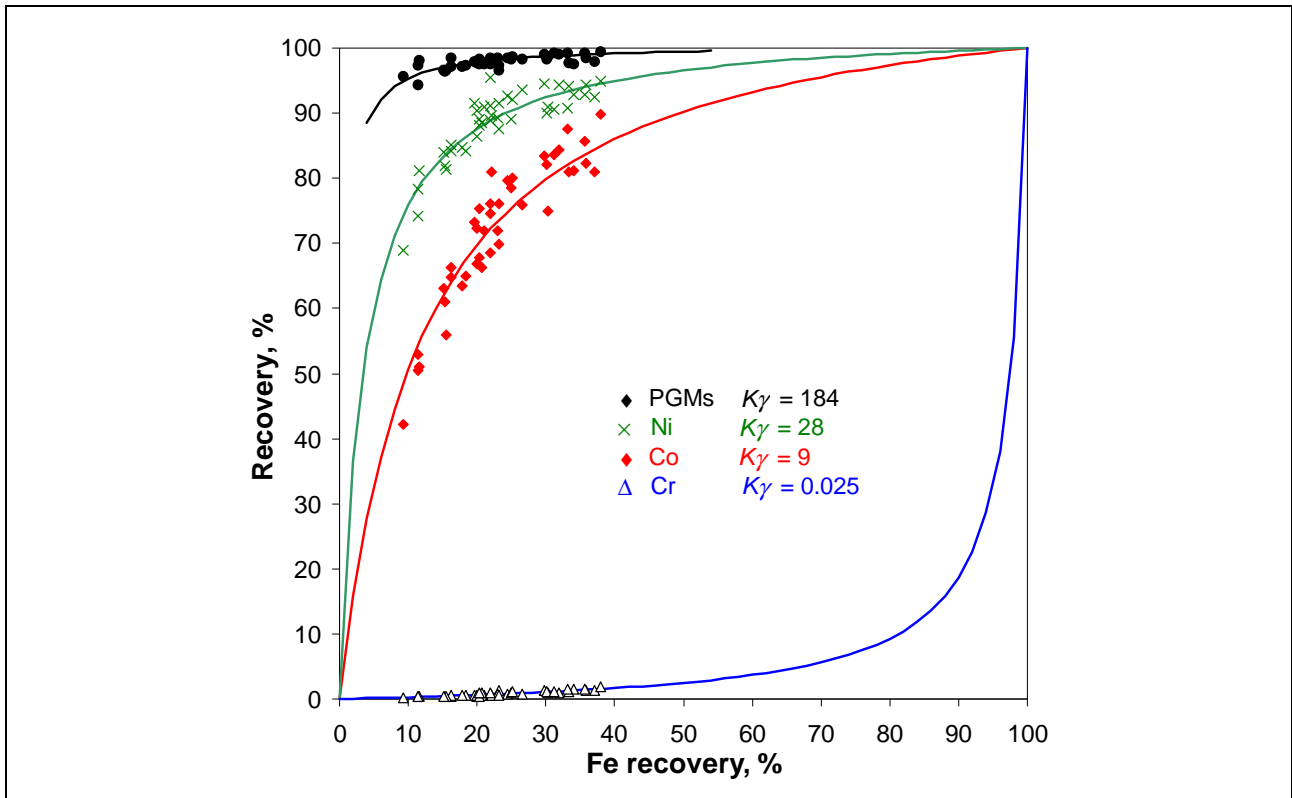

Figure 1: Recovery curves for PGMs ($K\gamma = 184$), Ni ($K\gamma = 28$), Co ($K\gamma = 9$), and Cr ($K\gamma = 0.025$)

Table 1: Typical slag composition from reductive smelting of PGM revert tailings

	Al_2O_3	CaO	Co	Cr_2O_3	Cu	FeO	MgO	Ni	SiO_2
Mass %	4.4	7.3	0.05	2.8	0.09	28.7	14.1	0.1	41.3

Table 2:   Typical alloy composition from reductive smelting of PGM revert tailings

	Fe	Ni	Cu	Co	Cr	S
Mass %	77	11	3.2	1.4	0.17	6.1

4   Application to Ferronickel Smelting

The smelting of nickel laterite ores to produce ferronickel [5, 6] 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 2 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. The alloy produced during this test work typically contained ~80 % Fe and ~20 % Ni, and the slag contained 10-15 % FeO and ~0.1 % Ni.

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, 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.)
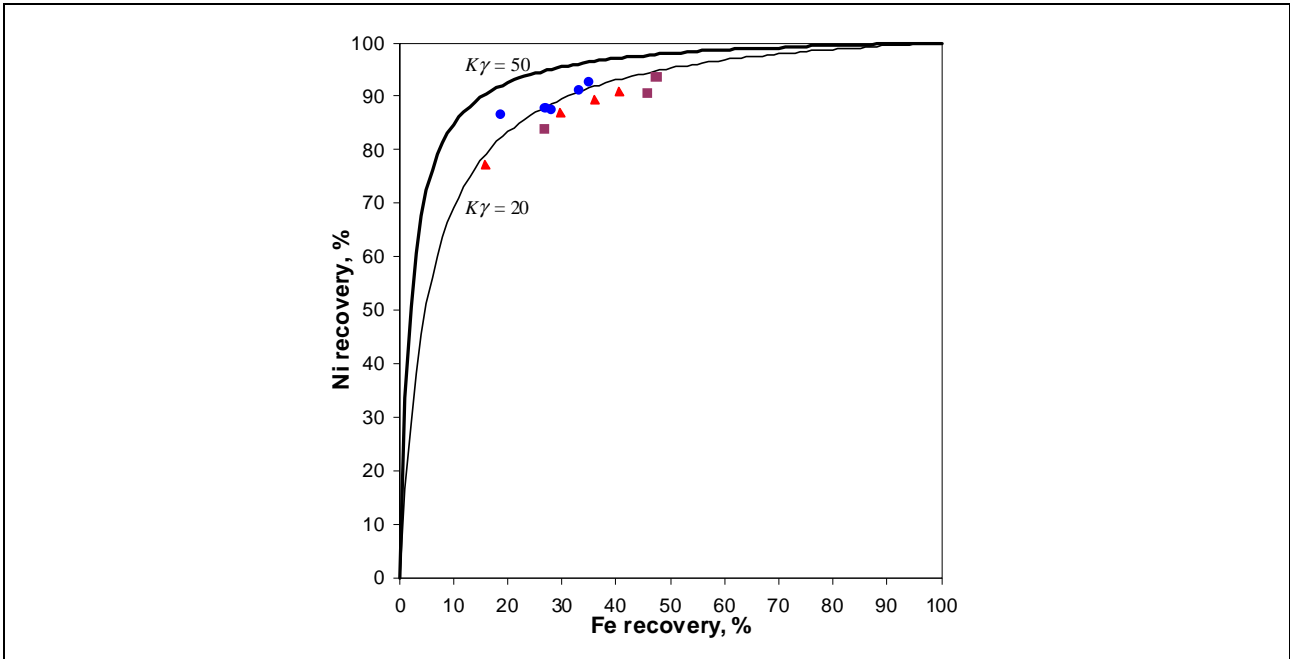
Figure 2:   Recovery curve example for Ni ($K\gamma$ = 20 to 50) in ferronickel smelting

5   Downstream Treatment of Alloys by Water Atomization

A notable feature of many of the iron-nickel alloys discussed here is that they are extremely tough, and 'unbreakable' for practical purposes. However, it is necessary to produce a product comprising small metal particles that are amenable to further downstream processing (either pyrometallurgical or hydrometallurgical). It is clear that the handling of ingots weighing hundreds of kilograms is not practical, and smaller sizes are required. In the case of a leaching process, it may be desirable to have a mean particle size (d_{50}) of less than 100 μm, whereas the injection of alloy particles into a pyrometallurgical reactor may require all particles to be less than 2 mm, for example. Water atomization was selected as an appropriate choice of technology for producing the small particles required. Table 3 shows a typical composition of the alloy used for a large-scale demonstration of atomization at Mintek.

Table 3:   Typical alloy composition for large-scale atomization work at Mintek

	Fe	Ni	Cu	Co	S
Mass %	77	15	4	2	2

Water atomization has a long history. It has been used for the production of copper powder since the 1930s, and for iron/steel powders since the 1950s. Testwork was undertaken by Mintek at Atomising Systems Ltd in Sheffield, UK during February 2008. A sample of 90 kg of alloy was treated in a 25 kg induction furnace, and batches of alloy were atomized at a rate of 5-7 kg/minute, using a 4 mm nozzle. The results of this testwork are summarised in Table 4, which shows that the mean particle size can be halved by doubling the water pressure (over the conditions of interest).

Table 4:   Mean particle sizes achieved at various pressures

Pressure, bar	50	100	195
d_{50}, µm	90	44	22

In the second half of 2012, Mintek commissioned a large water atomization plant to be used in conjunction with its 3 MW DC arc furnace. It is designed to atomize 6-ton batches of alloy. From the metal tap-hole of the DC arc furnace, molten alloy flows into a cylindrical refractory-lined ladle that is equipped with a porous plug through which nitrogen is introduced for stirring of the molten metal, as well as a slide-gate valve for discharging the molten metal. The full ladle is transferred by crane to a three-electrode AC ladle-heating furnace, where the temperature of the molten alloy can be controlled closely (independently of the operation of the smelting furnace). After reaching the desired temperature, the slide-gate valve at the bottom of the ladle is opened to discharge the molten alloy into a tundish. Careful control of the liquid level in the tundish provides for a constant pressure, and therefore a constant flow of molten metal in a thin stream through a nozzle into the water atomization vessel. High-pressure water jets impinge on the stream of molten alloy and smash it into fine particles. Further water freezes the metal particles. The resulting slurry of hot water and metal powder then requires dewatering. This is done initially by passing the slurry through a magnetic separator. The (still wet) solids are then transferred via a dewatering screw into an electrically-heated rotary kiln drier. Finally, the metal particles are sampled and packaged.

6   Conclusion

The recovery of nickel from oxidized feed materials can be accomplished by selective carbothermic reductive smelting in a DC arc furnace. The resulting iron-nickel alloy can be reduced in size by means of water atomization.

Acknowledgement

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