

9 STEEL INDUSTRY RAW MATERIALS AND WASTES

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9 STEEL INDUSTRY RAW MATERIALS AND WASTES

9.1 Iron and steel making

9.1.1 Iron and steel

Steel is an alloy of iron and carbon. It may contain up to 1.7% carbon, though generally it contains less than 0.5%. Steel is produced in a variety of forms, for different uses. Alloy steels contain metallic elements other than iron, such as chromium (present at 14% in stainless steel), nickel, vanadium, molybdenum, manganese, cobalt and tungsten. The chemical composition and properties of the main types of iron and steel are shown in Table 9.1.

9.1.2 Iron ore

Iron ores are principally oxides or carbonates of iron. Iron ore has been mined in Europe by both underground and surface mining methods. The main types of iron ore and where they can be found in Europe are shown in Table 9.2. Mining produces waste rock and soil which may be devoid of vegetation because of its poor nutrient status. Spoil from iron ore mining in Lorraine, eastern France contains pyrite and is a source of acid mine drainage (see Section 12.2.3).

Since the 1960s the exploitation of large deposits of high purity iron ore (63-65% Fe content) in western Australia and the Amazon has led to a dramatic reduction in iron ore mining in Europe, with European ore being replaced by imported ore, predominantly from Africa and Brazil. In 1990 the only significant European iron ore producers were France (Lorraine region) and Spain.¹²⁴ Production of iron ore is likely to decline further as steel production based on these ores is planned to switch to imported ores or production from scrap.¹²⁵

Some of the contamination of iron and steel sites by non-ferrous metals derives from the metal content of the iron ore. The metals which may be present as impurities in iron ore are shown in Box 9.1.

Table 9.1: Types of iron and steel

Type of iron/steel	Composition	Properties
Pig iron	High in carbon (3-4%) and impurities, including silicon, phosphorus, sulphur and manganese. Much of the carbon is in the form of graphite flakes which are a source of structural weakness.	Brittle, low melting point. Used for manufacture of other types of iron and steel.
Wrought iron	Virtually no carbon. Contains minute, parallel threads of slag.	Ductile, malleable, easily welded, corrosion free. High tensile but low compressive strength.
Cast iron	High in carbon and other elements. Slightly lower in impurities compared to the pig iron from which it is manufactured.	Brittle, cannot be forged or welded, but high compressive strength.
Carbon steels	Similar to wrought iron in that they contain very little carbon: mild steel <0.2%; medium steel 0.3-0.6%; high-carbon steel 0.6-1.7%. No slag threads.	Not as ductile or as easily welded as wrought iron, not corrosion free, but harder wearing and stronger.
Alloy steels	Small amounts of carbon and up to 50% of other metals (e.g. Al, Cr, Co, Mn, Mo, Ni, Ti, W, V).	Wide variety of properties depending on alloy.

9.1.3 Iron smelting

Ancient methods of iron smelting involved heating the iron ore in a charcoal fire within a clay furnace with limited air supply. On completion, the furnace had to be demolished to obtain the 'bloom' of wrought iron. Such furnaces were known as bloomeries. If the supply of air was increased the carbon from the charcoal and silicon from the

Table 9.2: Types of iron ore and principal deposits in Europe

Name	Chemical composition	Physical character	Principal deposits	Purity /impurities
Magnetite	Fe_3O_4	Dense, hard, black masses. Magnetic. Specific gravity 4.9-5.2.	Scandinavia, particularly Sweden.	72.4% Fe when pure, usually deposits contain 55-65% Fe. Purest type of iron ore. Free from sulphur and phosphorus.
Red hematite	Fe_2O_3	Red/black, hard massive lumps to soft powdery deposits. Specific gravity 4.9-5.3.	Sweden, UK (Cumbria), Spain (Bilbao).	70% Fe when pure. Usually deposits contain 60% Fe.
Brown hematite (limonite)	Fe_2O_3 with 8-20% water	Light yellow-brown to red/black. Soft, open, easily, smelted. Specific gravity 4.0-4.7.	France (Lorraine), Belgium, Luxembourg, Germany, Spain.	65-55 % Fe. High phosphorus content.
Carbonate ores (siderite)	FeCO_3	Grey/brown.	UK (East Midlands)	48% Fe when pure, deposits average 30%. High phosphorus content, high lime content.

Box 9.1: Non-ferrous metals found in iron ore²²

Non-ferrous metals which may be present as impurities in iron ore include:

Titanium	Zinc	Nickel	Vanadium
Magnesium	Lead	Arsenic	Chromium
Manganese	Copper	Tin	Boron

iron ore would combine with the iron, lowering its melting point so that the iron became liquid and flowed out of the furnace. This was at first undesirable, as the iron produced, known as pig iron, was brittle and unworkable. However, a method by which this iron could be refined to produce wrought iron was developed in the sixteenth century and production of pig iron from iron ore became the norm, with wrought iron subsequently produced from the pig iron.

The furnace producing pig iron from iron ore, the blast furnace, has changed little since it was first developed, although its size, efficiency and speed of throughput have greatly increased. The largest furnaces in Europe, built since the 1970s, have hearth diameters of around 14m, and working volumes of 4,000-5,000m³, and can produce over 10,000t of pig iron per day.¹²⁵ Figure 9.1 is a diagrammatic section through a blast furnace. Iron ore, coke and limestone are charged into the top of the blast furnace via a bell valve, which prevents loss of gases to the atmosphere during charging. A blast of air, sometimes containing fuel in the form of gas, oil or pulverised coal, heated to 600°C, is introduced near the bottom of the furnace. The coke burns to produce carbon monoxide which reduces the iron ore. Molten iron flows into the bottom of the furnace where it is removed via a tap. The iron may be run into moulds, known as pigs, or may be used directly, in its molten form, for the production of steel or cast iron. Impurities in the iron ore and coke combine with lime from the limestone to produce a molten slag which floats on top of the iron and is tapped off separately.

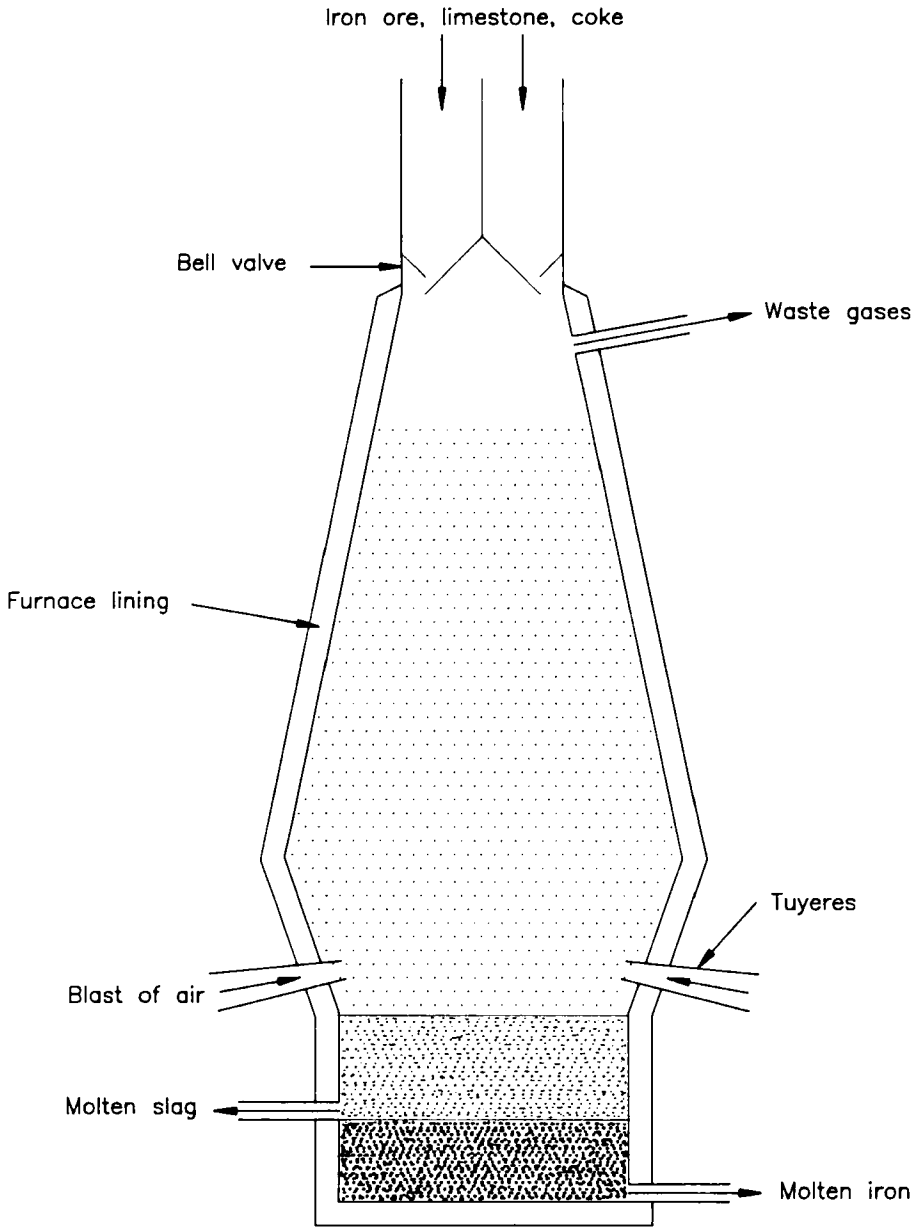


Figure 9.1: The blast furnace

The use of coke, rather than charcoal, for fuel was an important development in iron making, first introduced in the early eighteenth century. Coal could not be used as it softens under heat and would thus choke the furnace. Unlike charcoal, the coke contains sulphur which makes the pig iron produced unsuitable for wrought iron, a disadvantage before steel replaced wrought iron in nearly all its traditional uses.

Blast furnaces are operated continuously, with periodic tapping of slag and iron and charging of raw materials. The furnace is only shut down for renewal of the furnace lining. A modern blast furnace is shown in Photograph 9.1.

Small quantities of iron are also produced by direct reduction processes, which involve the removal of oxygen from iron ore, in the solid state, by gaseous or combustible reductants. Direct reduced iron (DRI) is generally added to electric arc furnaces (see Section 9.1.5) to make steel.



Photograph 9.1: Blast furnaces in Spain (source: Richards, Moorehead and Laing Ltd)

9.1.4 Iron casting

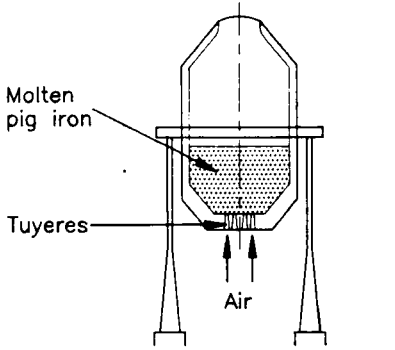
To produce cast iron, pig iron is remelted in a cupola, a furnace similar to the blast furnace, though generally smaller and operated as a batch process. High grade coke, low in ash and sulphur, is used as the fuel and a small quantity of limestone added to form a slag with some of the impurities in the iron. The molten iron is tapped off and run into moulds, formed from sand.

Cast iron has now been largely replaced by steel in most of the many uses it was put to in the nineteenth and early twentieth century. Casting, still commonly carried out with steel, is performed in a foundry.

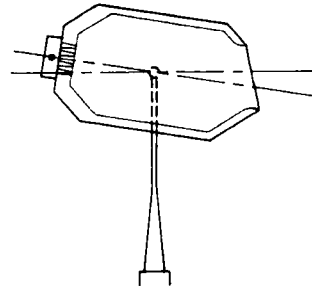
9.1.5 Steel making

The making of steel is a batch process by which the impurities present in the pig iron are removed. Measured quantities of carbon and other elements are then added to produce steel of the type required.

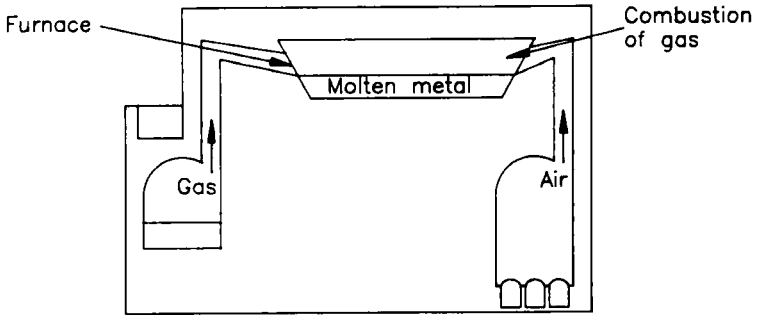
The oldest steel making process is the Bessemer process, developed in 1850. In this process, molten pig iron was loaded into a vessel, known as a converter (see Figure 9.2(a) and (b)). Air was then blown into the molten iron through a series of tuyeres in the bottom of the converter. The air oxidised the impurities such as carbon, silicon and manganese, and some of the iron. These impurities either left the converter as brown fumes or formed a slag which floated on top of the iron and was removed separately. In the original 'acid' process the converter was lined with silica bricks. Only iron low in sulphur and phosphorus could be used as these elements were not removed by the acid Bessemer process. In the 1880s a 'basic' version of the process was invented by Thomas and Gilchrist. Addition of a lime-rich flux was found to remove the unwanted elements from the steel. The furnace lining had to be made of a basic material (dolomite) to avoid reaction with the slag. A phosphate-rich slag was produced which could be used as a fertiliser. The process allowed steel to be made from the phosphorus-rich ores of France, Belgium, Luxembourg and Germany, where it is known as the Thomas process.



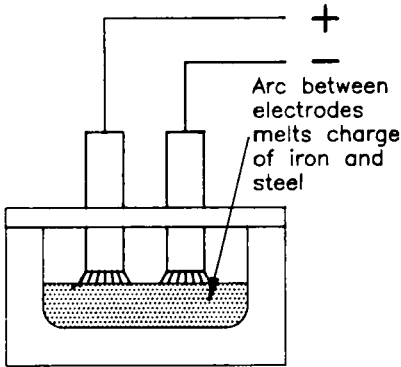
(a) Bessemer Converter turned up for blowing



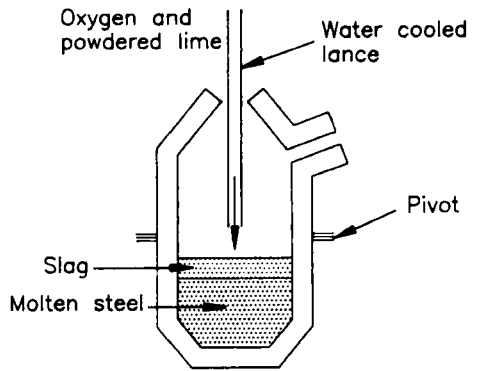
(b) Bessemer Converter turned down for loading and pouring



(c) Open hearth or Siemens-Martin furnace



(d) Electric arc furnace



(e) Basic oxygen or LD Converter

Figure 9.2: Steel making furnaces

In the first half of the twentieth century the main alternative to the Bessemer processes was open hearth, also known as 'Siemens-Martin', or just 'Martin'. In open hearth steel making the furnace is a shallow, crucible type. Heat to melt the iron is produced by the burning of gaseous fuel within the furnace (see Figure 9.2(c)). Acid and basic processes differ in the nature of the furnace lining and the addition of lime-based flux. The acid process requires low phosphorus pig iron whereas the basic process can use high phosphorus pig iron, but unlike the basic Bessemer process, phosphorus is not essential. Steel scrap as well as pig iron can be used in open hearth steelmaking. In the basic open hearth process fluorspar is added with the limestone as a flux. The fluorspar absorbs sulphur and makes the slag more fluid, but it destroys the value of the slag as a fertiliser as it renders the phosphate in the slag insoluble. Less iron is lost through oxidation with the open hearth than with the Bessemer process. Open hearth steel making is still carried out in Eastern Europe and India.

Pure oxygen became available in large quantities after 1945 and in 1953 a steel making process which used pure oxygen rather than air was developed in Austria. It was called the Linzer-Dusenverfahren (LD) process and is also known as the Basic Oxygen Steel (BOS) process. A converter, similar to that used in Bessemer steel making is used but, rather than air being introduced through the bottom of the vessel, a lance through the top of the vessel blows a blast of pure oxygen with powdered lime on to the charge of molten pig iron (see Figure 9.2(e)). Oxidation of impurities in the pig iron produces heat so no additional heating is required. Up to 30% of the charge can be cold scrap or iron ore. In later modifications of the process oxygen may be blown from the sides or bottom as well as the top of the converter. The process combines the fast production rate of Bessemer with the high quality product of open hearth and it is now the major steel making process. The BOS process is used for making bulk steel at large integrated steel works where molten pig iron from blast furnaces can be fed directly into the converter. In 1991 oxygen steel making accounted for 67.9% of steel production in the European Community.¹²⁴

Electric steel making uses electricity to provide the energy to melt a charge of iron and steel scrap and produce steel of the desired quality. In the electric arc furnace (see Figure 9.2(d)) the metal is placed in the arc between two carbon electrodes. The heat of the arc is sufficient to melt the metal charge and impurities present in the metal form a slag with added lime and fluorspar. In the high frequency induction furnace a high frequency AC current in a copper coil surrounding the furnace induces a similar current in the metal within the furnace. This current is concentrated in the surface of the metal, creating heat which melts the metal. The generation of heat in electric furnaces does not depend on combustion processes so the atmosphere of the furnace can be controlled, enabling conditions to be chemically reducing if necessary. Chemically reducing conditions allow the melting of steels containing easily oxidisable elements such as chromium, manganese and vanadium without loss of these elements, to produce high quality alloy steels. Electric furnaces are generally smaller than oxygen furnaces and can take a cold charge of 100% scrap. Such furnaces can therefore be used at non-integrated steel works where a supply of molten pig iron is not available. In 1991 electric steelmaking accounted for 31.6% of European Community steel production.¹²⁴

9.1.6 Processing of steel

Crude steel from the furnace is first transferred by casting, rolling and/or forging into semi-finished or intermediate products such as ingots, slabs, blooms or billets. These products are known as 'semis' and they may be sold to steel processing companies or may be further processed at the steel-making works. Such further processing may include hot or cold rolling, drawing to form wire, cutting, machining and coating with metallic or plastic materials. The major processes are described in the following sections.²⁴³

Casting

Liquid steel from the furnace may be cast into ingots by pouring into individual moulds made of pig iron. Once solidified, the ingots of steel are taken from the moulds and placed in soaking pits to be reheated to the temperatures suitable for hot rolling. The soaking pits give an even temperature distribution within the ingots.

Alternatively, continuous casting may be employed. In this method the liquid steel in the ladle is tapped into a vessel known as a tundish. Nozzles in the tundish are then opened to allow the steel to flow into moulds made of copper which are cooled by water. The steel is removed from the mould when it is partly solidified and carried on a series of rollers through sprays of water, to cool it further. The steel is cut into lengths and it is either cooled and inspected, or passed immediately to a reheating furnace prior to hot rolling.

Hot rolling

The ingots, or lengths of steel from continuous casting, are reduced in thickness and sometimes in width, with concurrent elongation, by passage through the rolling mill. Scale, consisting of oxidation products, forms on the surface of the steel during reheating prior to rolling. This scale is broken up by the action of rolling and is washed away by the water used to cool the rolls.

Pickling

After hot rolling the metal cools and a thin scale forms on the metal surface. This scale must be removed by pickling in an acid bath before further processing is carried out. Sulphuric acid or, less commonly, hydrochloric acid is used. Particularly acid-resistant steels, such as stainless steel, require the use of stronger acids, such as mixtures of hydrofluoric and nitric acids. After pickling the steel is rinsed and coated with oil to prevent further scale formation.

Cold rolling

The flat products produced by hot rolling are processed further by cold rolling to produce products such as bright sheet, angles or sections or wire products (by cold drawing or twisting). Oil, or mixtures of oil and water are used to cool the rolls and to provide lubrication. After cold rolling the oil is removed from the steel products by rinsing, electrolytic treatment in an alkaline solution and then washing to remove the alkali.

Coating

Zinc, tin, aluminium, lead, brass, cadmium, paint and various types of plastic may all be applied to steel products as a protective or decorative coating. Coating with zinc, known as galvanising, may be done electrolytically or by dipping the steel in liquid zinc. Coating processes are carried out in a number of stages, several of which involve cleaning the metal surface. These stages include rinsing, alkaline treatment, pickling and oiling.

9.1.7 Integrated steel works

The production of steel is an industry where great increases in efficiency have been achieved through economies of scale, so that increases in steel production since the 1950s have been achieved with larger but fewer steel works. These large works are generally 'integrated'; all the processes involved in steel production, such as smelting of iron ore, burning of limestone to produce lime, coal carbonisation to produce coke, steel making and steel processing, are located on the same site. The products of one process feed directly into the next process, so that, for example, molten pig iron from the blast furnaces feed into the converter to be made into steel (see Section 17.9). In this way heat losses are minimised and efficiency is increased by utilisation of heat or gases generated by one process in other processes. Underground and overground ducts, pipes or conveyor belts transport gases and materials from one part of the site to another.

In many steelmaking towns, such as Seraing near Liege, Belgium, the town and steelworks have grown together. In such places, ducts and conveyors cross residential and commercial areas of the town to connect different sites of the local steel company.

9.2 Wastes from iron and steel making

9.2.1 Introduction

The major processes which take place at iron and steel works, together with their associated raw materials, products and wastes, are shown in Table 9.3.

The principal type of waste from steel making in terms of volume is slag. There are various types of slag, described in Section 9.2.2. Slag has become regarded as a useful by-product rather than a waste material, although this has not always been so, particularly in Britain where large tips of waste slags are found at some former iron and steelworks sites. Flue dusts and refractory linings from furnaces are also significant waste streams, of which deposits may be found at old sites. Coal carbonisation, used to make coke is likely to have been the greatest source of contamination found at steel and iron sites. Coal carbonisation is dealt with in Chapter 10.

9.2.2 The characteristics of slags

Introduction

Slags are synthetic rock-like materials formed by the fusion of the non-iron constituents of iron ore, or the impurities present in the iron, with the limestone flux during steel making. The amount of impurities to be removed is much greater at the iron smelting stage, in the blast furnace, than at the steel making stage, so for a given amount of steel produced from iron ore the volume of blast furnace slag is much greater than the volume of steel slag.

Table 9.3: Processes, raw materials, products and wastes involved in production of steel

Process	Raw materials	Product	Wastes/by-products
Iron ore mining		Iron ore	Waste rock
Iron smelting (in blast furnace)	Iron ore Limestone Coke Air	Pig iron	Blast furnace slag Flue dusts Ash Refractory linings
Steel making	Pig iron and/or steel and iron scrap	Steel	Steel slag Flue dusts Refractory linings
Iron casting	Pig iron Coke Moulding sand	Cast iron	Foundry slag Moulding sand
Processing of steel	Crude steel	Steel products	Spent acids and alkalis, hydroxide sludges, spent plating solutions, mill scale, oils, solvents, paints, non-ferrous metals
Coal carbonisation (see Chapter 10)	Coal	Coke Coal gas	Tars Benzole Naphthalene Ammoniacal liquors Spent oxide Sulphate

Blast furnace slag

Blast furnace slag consists of silicates and alumino-silicates of lime.¹⁴⁶ The major mineral component is melilite. This is a solid solution with the end members gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) and akermanite ($2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$). Melilite is a stable mineral with good strength

properties, responsible for the good engineering properties of blast furnace slag as roadstone, fill material and concrete aggregate.^{179, 237} The rate and manner of cooling of molten slag from the blast furnace can be varied to produce three different forms of solid slag, as described in Box 9.2.

The few problems which have arisen through the use of blast furnace slag are associated with the sulphur content of the slag. Blast furnace slag generally contains around 1.5% total sulphur, with over 2% in older slags. The sulphur is derived from the coke used in the furnace. High concentrations of water-soluble sulphate may result in the formation of sulphotoaluminates such as ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 30\text{-}32\text{H}_2\text{O}$).²³⁷ The formation of this secondary mineral is accompanied by an increase in volume of approximately 120%, and may cause ground heave.

High concentrations of sulphate may also result in the chemical attack of concrete (in which sulphotoaluminate formation is also involved), particularly if the concrete is placed in contact with the slag in a

Box 9.2: Forms of blast furnace slag¹⁴⁶

Three different forms of blast furnace slag are produced by different methods of cooling the slag:

Air cooled	Slag which has been allowed to solidify under ambient conditions, producing a crystalline structure similar to that of natural rock. The slag is generally crushed and graded to produce aggregate of the desired size.
Foamed, or expanded	Introduction of water under controlled conditions whilst molten slag is tipped into a container, produces many air pockets within the slag, giving a strong, lightweight aggregate.
Granulated	Slag which has been cooled rapidly with an excess of water to produce glassy sand-like material.

waterlogged situation. The presence of reduced forms of sulphur result in discolouration of the slag and odour problems. A greenish tinge is common and the foul-smelling gas, hydrogen sulphide, may be produced. Leaching of sulphur compounds from blast furnace slags cause the most common water pollution problems associated with the use of slags, although these problems can be largely avoided by not placing the slag in situations where water can drain through them.⁸³

Steel slags

Steel slags contain more iron, as free metal and as oxides, than blast furnace slag. This iron gives steel slags a greater density, and the potential to be magnetic. Unlike blast furnace slags steel slags contain very little sulphur. The chemical composition of steel slags, even from the same process, tends to vary more than for blast furnace slags.

Steel slags may derive from acid or basic steel-making processes. Slags from acid processes contain silica with some lime. However, these slags are rarely encountered as basic processes have been responsible for nearly all European steel production in the twentieth century. Basic steel slags are high in lime, and contain calcium silicate, solid solutions of calcium oxide and ferrous oxide, and calcium ferrite.^{83, 237} Unlike blast furnace slag some 'free', uncombined lime (CaO) and magnesia (MgO) may also be present, particularly in slags from oxygen steelmaking.²² These oxides can react with water to form hydroxides, a reaction which is accompanied by a large increase in volume. This reaction can give rise to a greater degree of expansion and is a more common problem associated with the use of slags than the sulphoaluminate expansion mechanism of blast furnace slags (see Box 9.3).

Hydration of calcium oxide has been found to be responsible for the expansion of steel slag over the first year subsequent to production, with hydration of magnesium oxide a slower, longer term reaction, responsible for the continued expansion over a number of years. The heat produced by these hydration reactions may also result in spontaneous heating in slag fill.²³⁶

Box 9.3: Building damage caused by expansive steel slags

Building damage caused by expansive steel slag was reported in 1969.⁶⁴ A single storey building, constructed in 1962, had developed cracks followed by buckling of window frames and interior metal and glass partitions. The damage was found to be caused by the differential movement of the floor slab and interior and exterior columns. The latter rested on spread footings at 1.5m depth whilst the concrete floor slab was cast on compacted fill consisting of slag from a steel mill. Level measurements revealed that the floor slab was rising rather than the footings sinking. The absence of any voids between the floor slab and an underground service tunnel indicated that the movement was caused by swelling of the slag fill. In autoclave tests open hearth slag from the steel mill was found to expand by 10% and it was concluded that this was due to hydration of calcium and magnesium oxides.

Following publication of this paper fourteen other cases of building damage caused by expansive slag were reported in the same journal.⁶⁵ The amount of expansion reported was as much as 20%, with rises of 220-370mm beneath floor slabs and 600mm beneath pavement. The causes of the damage were not always recognised, often being wrongly diagnosed as differential settlement or expansive clays.

Slags which are susceptible to expansion can be used in situations where expansion can be tolerated, such as screening bunds, or as aggregate on unsurfaced roads, where steel slag has the advantage of not suffering the discolouration of blast furnace slag. Steel slag has excellent skid resistance properties and is used for roadstone, sealed with an asphalt coating to exclude water.^{84, 179} Slag from basic Bessemer (or Thomas) processes, used widely in Germany and France, was rich in phosphate and was valued as a fertiliser. Now that oxygen steelmaking has replaced the Bessemer process, and low phosphate imported ores have replaced the local high phosphate ore, phosphate is added to some steel slag in the Ruhr area so that it can be sold as a fertiliser.²³⁹ Use of steel slag as a fertiliser is described in Box 9.4.

Calcite can be formed if steel slag is placed in waterlogged situations.⁸³ The highly alkaline pH (10-12) of steel slags may cause surface and groundwater to be alkaline.²²⁵

9.2.3 Slags as a substrate for plant growth

Because slags have been so widely re-used, large quantities of waste slags have not generally accumulated. The lack of large slag heaps in need of treatment has meant that there has been little study of them as a substrate for plant growth. Where attempts have been made to vegetate slags a principal difficulty has been with those slag heaps which are comprised of large blocks of fused slags. The lack of fine-grained particles has meant that moisture holding capacity is negligible and vegetation has been slow to establish and difficult to maintain. Some very old blast furnace slag heaps have become vegetated naturally (see Photograph 9.2) but where slopes are steep even on old tips vegetation has not established. Old acid slag heaps tend to take on the vegetation characteristics of the surrounding land. Where slag and other wastes from basic steel making

Box 9.4: Basic slag as a fertiliser

Basic slag was used as a fertiliser in many steel making areas. Its principal benefits were:

- alkalinity. Basic slag has a moderate liming effect;
- source of phosphate. The phosphate in slag is only sparingly soluble. Slag was therefore useful as a 'slow release' supply of phosphate, one application often sufficing for 3-4 years on grassland;
- low cost.

These properties are particularly beneficial on soil-forming materials such as colliery spoil or other inert wastes where vegetation establishment is required. Basic slag (often enriched with phosphate) is now imported for fertiliser use into some European countries where it was once a by-product.



Photograph 9.2: A heap of blast furnace slag in South Wales with some natural vegetation (source: Richards, Moorehead and Laing Ltd.)



Photograph 9.3:
White Mullein (*Verbascum lychnitis*) on
blast furnace slag (source: Richards,
Moorehead and Laing Ltd)

processes has been deposited, naturally established vegetation can be of some ecological value (see Box 9.5).

9.2.4 Assessment of slags

Over the years more and more slag has found a productive use and slags have come to be viewed as a valuable by-product of iron and steel making. Slag is, however, likely to be encountered on derelict iron and steel sites as it will have been used as an aggregate in concrete and as a general fill material. There may also be areas used for disposal of material which was considered to be unsuitable for reuse at the time of its production. Different types of slags and other wastes from the site, such as refractory linings and flue dusts, are likely to be mixed together in such dumps. The assessment of these tips presents a number of problems, especially the difficulty in obtaining representative samples for subsequent analysis. A wide variety of different types of slags of different ages may be present, and cementation of some slags may make it difficult to penetrate with ground investigation equipment. Indeed, in some instances even heavy earth moving equipment may encounter problems in excavating highly cemented slags.

Box 9.5: Wildlife value of steel wastes

The alkaline nature of the slags from steel manufacture can result in colonisation by vegetation of significant ecological value. At one site in North Wales where a steelworks is situated on an estuary, the combination of the calcareous influence of the slag and the marine influence has resulted in the development of an ecologically interesting flora. The plants found include White mullein (*Verbascum lychnitis*) a relatively uncommon plant in the United Kingdom and which is only found in the vicinity of the steelworks on steelworks slag and the waste from the alkali industry (see Photograph 9.3). The wildlife value of the site as a whole is enhanced by the colonisation by flora and fauna of the former steelworks lagoons which have become very rich in bird life and support one of the largest colonies of breeding common terns in the United Kingdom.

Volumetric instability

Although slags present at former steel sites may be over 50 years old this does not mean that reactions causing expansion (described in Section 9.2.2) will no longer occur. This is particularly so if the slag is disturbed, so that large lumps are broken up, exposing unreacted material to water and bringing materials together in new combinations. Old deposits of slags should be disturbed as little as possible, but if they are to be placed in confined situations, such as beneath buildings, an assessment of their volumetric stability should be made.

Assessing the volumetric stability of slags is not a simple matter. The mineralogy of the slags should be determined by techniques such as optical microscopy and X-ray diffraction, and the chemical composition determined by chemical analysis. In particular the amounts of total sulphur, sulphate, free lime and magnesia present should be measured. Specialist techniques, such as thermal analysis, are required to distinguish the oxides, lime (CaO) and magnesia (MgO), from their hydroxides (Ca(OH)₂ and Mg(OH)₂).²³⁷ Information gained from these investigations can be used by experienced personnel to make an assessment of how likely the slag is to undergo expansive reactions. Accelerated expansion tests should then be carried out on representative samples of the slag material. The simpler test procedures which have been developed for this involve immersion of compacted samples of slag in a water bath which is maintained at an elevated temperature.⁸² However, some work suggests that expansion is greater if the slag is in contact with water vapour rather than immersed in a water bath, as in the latter case the hydroxides are formed in solution and tend to fill up the void spaces in the crystal structure, whereas in the former the crystals are pushed apart.¹⁵⁶ Examples of accelerated expansion tests are described in Box 9.6.

If expansion is observed in an accelerated expansion test it indicates that there is a risk that the slag may expand. The precise degree of expansion cannot be predicted, nor can the timescale over which such expansion will occur. During reclamation of a slag bank in Hartlepool, North-East

Box 9.6: Accelerated expansion tests

A test procedure developed in the United Kingdom²³⁸ exposes samples of slag to carefully controlled fluctuating conditions of temperature and humidity within a climatic cabinet. The test is usually carried out over a period of 14 days and, unlike tests where the sample is immersed in water, it detects expansion due to formation of sulphoaluminate type minerals as well as the hydration mechanisms found in steel slag.

An accelerated expansion test which uses steam has also been developed in Germany, where it is used to assess steel slags, from the LD process.¹⁴⁷ The test apparatus has two compartments, the lower of which contains water which is heated to boiling point. The steam generated passes through the upper compartment, which contains a compacted sample of slag. This upper chamber is surrounded by a heated jacket, at 102°C, to prevent condensation of water vapour. A meter measures movements in the upper surface of the slag sample. Expansion has been observed to be hyperbolic, tending towards a maximum value in around 24 hours. Comparison of maximum expansion with free lime content of the slag sample revealed that expansion was minimal, (3% or less) if the free lime content was less than 7% by weight. This work has led to specifications for use of steel slag in road construction in the state of North-Rhine Westphalia.

England, site levels were monitored after earthworks had been carried out to prepare the site for redevelopment. Some of the slag from the bank was known to be expansive as its use in a local road scheme had led to ground heave. The observed rise in levels was generally less than that found in concurrent laboratory real-time expansion tests, but expansion was still continuing after three years.^{77, 78} During later development of the site slag was removed over areas where buildings were to be located.²³⁸

9.2.5 Leaching of metals from slags

Slags contain metals derived from iron ore, coke and limestone. Steel slags may also contain some of the metals used in alloy steels. Metal concentrations of some blast furnace and steel slags are shown in

Table 9.4: Metal content of slags (from Barry, 1985²²)

Sample:	Blast furnace slag				Steel slag			
	A	B1	B2	C	D	E	F	
TOTAL CONCENTRATIONS (mg/kg)								
Antimony	ND	ND	ND	ND	210	64	220	
Arsenic	ND	ND	87	3	ND	ND	ND	
Barium	200	100	200	400	700	70	100	
Cadmium	10	6	8	9	7	4	9	
Chromium	162	65	55	60	420	96	752	
Copper	188	90	60	4400	32	17	20	
Fluorine	9	1	0.8	0.4	9.5	4.8	0.7	
Lead	63	56	48	61	70	38	80	
Magnesium	37360	44040	54800	60980	4542	20902	20370	
Manganese	18800	2580	2210	3620	44900	12600	43800	
Mercury	1.7	ND	ND	ND	ND	ND	ND	
Nickel	50	20	30	17	140	50	120	
Selenium	24	ND	80	57	ND	ND	16	
Thallium	23	95	108	90	53	34	58	
Zinc	780	20	25	1160	38	41	54	
EXTRACTABLE CONCENTRATIONS (mg/kg)								
Hot water	Boron	5.5	3.0	3.0	4.0	3.5	3.0	3.5
0.5M acetic acid	Copper	0.3	0.5	0.8	0.6	0.7	-	0.3
	Nickel	0.2	0.4	1.6	1.0	3.0	5.0	0.4
	Zinc	3.6	2.0	3.2	3.4	2.8	8.2	3.2
0.5M ETDA	Copper	0.2	1.3	0.9	1.3	0.1	-	0.7
	Nickel	1.3	0.9	1.4	1.0	1.8	-	2.0
	Zinc	8.9	2.7	4.8	2.9	1.0	-	1.2

Notes: B1 and B2 are 'blind' repeat analyses
 ND not detected
 - not determined

Table 9.4. Many of the metals in slags, such as copper, chromium, lead, zinc and nickel, are potentially toxic to people, animals or plants. However, slags have a pH of 10-12 (though this may fall to pH 8 on weathering) and this alkaline pH and the complexing of metals with calcium silicates ensures that these metals are present in insoluble forms. Leaching studies have shown that metals are not readily leached from slags.^{83, 127, 141}

9.2.6 Flue dusts

Flue dusts consist of the particulate matter removed from the gases emitted by furnaces of iron and steel production. The coarse-grained material, of a particle size similar to that of sand, trapped by primary dust catchers, is usually returned to the blast furnace after sintering, a process which agglomerates fine-grained particles so they can be used in the furnace without impeding the flow of air. Recycling of flue dusts in this way recovers some of the iron lost in steelmaking and the coke lost in the dust from the blast furnace. However, flue dusts also contain non-ferrous metals so continuous recycling of all dust cannot be practised as it would lead to the accumulation of such metals in the blast furnace.

Fine-grained dusts, collected in bags, scrubbers, precipitators and cyclones may have been disposed of in lagoons, where their physical nature may result in soft ground conditions. Excavation of such fine-grained materials is likely to produce high concentrations of air-borne dust, a health and safety hazard. Chemically, dusts are likely to be enriched in metals such as lead, zinc, nickel, copper, cadmium, chromium, arsenic, alkali metals, and halides.^{189, 225}

Flue dusts are often the chief sources of inorganic contamination at iron and steel sites and, unlike slags, their metal contents may be leachable. In a study of the leaching of metals from wastes of steel manufacture,¹²⁷ flue dusts from electric steel making were found to be the only waste which gave rise to leachate containing elevated concentrations of metals such as lead, zinc and chromium. The free lime content of the dusts was found to be the major factor determining metal solubility.

Dusts from electric arc furnaces frequently contain up to 20% lead and zinc, originating from the high percentage of scrap metal used in such furnaces. In the USA electric arc furnace dust is classified as a hazardous waste and it must be treated chemically or thermally to remove or stabilise the leachable toxic metals. One such thermal process operating in Europe, the Waelz process, involves heating the dust to high temperatures, with coal and sand. Lead and zinc are vaporised and reclaimed to give a residue containing 60-70% lead and zinc in an oxidised form. Other constituents of the furnace dust form an innocuous slag with the sand.²³² A hydrometallic process involving alkaline leaching, which produces a metallic zinc powder, has also been developed.²⁵⁶

9.2.7 Other wastes

The refractory materials used to line furnaces form a significant part of the wastes likely to be found on iron and steel sites. They will almost certainly be contaminated by metals. Refractories from the blast furnace can also contain cyanides.²⁴³

Sand used for forming moulds for casting of iron and steel, may contain phenolic binders. Large volumes of this sand, used as a fill material has been found at some sites.¹²⁹ Foundry and moulding sand may also contain expansive steel slag, giving risks of ground heave.⁶⁵

The processing and treatment of steel results in various types of wastes, for example:^{22, 189, 243}

- spent pickling acids (liquors containing, typically, 10% unreacted sulphuric or hydrochloric acid and 5% dissolved iron,²¹¹
- hydroxide sludges, formed on neutralisation of spent acid solutions, containing iron sulphate or chloride;
- spent plating solutions;
- galvanising scums;

- wastes from metallic coating of steel, which may have used tin, molybdenum, zinc, vanadium, nickel, copper, chromium, cadmium, lead or aluminium;
- emulsified mineral oils from cold rolling of steel;
- waste plasticisers, glues and paints used in coating of steel products.

Substances used in steel production may be present as contaminants at former steel sites. For example, selenium is used as an additive in ferrous metals as it aids casting and improves the machinability of steels. This toxic element, which is chemically similar to sulphur, has been found at elevated concentrations in ground beneath former steel making plant.

Iron and steel sites also contain the wastes common to a wide range of industrial sites. These materials include asbestos, used for lagging of pipes and buildings, ash from coal burning, and waste oils and lubricants.

Areas which were used for storing scrap are likely to be contaminated with materials associated with that scrap, such as paints, oils and non-ferrous metals.

Iron and steel production sites have typically been developed over a long period of time, with several generations of plant following on from each other. In many cases such sites were originally associated with coal or iron ore mines. Shafts and areas of unstable ground may thus be present, sometimes overlain by areas of filled ground several metres deep. Frequently encountered problems, in addition to those caused by the presence of the wastes and raw materials described above, are the presence of massive foundations, underground voids, ducts and pipework. These aspects have been discussed in Chapter 4, under the subjects of demolition and site clearance.