

National Certificate of Educational Achievement TAUMATA MĀTAURANGA Ā-MOTU KUA TAEA

Exemplar for Internal Achievement Standard

Chemistry Level 2

This exemplar supports assessment against:

Achievement Standard 91163

Demonstrate understanding of the chemistry used in the development of a current technology

An annotated exemplar is an extract of student evidence, with a commentary, to explain key aspects of the standard. It assists teachers to make assessment judgements at the grade boundaries.

New Zealand Qualifications Authority

To support internal assessment

	Grade Boundary: Low Excellence
1.	For Excellence, the student needs to demonstrate comprehensive understanding of the chemistry used in the development of a current technology.
	This involves an evaluation of how the chemistry influenced the development of the technology.
	This student has explained the chemistry and the reactions occurring that produce iron and steel, including an explanation and evaluation of the involvement of energy in exothermic and endothermic reactions (1). They have explained how the problem of the high titanium and vanadium content is overcome and explained why limestone is used in the reaction (2). There was low-level evaluation of the chemistry of using the reaction between oxygen and limestone and its influence on the development of steel (3).
	For a more secure Excellence, the student could write equations for the reactions that produce titanium oxide and calcium oxide (4), and for the reactions between oxygen and limestone (5).

Steel from Iron Sands in New Zealand

Iron in New Zealand is used to make some of the above products. Steel is used in these products as it is strong and will last a long time.

Steel in New Zealand is obtained from the iron sand which is found on the west coast of the north Island. These were formed from volcanic activity and were first noticed in 1841. The hope then was that New Zealand may become the Britain of the south in terms of the production of iron and steel. Samples of these iron sands were sent overseas and attempts were also made to obtain iron from these samples. In 1853 Stensons from Messers Stenson and Co iron masters in Northampton noted difficulty in working with these iron sands.

The way iron was obtained at the time was to heat the iron ore with coal in a blast furnace. The oxygen in the iron oxides was transferred to carbon and carbon monoxide contained in the coal. In this way the iron oxide was reduced by a decrease oxidation number (or a removal of oxygen) and iron was formed. Any impurities in the iron ore would float above the molten iron and could be removed. This layer is referred to as slag.

The problem with the New Zealand iron sands was that the sands themselves were very fine and they blocked the flow of hot air into the furnace. In addition the New Zealand iron sands were rich in titanium compounds. When heated in a blast furnace titanium oxide was formed. This has a high melting point and a thick pasty layer formed beneath the slag. This layer blocked the tap holes which were used to remove the molten iron and waste slag. Other iron sands worldwide do not have this high titanium content. An early blast furnace was built near Nelson in the 1870's but again problems were found with the slag which was



very viscous.

In the 1900's professor John Cull carried out his own experiments to see if he could overcome these difficulties. He used magnetic techniques to concentrate the iron compounds in the iron sands. He then reduced the iron oxide directly at a temperature below the melting point of the iron. He then transferred this directly to an electric arc furnace where he carried out further reduction in the absence of air. He added lime as a flux and successfully separated the slag from the iron. The early experiments were carried out in the backyard of his parents' home in Christchurch. He discovered that iron could be obtained by using electric means but the earlier reduction at the lower temperatures required considerably less energy. He was able to do this because at lower temperatures titanium compounds were not formed. In addition limiting the amount of oxygen and controlling the amount of

PROF. CULL.

carbon this also prevented the formation of titanium compounds. This was to be the basis of how iron and steel would be made at Glenbrook years later.

In 1969 the steel mill at Glenbrook was opened. This mill now produces so much iron and steel that New Zealand now exports more steel than it imports. An important part of this process is what occurs in the rotary kiln.

Preheated coal, with limestone and the primary concentrate (ore after magnetic and gravity separation techniques along with pre-treatment in hearth furnaces) is fed into the rotary kiln. These kilns are 65 metres long and 4.6 metres in diameter. In the final part of the kiln (on the first part preheating occurs) the following chemical reactions occur:

1.
$$C + O_2 \rightarrow CO_2 \quad \Delta H = -393 \text{ kJ mol}^{-1}$$

The coal is the source of carbon. This reaction is exothermic and produces heat which is used to make further reactions occur. The carbon dioxide produced reacts with more carbon to produce carbon monoxide.

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

This reaction is endothermic and so the energy produced in reaction one helps this reaction occur.

3. 2CO + O₂ \rightarrow 2CO₂ ΔH = -564 kJ mol⁻¹

Again an exothermic reaction which produces more heat which can be used.

4. Fe₃O₄+ 4CO \rightarrow 3Fe +CO₂ ΔH = -10 kJ mol⁻¹

During these reactions titanium dioxide is also formed. The mixture is now 70% iron.

At this point the mix is poured into melters and more limestone is added. The limestone reacts at these high temperatures producing calcium oxide. This calcium oxide acts as a flux which removes any acidic sulphur, phosphorous oxides, in addition to any other impurities such as silicon and titanium oxides. The energy is provided by carbon electrodes and the amount of air is monitored as earlier suggested by Professor Cull years ago.

The mix in now poured into various further ladles. In the first vanadium is removed by blowing oxygen into the mix and forming oxides which is removed as slag. Then in a further ladle the remaining molten steel has further oxygen blown into it using the Klockner Oxygen Blown Maxhutte (KOBM) process. In this process oxygen is blown in at the top and the bottom of the ladle. The chemistry behind this process is that oxides are produced. These oxides are either liberated as a gas or react with the limestone to form a slag which floats on the surface of the liquid metal and is easily removed. The reaction of oxygen and limestone to remove impurities improved the quality of steel and influenced the development of steel as a technology. This process is unique to Glenbrook. In a normal blast furnace oxygen is normally blown in at just the top. 70 tonnes of steel has 1500 litres of oxygen blown in at the bottom and 2500 litres per second at the top of the ladle. This is more technically complex than other furnaces. Oxygen is required at the top and bottom because of the high content of titanium and vanadium in the iron which was part of the original ore. From here argon is blown into the steel to mix it evenly. Argon is an unreactive gas as it is in group 18 of the periodic Table. Elements in this group have a full outer shell of electrons and are unreactive. In the final step any alloying elements are added in the furnace and again mixing is achieved by blowing in argon. The metal is then cut into slabs and allowed to cool. Further treatments are then carried out depending on what the steel is going to be used for.

5

3

1

1

2

	Grade Boundary: High Merit
2.	For Merit, the student needs to demonstrate in-depth understanding of the chemistry used in the development of a current technology.
	This involves making and explaining links between the chemistry and the development of the technology using chemistry vocabulary, symbols and conventions.
	This student has gathered, processed and interpreted information detailing how steel is made at Glenbrook. Information regarding the history is presented which includes the early problems associated with the high content of titanium in the iron sands. Links between the chemistry and development of steel are made and explained by the use of calcium oxide (1), the use of oxygen being blown in both at the top and bottom of the ladle (2), and the use of argon gas (3) and the use of exothermic reactions (4).
	To reach Excellence, the student could provide an evaluation of how chemistry influenced the development of steel.

Steel making in New Zealand

In 1841 it was noted by The Plymouth Company in Taranaki that "from certain indications, iron will be found in large quantities in this neighbourhood". Settlers saw this as a potential source of iron. However the extraction of iron from these "iron sands" proved frustrating and a lot of time was put into efforts to access this source of iron. In fact it took over a hundred years to develop the technology and expertise to make iron and hence steel from this abundant source of iron located mainly along the West Coast of the North Island.

In the 19th century iron was extracted around the world from iron ore by using a blast furnace. The iron in iron ore is normally in the form of iron oxides. In a blast furnace these iron ores are heated with coke (different forms of carbon, sometimes charcoal). The oxygen in the iron oxides is transferred from the iron oxides to the carbon. In this process the iron oxides are reduced (removal of oxygen) to iron and the carbon is oxidised (gain of oxygen). The coke serves two purposes. One is to provide the reductant and the other is to provide the source of energy required. The iron formed is molten due to the heat and forms at the bottom of the furnace. Any other impurities (slag or waste) form on the top and these can be removed. The problem with the iron sands found in New Zealand is that as well as containing iron they also contain titanium, vanadium and other impurities. The titanium dioxide present has a high melting point and this blocks the holes in the blast furnace. In addition iron produced which contains large amounts of impurities can brittle.

In 1969 a steel mill was opened at Glenbrook (60 Km south of Auckland). This site was chosen as it was close to Waikato North Head where the iron sands are mined and also close to Huntly (a source of coal). The iron sands are concentrated by magnetic and gravity methods, and are then mixed with water and pumped 18km to the Glenbrook site.

The hearth Furnace

This primary concentrate (PC) is mixed with limestone and coal in a hearth furnace. In this furnace the PC is preheated and volatile matter in the coal is removed. If these gases were not removed they would interfere with some of the processes further down the line. These waste gases are burnt to make steam to generate electricity for energy later on. At this stage the mix is heated to 650 degrees.

The rotary Kilns

It is in these kilns the iron oxides in the PC are reduced to iron. Preheated coal, with limestone and the PC is fed into the rotary kiln. These kilns are 65 metres long and 4.6 metres in diameter.

In the final part of the kiln (on the first part preheating occurs) the following chemical reactions occur:

1. $C + O_2 \rightarrow CO_2 + heat$

The heat produced by this strongly exothermic reaction is used to fuel the process.

2. $CO_2 + C \rightarrow CO$

This reaction requires heat.

- 3. $2CO + O_2 \rightarrow 2CO_2$
- 4. $Fe_3O_4 + 4CO \rightarrow 3Fe + CO_2$

Carbon monoxide is the main reducing agent. During these reactions titanium dioxide is also formed. The mixture is now 70% iron.

Melters

This reduced primary concentrate (RPP) is then poured into melters, along with limestone. The purpose of the limestone is to provide calcium oxide. Calcium oxide is produced by decomposition of calcium carbonate (CaCO₃ \rightarrow CaO + CO₂). The calcium oxide reacts with any acidic sulphur, phosphorous oxides or any acidic oxide like silicon dioxide, which can harm steel at high temperatures. The reaction with silicon dioxide is: CaO + SiO₂ \rightarrow CaSiO₃. This chemical process has been introduced into the steel making process to further develop it.

The temperature is raised to 1500 degrees. The energy is provided by large carbon electrodes. Two layers form. The lower layer is molten iron with some dissolved elements notably carbon. The upper layer known as slag (waste) contains TiO_2 , Al_2O_3 , MgO, CaO, SiO_2 and some vanadium oxides. The molten iron and slag is tapped off through holes.

Steel making

Before steel making any vanadium is recovered. This is done as the vanadium rich slag formed can be sold and steel with too much vanadium content can be too hard. In this process oxygen is blown into the mix. This oxidises any silica, titanium, manganese, and vanadium which then forms a slag that floats and can be removed.

The remaining molten steel has further oxygen blown into it using the Klockner Oxygen Blown Maxhutte (KOBM) process. In this process oxygen is blown in at the top and the bottom of the ladle. This process is unique to Glenbrook. In a normal blast furnace oxygen is normally blown in at just the top. 70 tonnes of steel has 1500 litres of oxygen blown in at the bottom and 2500 litres per second at the top of the ladle. This is more technically complex than other furnaces. Oxygen is required at the top and bottom because of the high content of titanium and vanadium in the iron which was part of the original ore. In vanadium recovery, oxygen is blown over the surface of the molten metal where it oxidises silicon, titanium, manganese and vanadium to form a slag that floats on the surface. Argon gas is used to stir the molten metal. Argon is used because it is non-reactive. Other iron sands around the world do not have this high content of these two metals.

The slag is removed. The metal is then cut into slabs and allowed to cool.

The technologies involved in these entire processed have all been refined and developed further since 1969. Since 1991 New Zealand has exported more iron and steel than it imports. In 2004 60% of Glenbrook steel was exported.

2

3

	Grade Boundary: Low Merit
3.	For Merit, the student needs to demonstrate in-depth understanding of the chemistry used in the development of a current technology.
	This involves making and explaining links between the chemistry and the development of the technology using chemistry vocabulary, symbols and conventions.
	This student has gathered, processed and interpreted information detailing how steel is made at Glenbrook. Information regarding the history is presented which includes the early problems associated with the high content of titanium in the iron sands (1). Links between the chemistry and development of steel is made. There is explanation of the reduction process that is used in the rotary kiln and the use of lime in the process (2).
	For a more secure Merit, the student could provide more explanation of the chemistry that is involved in the development of steel production, such as explaining the use of the exothermic reaction that produces CO_2 (3).

The steelmaking process in New Zealand

James Cook first noted the dark sands on the coast of the west coast of the North Island. The dark sands he noted were dark because of the presence of iron and formed due to volcanic activity.

Numerous attempts were made in the late 19th century to the 1950's to obtain the iron from these iron sands. There was limited success and it was uneconomic. In 1959 the New Zealand government established New Zealand steel Limited to investigate further an economic way to obtain this iron and hence steel. This resulted in a steel mill at Glenbrook near Auckland. This mill produces 90% of New Zealand's steel needs. The rest is exported.

The mill at Glenbrook contains multi hearth furnaces, rotary kilns, and melters, in addition to further ladles. The set up at Glenbrook is unusual as in most places in the world a blast furnace is used to obtain iron from iron ore. The technology at Glenbrook was developed because of the makeup of the New Zealand iron sands. These iron sands contain a larger than normal amount of titanium, vanadium, and silica type compounds. These compounds cause a problem in blast furnaces as they make the slag (waste products of the steel making process) difficult to separate from any molten iron.

The iron sand concentrate from the mine is fed into the multi hearth furnaces, with some coal and lime. When the concentrate leaves the multi hearth furnaces it is now dry and the coal has been converted to char. Char is coal that has had its more volatile content driven off. The heat produced from this process is used to help make electricity. This char is therefore mainly just carbon which is used in the rotary kilns to reduce the iron sand concentrate.

The reactions that occur in the kiln are

 $C + O_2 \rightarrow CO_2$ $CO_2 + C \rightarrow 2CO$ $Fe_3O_4 + C \rightarrow 3FeO + CO_2$ $FeO + CO \rightarrow Fe + CO_2$ $Fe_3O_4 + 4C \rightarrow 3Fe + 4CO$

It is the carbon and the carbon monoxide that is formed that reduces the different types of iron oxide. The carbon monoxide is formed by the reaction of the carbon in the char with the oxygen. The amounts of carbon (char) and oxygen that is fed into the rotary kiln is controlled so that the required amounts of carbon monoxide are present to reduce the iron oxides. This is reduction because the iron oxides have oxygen removed by the carbon and carbon monoxide which are oxidised (gain of oxygen).

The lime is added as it breaks up into calcium oxide with heat. This calcium oxide is added to help form the slag and also react with any acidic oxides that are formed from sulfur and phosphorous that were present in the coal.

The product of this is known as reduced primary concentrate and it is poured into melters and ladles which is further refined to steel. The steel is cut into slabs and coils.

These slabs and coils are then processed further and it at this stage that scale forms on the surface of the steel. Scale is oxidised iron from the steel. It is formed from this iron reacting with oxygen from the air.

This scale needs to be removed. The process of removing the scale is called "pickling". Hydrochloric acid is used to remove this scale. The process is carried in three deep bath tanks. The following three reactions occur depending on the type of iron oxide formed.

 $\begin{array}{l} Fe_2O_3 + Fe + 6HCl \rightarrow 3FeCl_2 + 3H_2O \\ Fe_3O_4 + Fe + 8HCl \rightarrow 4FeCl_2 + 4H_2O \\ FeO + 2HCl \rightarrow FeCl_2 + H_2O \end{array}$

In the first two reactions the iron is from the steel under the scale. The amount of iron that reacts needs to be controlled or too much of the iron is lost in the process. This is done by using inhibitors. If the acid cannot react with this iron then the reaction is much slower. These reactions occur faster at higher temperatures but there is a "trade off" here as if the temperature is too high the acid breaks down into hydrogen chloride vapour. It has been found that the best way to control this process is to vary the time that the steel is picked for.

	Grade Boundary: High Achieved
4.	For Achieved, the student needs to demonstrate understanding of the chemistry used in the development of a current technology.
	This involves processing and interpreting information to provide an account of the chemistry used in the development of a current technology using chemistry vocabulary, symbols and conventions. This may also include an account of the historical development of the technology.
	This student has outlined some history of the process and used chemistry vocabulary, symbols and conventions (1). They have provided an account of the chemistry used in the development of steel by outlining the problem of high concentrations of titanium oxides and the chemistry used to overcome this as the technology developed (2). The links between chemistry and the development of steel have been made.
	To reach Merit, the student could explain the link between the reduction of iron oxides and oxidation process and the development of the technology (3).

Iron sands were first noticed on the West Coast of New Zealand in 1841. It was known at this time that iron could be obtained from such iron sands. Up to this time iron was obtained from such iron ores in a blast furnace. In a blast furnace the iron sand (iron ore) is heated with charcoal or coke. The carbon in the coke or charcoal reacts with the oxygen in the iron sands leaving just iron.

Carbon in coke + iron ore (iron oxides) + heat \rightarrow carbon oxides + iron. This is done in a series of chemical reactions, see below.

 $\textbf{C}_{(s)} \textbf{+} \textbf{O}_{2(g)} \ \rightarrow \ \textbf{CO}_{2(g)}$

 $\textbf{CO}_{\!\!\!2\,(g)} + \textbf{C}_{\,(s)} \ \rightarrow \ \textbf{2CO}_{\,(g)}$

 $\textbf{3CO}_{(g)} + \textbf{Fe}_2\textbf{O}_{3(s)} \ \rightarrow \ \textbf{2Fe}_{(l)} + \textbf{3CO}_{2(g)}$

As well as iron oxides in the ore there can be other elements and compounds called impurities. When the irons and are heated in a blast furnace these other impurities melt and float on top of the iron. This unwanted stuff is known as slag.

This traditional method of using a blast furnace though did not work with these New Zealand iron sands, as it did with other iron sands around the world. This was because the New Zealand iron sands contained high amounts of titanium. This titanium was in the form of titanium oxide. In a blast-furnace, the titanium (IV) oxide (TiO2) in titanomagnetite ore is reduced to titanium nitride (TiN), titanium carbide (TiC) and the titanium (II) oxide (TiO). These products have high melting points and form a paste that blocked any holes that were used to remove either the molten iron or the slag and everything in the blast furnace became clogged up. The last attempt at using a blast furnace was between 1914 and 1919 by J.A. Heskith for the New Zealand iron ore smelting and manufacturing company. He noted that "titaniferous accretions built up in the hearth and gradually prevented tapping." Again problems occurred with titanium oxides clogging up the holes from which slag and purified iron was removed. The trick then was to come up with some method that made the iron and hence steel but prevented the titanium compounds with the high melting points from forming.

The method developed involved using a rotary kiln followed by an electric melter. Both of these processes involved the reduction of iron oxides, either directly or indirectly.

A primary concentrate is prepared. This is done using magnetic means and preheating with limestone and coal. This primary concentrate is fed into the rotary kiln. At Glenbrook there are 4 of these, and they are 65 metres long. This process is carried out at a temperature lower than what the reactions that form the titanium compounds occur at. This way this slag that clogs the holes up that are used to "tap off" the iron and slag do not become blocked. Once the more purified concentrate that has been tapped off is poured into the electric melters the temperature can be increased. Further reduction occurs in the melters (electric arc furnaces). From here any other elements that are still present as impurities are removed. This is done by controlled blowing of oxygen over the concentrate for oxidation. Once oxides are formed they can be removed. Now that almost pure iron has been obtained it can be made into various steel products. These products include hot and cold rolled steel, colour steel, zinc lume, pipe and hollow sections of steel.

1

1

2

3

	Grade Boundary: Low Achieved
5.	For Achieved, the student needs to demonstrate understanding of the chemistry used in the development of a current technology.
	This involves processing and interpreting information to provide an account of the chemistry used in the development of a current technology using chemistry vocabulary, symbols and conventions. This may also include an account of the historical development of the technology.
	This student has provided an account of the chemistry used in the development of steel and included an account of the history of the process and used some chemistry vocabulary, symbols and conventions (1). They have outlined the problems, namely, the high concentrations of titanium oxides and impurities in iron and described how chemistry was used to solve the problems and develop the production of steel (2).
	For a more secure Achieved, the student could make use of a wider range of chemistry vocabulary, and describe the process in the melter as oxidation, and the process in the rotary kiln as reduction.

Steel is used worldwide and in New Zealand for a number of uses. Steel is used mainly in the construction industry. This is because of its strength and durability. Throughout the world over 700 million tonnes of steel is produced each year. In New Zealand about 675000 tonnes of steel is produced each year. Most of this is used in New Zealand with about 90% of the steel used in New Zealand being produced in New Zealand while the rest is exported.

In New Zealand steel is produced at the Glenbrook mill 40km from Auckland. This mill was established in the 1960's and has been continually updated ever since.

New Zealand has a rich source of iron compounds from which steel is made. These are found in the black iron sands on the west coast of the North Island. These were first noticed by James Cook himself.

Traditionally iron is obtained from iron sands by a blast furnace. Over 95% of the worlds iron is obtained this way. In a blast furnace the iron sands are reacted with carbon. This carbon can be in the form of coke of charcoal. When this reaction occurs at heat the iron oxide is reduced to iron and carbon is oxidised to carbon monoxide or carbon dioxide. The iron oxides are reduced as the iron in the iron oxides goes from a lower oxidation number to a higher one. The opposite happens with the carbon.

The reactions are

 $C+O_2 \rightarrow CO_2$

 $C + CO_2 \rightarrow 2CO$

 $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

The problem with the New Zealand iron sand is the presence of titanium oxides. These titanium oxides get involved and inhibit the process of iron production. They do this as they block up the holes in the blast furnace by which the iron is removed. The iron is in a molten form and is removed through holes in the furnace. However it is these holes that the titanium oxides block.

Up till the 1920's the blast furnace was tried in New Zealand. While some iron was obtained it was uneconomical due to the problems described above with the titanium oxides.

A new method was needed that prevented this and also removed any other impurities present in the iron sands or that are formed from the iron making process. This method involved the use of a rotary kiln. A rotary kiln is almost 100 metres long and has holes in the side of it at uniformed points. Purified treated iron is poured into these kilns. In these kilns the supply of air is controlled. This is to control what is formed The carbon that reacts also produces heat which is used to fuel the process. The temperature is also controlled. By controlling the temperature the iron production is maximised and the holes are not blocked by titanium compounds.

The iron formed then goes into a melter for further purification. From here the even more purifiesd iron goes into a ladle where oxygen is blown in using the Klockner oxygen manchette process. This it to help remove other impurities. The iron produced is then developed into various steel products.

1

1

2

	Grade Boundary: High Not Achieved
6.	For Achieved, the student needs to demonstrate understanding of the chemistry used in the development of a current technology.
	This involves processing and interpreting information to provide an account of the chemistry used in the development of a current technology using chemistry vocabulary, symbols and conventions. This may also include an account of the historical development of the technology.
	This student has processed and interpreted information and has provided an account of some of the chemistry that is used in the development of steel (1). There is also limited use of chemistry symbols and conventions (1).
	To reach Achieved, the student could provide an account of more of the chemistry that is used in the development of steel, such as the reduction process developed in the rotary kiln to remove impurities (2). Also, more chemistry vocabulary could be used.

2

Steel making in New Zealand

Steel is a very strong metal and as a result it is used in industry where strength is required like in the picture above.

Steel is made from iron. Steel is iron that has had carbon added to it to add to its strength and durability.

The problem with making steel is obtaining iron. Adding the carbon is not difficult. In New Zealand iron is obtained from the iron sand deposits found on the beaches of the west coast of the North Island. These deposits are sometimes referred to as black iron sands. It is the iron content that makes them black.

When iron sands are heated with carbon and limestone iron can be formed.

Carbon + iron sands \rightarrow iron + carbon oxides.

The iron sands contain oxygen with the iron and in this process the oxygen is removed. That is Fe_3O_4 reacts with carbon to make Fe. The limestone is added as when limestone is heated it makes carbon dioxide which is involved with the process.

 $CaCO_3 + heat \rightarrow CaO + CO_2$

Normally this process is carried out in a blast furnace. However at the Glenbrook steel mill this is not the case and some new technology was required. This is because the iron sands in New Zealand contain impurities not found elsewhere in the World. These impurities react when heated and block the furnace up.

1

The iron which is melted in the process is normally removed through these holes. But as mentioned the holes get blocked up by the impurities. Because of this additions to the method are required.