Steel refers to any iron-carbon alloy, although steels usually contain other elements as well. In New Zealand steel is made by BHP NZ at Glenbrook, where about 90% of New Zealand's annual steel requirements are produced.

Iron occurs mainly as oxide ores, though it is also found in smaller quantities as its sulfide and carbonate. These other ores are usually first roasted to convert them into the oxide. On a world scale the most important ore is haematite ( $Fe_2O_3$ ), but in New Zealand the starting materials are magnetite ( $Fe_3O_4$ ) and titanomagnetite ( $Fe_2TiO_4$ ). The oxides are reduced with carbon from coal, through the intermediate production of carbon monoxide.

The carbon initially burns in air to give carbon dioxide and the heat, which is necessary for the process. The carbon dioxide then undergoes an endothermic reaction with more carbon to yield carbon monoxide:

 $\begin{array}{rcl} C &+ & O_2 &\rightarrow & CO_2 \\ C &+ & CO_2 &\rightarrow & 2CO \end{array} \qquad & \Delta H = -393 \text{ kJ mol}^{-1} \\ \Delta H = +171 \text{ kJ mol}^{-1} \end{array}$ 

The oxide ores are then principally reduced by the carbon monoxide produced in this reaction, the reactions involving very small enthalpy changes:

 $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2 \quad \Delta H = -22 \text{ kJ mol}^{-1}$  $Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2 \quad \Delta H = -10 \text{ kJ mol}^{-1}$ 

In conventional ironmaking this reduction occurs in a blast furnace, whereas in New Zealand a rotary kiln is employed for direct reduction, followed by indirect reduction in an electric melter. This technology is used because the titanium dioxide present in the ore produces a slag which blocks conventional blast furnaces as it has a high melting point.

The iron produced in this way always contains high levels of impurities making it very brittle. Steel making is mainly concerned with the removal of these impurities. This is done by oxidising the elements concerned by blowing pure oxygen through a lance inserted into the molten alloy. The KOBM (Klockner Oxygen Blown Maxhutte) used for this in New Zealand is unusual because oxygen is also blown through holes in the base of the converter. The oxides produced are either evolved as gases, or combine with limestone to form an immiscible slag which floats on the surface of the liquid metal and so is easily separated.

# INTRODUCTION

Steel is a term given to alloys containing a high proportion of iron with some carbon. Other alloying elements may also be present in varying proportions. The properties of steel are highly dependent on the proportions of alloying elements, so that their levels are closely controlled during its manufacture. The properties of steel also depend on the heat treatment of the metal.

Steel is by far the most important metal, in tonnage terms, in the modern world, with the annual global production of over 700 million tonnes dwarfing the approximately 17 million tonnes of the next most prolific, aluminium. The low price and high strength of steel means that it is used structurally in many buildings and as sheet steel it is the major component of

motor vehicles and domestic appliances. The major disadvantage of steel is that it will oxidise under moist conditions to form rust. A typical steel would have a density of about 7.7 g cm<sup>-3</sup> and a melting point of about  $1650^{\circ}$ C.

The New Zealand production of about 650 000 tonnes per year at Glenbrook, 40 km southwest of Auckland, is minimal on a world scale, being less than 1% the output of the major producing countries. However, the two main stages in the production of steel in New Zealand are both unusual, making the overall process almost unique. New Zealand is also one of the few countries that has increased steel production over the last decade. Its current share of the domestic steel market is about 90%.

## THE MANUFACTURING PROCESS

Iron ore is converted to steel via two main steps. The first involves the production of molten iron and the second is that of actual steel manufacture. The details of these steps are outlined below.

## Step 1 - The production of molten iron

The Primary Concentrate is mixed with limestone and coal and heated. The iron oxides are reduced in the solid state to metallic iron, which then melts, and the impurities are removed either as slag or gas. The flow diagram for this process is shown in **Figure 1**.



Figure 1 - The production of molten iron

### The multi-hearth furnaces

There are four multi-hearth furnaces, each of which feeds a rotary kiln. The furnaces preheat the materials fed into the rotary kiln and reduce the amount of volatile matter present in the coal from about 44% to about 9%. This is important because the large volumes of gas produced during the emission of the volatile matter would otherwise interfere with the processes in the rotary kiln.

There are 12 hearths in each furnace and the feedstock passes down through these. In the first three hearths, hot gases from the lower stages preheat the material in the absence of air to about  $450^{\circ}$ C. Air is introduced in hearths 4 to 9 to allow combustion of the volatile

material, so as to increase the temperature to about  $650^{\circ}$ C. The supply of air is adjusted to control the percentage of residual volatiles and coal char in the product. In the final hearths (10 - 12) the char and the primary concentrate equilibrate and the final temperature is adjusted to  $620^{\circ}$ C. The total residence time in the multi-hearth furnace is 30 - 40 minutes.

The multi-hearth furnaces also have natural gas burners at various levels. These are used to restart the furnace after shutdown and to maintain the temperature if the supply of materials is interrupted.

The waste gas from the multi-hearth furnace contains water vapour and other volatile compounds from the coal (e.g. carbon dioxide, carbon monoxide and other combustion products) as well as suspended coal and primary concentrate dust particles. These solids are removed and returned to the furnace. This gas along with gas from the melter (mainly carbon monoxide) is mixed with air and burnt. The heat so produced is used to raise steam for the production of electricity. As well as providing a valuable source of energy, this combustion of the waste gases is necessary to meet emission controls.

#### The rotary kilns

There are four rotary kilns. Here about 80% of the iron of the primary concentrate is reduced to metallic iron over a 12 hour period. The kilns are 65 m long and have a diameter of 4.6 m, closely resembling those used for cement production.

The pre-heated coal char and primary concentrate from the furnaces is mixed with limestone and fed into the kiln. In the first third of the kiln, known as the pre-heating zone, the feed from the multi-hearth furnace is further heated to 900 - 1000°C. This increase in temperature is partly a result of the passage of hot gases from further along the kiln and partly a result of the combustion of the remaining volatile matter in the coal.

The last two-thirds of the kiln is known as the reduction zone, and is where the solid iron oxides are reduced to metallic iron. In this region the air reacts with the carbon from the coal to produce carbon dioxide and heat:

 $C + O_2 \rightarrow CO_2$   $\Delta H = -393 \text{ kJ mol}^{-1}$ The carbon dioxide then reacts with more carbon to produce carbon monoxide, the principal reductant, in an exothermic reaction:

$$C + CO_2 \rightarrow 2CO$$
  $\Delta H = +171 \text{ kJ mol}^{-1}$ 

Some of the carbon monoxide burns with the oxygen to produce heat, whilst the remainder reduces the magnetite<sup>1</sup> to iron in a reaction that is almost thermochemically neutral.

 $2CO + O_2 \rightarrow 2CO_2 \qquad \Delta H = -564 \text{ kJ mol}^{-1}$ Fe<sub>3</sub>O<sub>4</sub> + 4CO  $\rightarrow$  3Fe + 4CO<sub>2</sub>  $\Delta H = -10 \text{ kJ mol}^{-1}$ 

$$FeO + CO \rightarrow Fe + CO_2 \qquad \Delta H = -10 \text{ kJ mol}^{-1}$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2 \qquad \Delta H = -22\text{ kJ mol}^{-1}$$

<sup>&</sup>lt;sup>1</sup>Magnetite can be regarded as 1:1 combination of wustite (FeO) and haematite (Fe<sub>2</sub>O<sub>3</sub>). The separate reduction processes from these two components are:

In a similar manner the titanomagnetite is reduced to iron and titanium dioxide. The product from the kiln is known as **R**educed **P**rimary Concentrate and Char (RPCC) and is nearly 70% metallic iron. Unchanged ore, unburnt char, titanium oxide and coal ash accout for the rest of the mixture. This hot (950°C) mixture is then discharged to the melters.

In this latter part of the kiln the temperatures can reach 1100°C. Higher temperatures would lead to an increase in the percentage reduction of the concentrate, but unfortunately they also produce accretions of solids on the walls of the kiln which reduce its efficiency and damage the refractory lining.

Air is injected into the kiln at nine evenly spaced points along its length. In the kiln the limestone is converted to lime (calcium oxide) which then acts as a flux in the melters. The waste gases from the kiln are scrubbed to remove solids and burnt to remove any flammable compounds before being vented to the air. There are currently plans to use the energy from this process for the co-generation of electricity.

### The melters

The hot reduced primary concentrate from the kilns is fed into two melters. These are about 27 m by 12 m and hold a total charge of 1000 tonnes of iron and 900 tonnes of slag. Lime and primary concentrate may also be added to control the composition of liquid iron in the melter. The lime reacts predominantly with sulfur from the coal. Power is supplied by three continuously renewed carbon electrode pairs, which pass a large three-phase a.c. current through the contents of the melter. The potential difference across an electrode pair is 300 V and current is typically 60 kA.

The temperature in the melters rises to 1500°C, and this causes the reduced primary concentrate to melt and form two layers. The lower layer is of molten iron with some elements, especially carbon, dissoved in it. The upper layer is liquid oxide slag and this supports the solid feed. During the melting process reduction of the remaining iron containing compounds occurs. The electrodes are immersed in the molten slag and, becasue its electrical resistance is much greater than that of iron, most of the heat is generated in this layer.

One problem affecting the melters is that the refractory lining is subject to attack by the molten slag. In order to combat this, the solid feed in introduced around the perimeter of the melter to provide a protective barrier. The gas produced in the melter is mainly carbon monoxide and this presents both toxic and explosion hazards. It is recovered and burnt for co-generation of electricity.

Molten iron and slag are both tapped periodically by drilling a hole through the refractory sidewalls at special tapping points, higher up for the slag and lower down on the opposite side for the molten iron. The slag from the melter is approximately 40% TiO<sub>2</sub>, 20% Al<sub>2</sub>O<sub>3</sub>, 15% MgO, 10% CaO and 10% SiO<sub>2</sub> with smaller amounts of sulfides and oxides of iron, manganese and vanadium.

After cooling and the recovery of the metal trapped in it, the slag is sold. It is mainly used as a substitute for quarried rock in applications such as road construction.



Figure 2 - The steel making process

## Step 2 - Steel making

The steel making process is shown in Figure 2.

### Vanadium recovery

Before conversion into steel, vanadium is recovered from the molten iron. This is done firstly because of the value of the vanadium rich slag produced (15% vanadium as  $V_2O_5$ ) and secondly because a high vanadium content can make the steel too hard.

In the vanadium recovery unit a ladle containing 75 tonnes of molten iron has oxygen blown over the surface, where it oxidises silicon, titanium, manganese and vanadium to form a slag that floats on the surface. At the same time argon is blown through the molten metal to stir it. When the composition of the molten metal has reached the required vanadium specification, the slag is scraped off, cooled and crushed.

Additional advantages of this pre-treatment are that it causes the molten metal to reheat, so permitting temperature control, and, if required, the procedure can be modified by the addition of lime to reduce sulfur levels.

## The Klockner Oxygen Blown Maxhutte process

The KOBM steel making process, like most modern processes involves oxidising dissolved impurities by blowing oxygen through the molten metal. The KOBM is unusual in that it blows oxygen through the bottom of the furnace as well as through a lance inserted from the top. This type of furnace was selected for Glenbrook becasue of its capacity to cope with high levels of titanium and vanadium coupled with its very fast turn round time. The disadvantage of this type of furnace is that it is technically rather more complex than those that are blown only by a lance.

The KOBM is initially charged with about 6 tonnes of scrap steel. 70 tonnes of molten metal from the vanadium recovery unit is then added. Oxygen is then blown through six holes in the base of the furnace, at a total rate of about 1500 litres per second. Oxygen is also blown through a lance inserted from the top of the furnace at a rate of over 2500 litres per second.

The oxygen oxidises the elements other than iron (including any free carbon) to their oxides. In this way contaminants are removed as the oxides form a slag which floats on the surface of the molten metal. Powdered lime is blown in to help with slag formation and this particularly reduces the levels of sulfur and phosphorous by combining with their acidic oxides. Due to its low melting point, iron(II) sulfide (FeS) is particularly harmful to the high temperature properties of steel. So sulfur level must be reduced before further processing. Typical levels of the major elements in the metal fed into the furnace and in a typical steel are shown in **Table 1**.

	С	S	Р	Ti	Si	V
Hot metal	3%	0.04%	0.07%	0.8%	0.08%	0.3%
Steel	0.03%	0.02%	0.01%	nil	nil	0.005%

Table 1 -	Compositions	of steel and	the metal from	which it is made
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The molten iron is analysed just before being added to the furnace and the temperature taken. This determines the length of the oxygen blow and it also to a certain extent affects the amount and composition of the scrap added. The length of the oxygen blow required is also judged by moitoring the CO:CO<sub>2</sub> ration in the gases from the furnace. Blow times vary, but 15 minutes would be typical. During the oxygen blow the temperature would typically rise from 1500°C to 1700°C owing to the exothermic reactions that are occuring.

The slag is firstly tipped off and, after cooling, it is broken up so that the iron trapped in it can be recovered magnetically. The slag, which contains sulfur and phosphorous and has a high lime content, is then sold for agricultural use. Aluminium, which removes excess dissolved oxygen, and alloying materials, such as ferro-silicon and ferro-manganese (which increase the hardness of the steel) are added at this point so that they are well mixed as the molten metal is tipped into a ladle. The whole cycle in the KOBM takes about 30 minutes.

The Glenbrook site also has an electric arc furnace for steel making, the feed for this being mainly scrap steel. The cycle time for the final charge of 75 tonne is about  $3\frac{1}{2}$  hours, so that is only responsible for a small fraction of the total steel production. It is, however, a very flexible process and it may be economically used to produce small batches of specialised steel.

## Ladle treatment

The final stage of steel making is the ladle treatment. This is when fine adjustments are made to bring the composition of the molten steel, from either furnace, into line with the required composition. The bulk of the alloying elements are added in the furnace and, after blowing argon hrough the molten metal to ensure homogeneity, the temperature is measured and a sample removed for analysis after stirring. The analysis by optical emission spectrometry, which measures the levels of 15 elements, takes about five minutes. Alloying materials are added to adjust the composition. If the metal requires cooling, scrap steel is added. If the temperature is too low, aluminium is added and oxygen blown through. When all adjustments are complete argon is blown through once again to ensure mixing and the ladle taken to the continuous casting machine. Here it is cast into slabs of 210 mm thickness and a width of between 800 and 1550 mm. This slab is cut into lengths of from 4.5 m to 10 m and sent for further processing. Most of the production is converted to steel coil.

## **ANCILLARY PROCESSES**

The major ancillary processes carried out by the plant involve the supply of raw materials, the processing of waste and the production of electricity. Even though waste heat is used to co-generate electricity on site, this only amounts to about  $12\frac{1}{2}\%$  of total consumption, so large amounts of electricity are purchased. Natural gas is also used as a minor energy source and this is brought to the site from Taranaki through a pipeline.

## Iron primary concentrate mining

This is obtained from the ironsand mine at Waikato North Head and is a mixture of magnetite (Fe<sub>3</sub>O<sub>4</sub>) and titanomagnetite (Fe<sub>2</sub>TiO<sub>4</sub>), and is thought to originate from the volcanic eruptions of Mt. Taranaki. It is mined by standard open cast methods and suspended as an aqueous slurry. The ironsand is a low grade ore, with sand and clay being the major impurities. The concentrated material typically contains 58% iron (i.e. 80% Fe<sub>3</sub>O<sub>4</sub>), 8% TiO, 4% Al<sub>2</sub>O<sub>3</sub>, 3½% SiO<sub>2</sub> and 3% MgO by mass with smaller quantites of calcium, phophorous and sulfur. Initial separation is effected by magnetic separators which rely on the magnetic properties of magnetite and tintanomagnetite. Further concentration is then achieved by gravity separators because these minerals are denser than most impurities. The slurry is then pumped though a 21 km long, 200 mm diameter pipeline to Glenbrook at a rate of 300 tonnes per hour. Here it is dewatered to a moisture level of ca. 5% and discharged onto a stockpile. Annual production of this material, known as Primary Concentrate (PC), is about 1.2 million tonnes.

### **Coal preparation**

This is sub-bituminous B and C grade mined by both open cast and underground methods at Huntly. The annual consumption of 750 000 tonnes per year is delivered by rail to Glenbrook. Here it is stored on a stockpile and then blended with primary concentrate as the feedstock for the multihearth furnaces. The aim of the blending is to achieve a consistent carbon-iron ratio.

### Scrap steel recycling

Much of the scrap steel used is waste from the production process. Steel is also purchased from scrap metal dealers, though it must be free from copper which is difficult to remove from molten steel and adversely affects its properties. The scrap steel is sorted into different grades according to alloy content.

### Limestone mining

This is mined near Otorohanga. Limestone chip is blended with the coal and primary concentrate to help form a slag in the reduction of the iron oxide. Some is also supplied in the form of lime (calcium oxide) for use in steel making.

### **Oxygen production**

This is manufactured by the fractional distillation of liquid air, which also produces nitrogen and argon. About 4000  $\text{m}^3$  of oxygen is consumed for each 75 tonne load of steel, giving an annual consumption of about 75 000 tonnes. Some of the nitrogen and argon is used in steelmaking. The excess liquid nitrogen is sold for freeze drying foods and the excess argon is mainly sold for use as a gas shield for welding processes.

## Electricity

The total annual consumption of electricity is 1000 GWh, the typical power demand being 130 MW. This is purchased from Electrocorp and brought to the site through overhead power lines operating at 110 kV.

The waste gases from various processes, particularly the multi-hearth furnaces and the melter are burnt to raise steam in four boilers. The steam is used to power two turbines each rated at 18 MW, which produce  $12\frac{1}{2}$ % of the electricity needed by the plant.

In the near future the on site generation of electrical power is to be considerably expanded and greater use made of waste gases from the rotary kilns. This will enable the plant to produce over half the total electrical power consumed.

# THE ROLE OF THE LABORATORY

In general the laboratory is responsible for quality control of the various stages of production and of the end product. The laboratory uses optical emission spectroscopy<sup>2</sup> to determine the sample composition of the molten metal in the melter, vanadium recovery unit, K.O.B.M. unit and casting machine and during the ladle treatment stage. The levels of carbon, silicon, manganese, tin, vanadium, sulfur, phosphorus, aluminium and nitrogen are closely monitored. The test only takes four minutes, enabling operators to adjust process parameters on the basis of test reports before problems become serious.

The nitrogen content in steel can also be found by heating the steel in a helium flushed electric furnace. As the temperature increases any nitrogen in the sample comes off and mixes with the helium carrier gas. The gas mixture is analysed by a thermal conductivity cell at the gas outlet.

Samples of ironsand and slag are analysed with X-ray fluorescence spectroscopy. The slag samples are fused with boron before testing.

The laboratory is also involved in daily testing of effluent water to ensure that all water released into the environment is safe.

# ENVIRONMENTAL IMPLICATIONS

Due to the nature of the steel making process, large amounts of solid, liquid and gaseous wastes are generated in the steel plant. Careful planning is necessary to ensure that these do not have a negative impact on the environment.

<sup>&</sup>lt;sup>2</sup>Optical emission spectrometry is also called atomic emission spectroscopy and is described in the sewage treatment article.

The steel mill requires 1.2 to 1.4 million tonnes of ironsand each year, which means that up to 10 million tonnes of pure sand must be mined. The non-magnetic sand is returned to the area from which it was mined, and marram grass and radiata pines planted to stabilise the deposits.

Wet scrubbers and baghouses are the principal means of controlling air pollution. The wet scrubbers (see oil refining article) wash the dust out of the hot process waste gases which result from iron and steel making while the cloth bags inside a baghouse filter dust out of the gas. The dust collection system is shared by the steel production and steel processing sections, and collects a total of between five and ten tonnes of dust every hour.

Extensive water recycling is used in the plant to minimise the quantity of waste water produced, and all waste water and stormwater is treated in settling ponds on site before being discharged into the Waiuku Estuary.

Article written by John Green (Kristin School) and Jeremy Batchelor (BHP NZ Steel) with additions by David Yuen following a visit to BHP NZ Steel.