

## 9 Novel process routes

### and clean energy

*If we could invent a new way to extract liquid metal from ore, could we find new emissions savings, or could we drive the reactions by electricity and find a source of clean electricity that would reduce our total emissions?*



**Napoleon III with his run-of-the-mill gold jewellery**

When eating as the guest of Napoleon III in the 1850's, basic dignitaries, Royal princes of the poorer countries, and ordinary nobles, had to make do with the day to day gold plates and think themselves fortunate. But when he wanted to put on a show, to mark the arrival of the King of Siam for instance, there was no choice—gold was simply too common. For a big splash, the Emperor would bring out his very best—the aluminium plates<sup>1</sup>.

Aluminium was first extracted from ore in 1825 by Hans Christian Oersted. On hearing about the metal, Napoleon III invested in its development so Henri Sainte-Claire Deville was able to begin commercial production in France. He used an inefficient chemical reduction process with huge costs: in the 1850's the metal was as expensive as platinum. Thirty years later, in Ohio in 1886, a 22 year old chemistry student Charles Hall, by passing electricity through a bath of molten cryolite into which he had poured aluminium oxide (alumina) powder, produced a few globules of aluminium metal. Entirely independently, Paul Héroult achieved the same result two months later. So the process, known ever after as the Hall-Héroult process, was commercialised, led to great reductions in cost and hence increases in application, and is the core of aluminium production today.

Steel making has a similar history, though we've been unable to find stories of Royal patronage. Iron has been in use for thousands of years, but its properties are impaired by naturally occurring impurities such as carbon, silicon and manganese. In 1855, the engineer and inventor Henry Bessemer patented an industrial-scale process to remove these impurities, by blowing air through the iron while liquid. Oxygen in the air reacts with the impurities to form either gases, which escape from the metal, or solid oxides, which collect as slag. As a bonus, adding air doesn't cool the liquid metal as might be expected, but instead the oxidation reactions produce heat, which improves the rate of reaction, and in turn this releases more heat, and so on. The resulting steel, which is purer than the original cast iron, has greatly improved properties, so Bessemer's invention opened the opportunity

for a great expansion in applications of steel. Bessemer's process remained in use for over a hundred years until Robert Durrer in Switzerland showed in 1948 that replacing the air with a stream of pure oxygen was more effective. Today's steel is made with Durrer's 'basic oxygen' process.

We've started with these two stories of step changes in the processes of making aluminium and steel because we want to make an informed guess about whether it's likely that further step changes will occur in the future. Is there another student in Ohio waiting to be stimulated by a great lecture to invent a new process? According to our friends in the department of Economics this question is easy: the answer is always yes, and the real question is "what incentive do you need to provide to stimulate the next improvement?" This sounds reasonable, and at present is certainly true for the fuel consumption of cars, but in processing materials there are fundamental physical limits that we just can't beat. Whatever the incentive, a standard 3 kilowatt kettle will never be able to heat a litre of water from 10°C to boiling point in under two minutes, and similarly there are absolute limits to the energy required to make steel, aluminium and our other key materials.

We saw in Chapter 7 that pursuing all options for energy efficiency and reducing the CO<sub>2</sub> intensity of existing processes is allowing us to inch our way towards the minimum energy required to produce liquid steel and aluminium, but could we make bigger gains by developing novel technologies?

## Novel processes for steel making

The world's steel makers are currently exploring three alternative ways to make iron—direct reduced iron, smelt reduction and electrolysis, and three options for using less coke—through substitution of other fuels, the use of hydrogen and through top gas recycling.

The earliest approach to making iron, from around 1,000 B.C., was to heat the ore without coke, over a fire of coal or natural gas. Hydrogen and carbon monoxide released on igniting the fuel allowed reduction (the removal of oxygen atoms from the iron oxides) and created 'sponge iron.' This precursor metal has a high concentration of carbon and other impurities, so the steel-makers of 3,000 years ago hammered, folded and hammered the sponge iron, while hot, to oxidise (and remove) carbon, and distribute other impurities uniformly through the metal. One option for novel production of steel is therefore to go 'back to the future', starting by reducing ore directly to sponge iron. This is now called direct reduced iron (DRI),

illustrated in figure 9.1, and because the reduction occurs at a lower temperature (typically 800–1,000°C) than in a blast furnace and does not require production of coke, it uses significantly less energy than the blast furnace. However, direct reduced iron has too great a concentration of carbon and impurities. It could be refined in a basic oxygen furnace, but this would be energy intensive as production of DRI is solid not liquid. Instead, DRI is fed (hot) into the conventional electric arc furnace used in secondary steel making. The total primary energy used by the DRI route is greater than that in conventional steel making because of the electric arc furnace, but total emissions are lower because coke is not used. However, most DRI sites use natural gas to heat and drive the reaction, and this gives off-gases with a high concentration of CO<sub>2</sub> which could be captured and stored. If the electric arc furnace was powered by ‘clean’ electricity, this would further reduce emissions to a low level.

Smelt reduction is a two stage process, with the first being similar to direct reduction leading to sponge iron. However, rather than continuing on to refine the sponge iron in an electric arc furnace, in smelt reduction, it is fed into a closely connected pool of molten iron, and through further heating, is melted, as seen in Figure 9.2. The reduction reaction (removal of carbon and impurities) from the

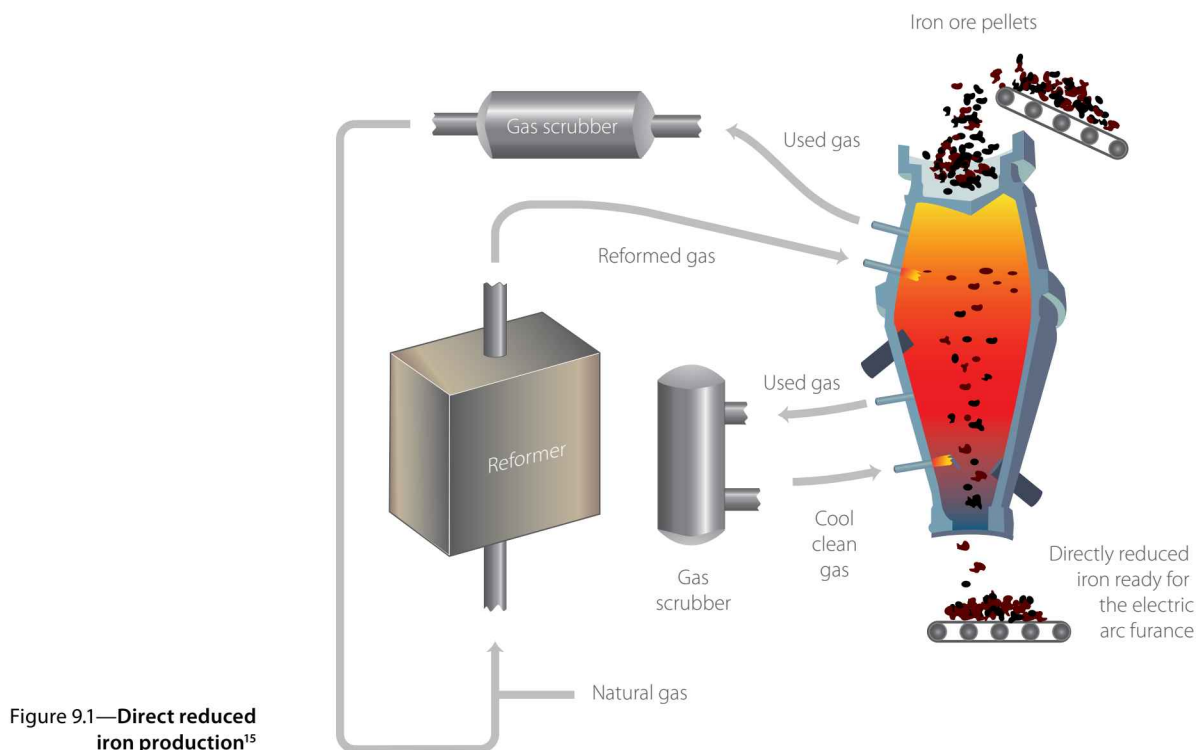


Figure 9.1—Direct reduced iron production<sup>15</sup>



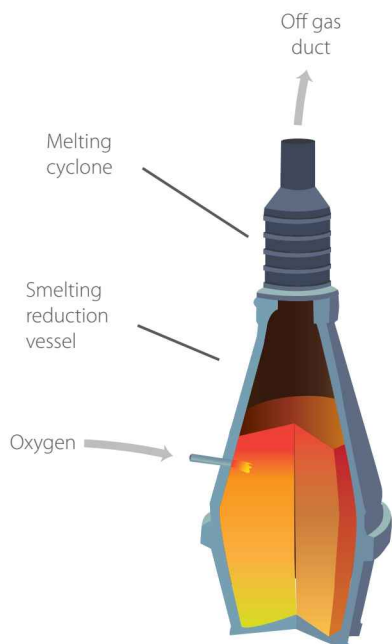


Figure 9.2—Smelt reduction process<sup>15</sup>

sponge iron occurs more rapidly in the liquid form, and is driven by direct injection of finely ground coal and oxygen into the liquid melt. The fine coal quickly turns into gas and combined with the oxygen, this drives the chemical reactions of reduction, and provides the required heat. Like DRI, the main efficiency of smelt reduction is the elimination of the coking process, but more energy is required as the process uses more coal and requires pure oxygen, which itself is an energy intensive product. Because oxygen rather than air is used in smelt reduction, and all other gases are fully combusted in the reduction vessel, the off-gases have a high concentration of  $\text{CO}_2$  so could be stored.

The third novel process route aims to produce iron from its ores by electrolysis. Two electrolysis technologies, shown in Figure 9.3, are being explored: electrowinning, in which a strong electrical current is passed into an appropriate liquid via a positive terminal made up of unrefined oxide, so that pure iron is electro-plated onto the negative terminal where the current flows out; iron ore pyroelectrolysis where current is passed from an inert positive terminal through molten iron ore, at  $1600^\circ\text{C}$  so that liquid iron will form at the negative terminal while pure oxygen is released. Electrolysis eliminates the need for coking and ore preparation, but is electrically intensive, so would only offer emission savings if powered by low carbon electricity, and as yet has been proven only at a very small scale.

Some of the coke used in conventional blast furnaces can be substituted by charcoal, biomass, or waste plastics, shown in Figure 9.4. As we saw in chapter 7, the coke provides support for the ore, generates heat, and releases carbon, to trigger the reduction reaction. Each of these substitute materials can achieve part of this function. Waste plastic, which is in effect oil, combusts to generate

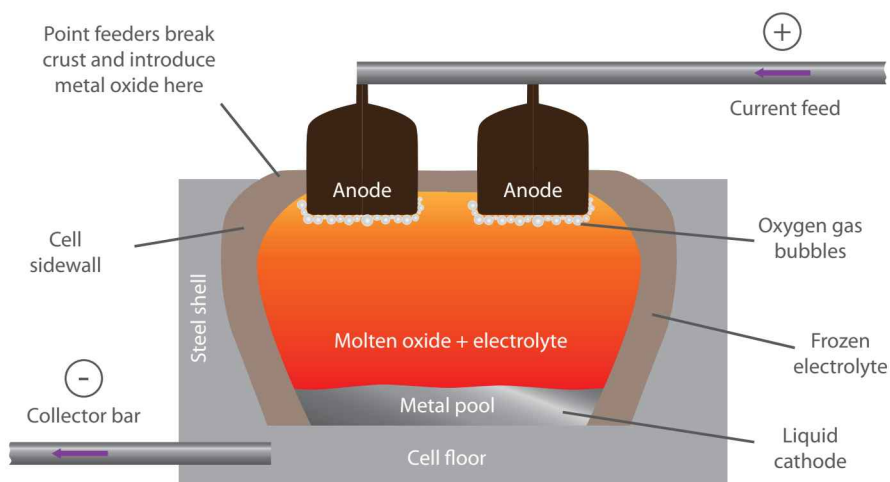


Figure 9.3—Schematic of iron ore pyroelectrolysis

heat, and we'll see later that even though any individual plastic can be recycled if well separated from other materials, waste plastics are often mixed together so incineration is potentially a good solution. Both biomass and charcoal are good substitutes, but an expansion in use is limited by the rate at which we can harvest biomass. If we replaced all coke in all 30Mt of our steel consumption in the UK, we'd need to use nearly half the surface of the UK for charcoal production<sup>2</sup>. So even though biomass substitution for coke is technically feasible, it isn't in any meaningful way a 'sustainable' solution.

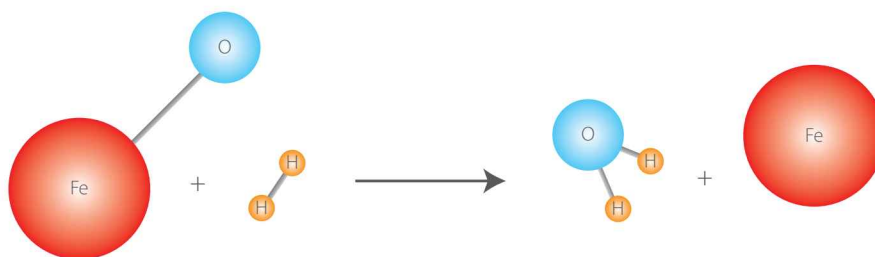
An alternative approach to coke substitution is to use hydrogen rather than carbon to drive the reduction reaction. This would eliminate process emissions, as the iron ore would react with the hydrogen to form iron and steam. However, the overall emissions impact of this option depends on how the hydrogen is produced and how the blast furnace is heated to its operating temperature. At present large-scale adoption of hydrogen substitution looks extremely unlikely, even by 2050<sup>3</sup>.



Figure 9.4—Possible fuel substitutes

A final option to reduce requirements for coke is to apply top gas recycling. The off gases from the blast furnaces contain a mixture of gases, including carbon monoxide (CO) and others. In top gas recycling, the CO is separated from the gas stream and recycled back into the blast furnace, where it can reduce the iron ore, to form CO<sub>2</sub>. In this case, the CO is acting as the reductant, rather than new coke. In a conventional blast furnace, preheated air is used to provide oxygen for combustion, so that a large volume of nitrogen is also present in the off gas, and this inhibits separation of the CO. If pure oxygen, rather than air is used, there is no nitrogen in the off gas and the separation of CO will be easier. Top gas

Figure 9.5—Reduction of iron ore with hydrogen



recycling reduces  $\text{CO}_2$  emissions from the blast furnace by 5 to 10%<sup>4</sup> but if oxygen rather than air is used, the blast furnace could be coupled with CCS. In this section we've looked beyond the best-available technologies of chapter 7. Existing blast furnaces could be modified to use less coke or to use top-gas recycling, and this would reduce emissions by up to 10%. Or, we might in future replace the blast furnace to extract metal from ore by direct reduction, smelt reduction, electrolysis or hydrogen reduction. Of these, direct reduction is widely used already in countries with natural gas supplies, and demonstrations of smelt reduction are planned (see the box story about the HIsarana pilot plant at IJmuiden in The Netherlands). We learnt from Josiah Gibbs that existing steel production is already impressively energy-efficient, so unsurprisingly none of these new processes would save much energy. Instead, they could be configured to release off-gases with high concentrations of  $\text{CO}_2$ , which could potentially be captured and stored.

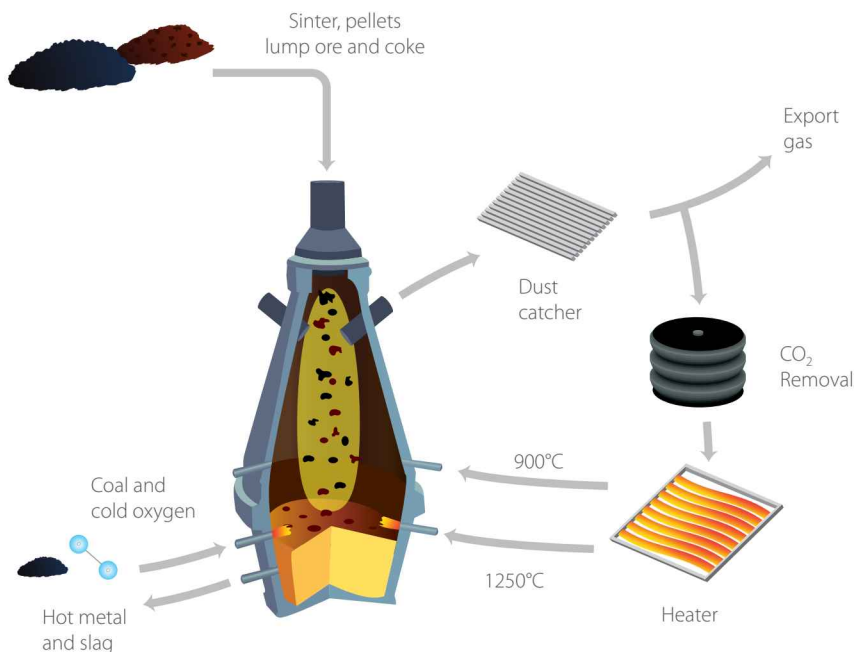


Figure 9.6—Top gas recycling<sup>15</sup>



## Novel processes for making aluminium

In order to reduce electricity consumption, developers in the aluminium industry aim to decrease the separation between anode and cathode in the Hall-Héroult cell. This could be achieved with inert anodes in conjunction with wetted drained cathodes and the anode-tilt system. Multipolar cells could increase productivity and two alternative chemical routes, carbothermic and Kaolinite reduction reactions, may lead to more efficient aluminium production.

The aluminium industry has been trying to develop inert anodes for at least 40 years. Many material options have been examined, particularly titanium diboride, an electrically conducting ceramic. In contrast with the carbon anodes in current use, inert anodes would not be consumed during electrolysis, eliminating both CO<sub>2</sub> and PFC (perfluorinated compound) emissions from carbon anode production and use. Furthermore, because an inert anode would not change shape in use, the separation between the anode and the cathode in the cells could be reduced giving improved energy efficiency. This would require care to avoid short-circuits between the anode (positive terminal) and the liquid metal in contact with the cathode (negative terminal). Two technologies aiming to reduce the chances of such short circuits are wetted drained cathodes<sup>5</sup>, and the anode-tilt system<sup>6</sup>.

Inert anodes could also lead to use of the multipolar cells, shown in Figure 9.7, with many anodes and cathodes in parallel in the same cell. This could increase productivity and electrical efficiency and could allow lower temperature operation of the cell.



### Hlsarna IJmuiden

Hlsarna, a pilot plant for steel production by smelt reduction has been constructed at IJmuiden in The Netherlands. Commissioning has begun and production of up to 60,000 tonnes per year may start by 2020<sup>7</sup>. Unlike the conventional blast furnace the Hlsarna process has two reduction stages: pre-reduction takes place in a cyclone converter furnace and then the final reduction takes place in a bath of molten oxide. Elimination of coke making and sintering steps should reduce the emissions of the Hlsarna process, and in future it could be combined with CCS technology.

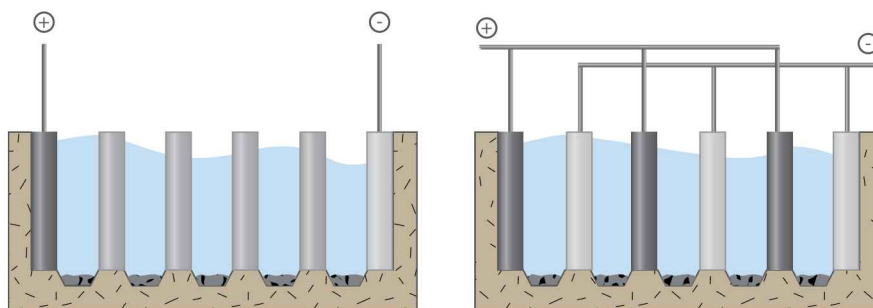


Figure 9.7—Multipolar electrolysis cell

Carbothermic reduction is a two-step process in which alumina and carbon react at around 1900°C to form an alumina-aluminium-carbide mixture, which is passed into a second reactor at about 2000°C, where the aluminium carbide is reduced by alumina to form aluminium. This process, shown in Figure 9.8, will produce more direct CO<sub>2</sub> than the existing route, but requires less electricity so gives an overall reduction in emissions. At present, development is inhibited by the high temperatures required. Alternatively, in Kaolinite reduction, alumina is first converted into aluminium chloride before reduction to aluminium in an electrolysis cell. Kaolinite reduction promises only a small reduction in CO<sub>2</sub> emissions, but can use lower quality ore than the Hall-Héroult process.

Electricity is a major cost in making aluminium, motivating intense research on the novel processes in this section for at least 40 years, yet they are still not ready for operation. It is unclear whether the industry can overcome the problems, so although 15-25% savings in emissions are forecast, we cannot yet plan for their implementation.

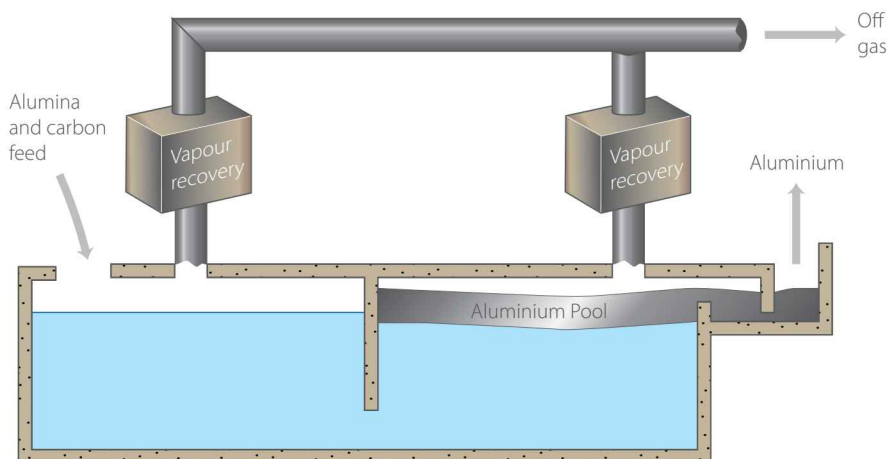


Figure 9.8—Carbothermic reduction



## Powering processes with 'clean' electricity

Both steel and aluminium making consume a lot of electricity. Our emissions would be reduced greatly if we could use 'clean' electricity, generated without emissions. To find out about that, we can turn directly to David MacKay's "Sustainable Energy without the hot air"<sup>8</sup>. Here's our very short summary:



Sheffield in the late 1800s, polluted by steelmaking

- There are many ways to generate energy 'renewably', for example from sunlight, wind, waves, tides, hydropower, plants or algae. All of them produce relatively little energy for a large commitment of land. The key numbers are summarised in Table 9.1 shown against our estimates of the total power use of a country divided by its surface area. To meet the UK's total energy requirements by renewable generation only, our most effective current options are either that we cover a quarter of all our land with solar cells, or that we cover more than half of our land with wind turbines. This won't happen.
- Nuclear power can deliver nearly carbon free electricity and is widely used. The main arguments against expanding nuclear power are that (i) we think it might not be safe, (ii) we will in due course run out of nuclear fuel and (iii) no electricity company can afford to insure a nuclear power plant, so in effect all nuclear electricity is subsidised by government, and the subsidy would be better used elsewhere. David MacKay provides clear evidence that (i) and (ii) are not right so while (iii) is true, it should only be used with a specific second part—where else should that money be spent? It seems that nuclear is probably a very good option for creating nearly carbon free electricity, and we should be very pleased we have the option.

Renewable electricity source	Power per unit area (W/m <sup>2</sup> ) <sup>9</sup>	Country	Energy consumption per unit area (W/m <sup>2</sup> ) <sup>10</sup>
Rain-water	0.2	Australia	<0.1
Plants	0.5	Brazil	<0.1
Wind	2	Canada	0.1
Offshore wind	3	China / USA	0.3
Tidal pools	3	France	0.6
Tidal streams	6	UK / Germany	1.3
Solar PV panels	5–20	Japan	1.9
Concentrating solar power (deserts)	15	World	0.1

Table 9.1—Land requirements for renewable electricity generation

- We discussed the first part of Carbon Capture and Storage (CCS) above for steel making—how do you generate a pure stream of CO<sub>2</sub> from steel making? With exactly the same motivation, developers of electricity generation stations are aiming to create pure streams of CO<sub>2</sub> when burning coal or gas. We'll discuss this further in the next chapter.

So, nuclear power is a mature technology that can be expanded relatively rapidly, Carbon Capture and Storage might be deployed in future but as yet doesn't operate at scale anywhere, and renewable sources are disappointingly intensive in land requirements. Is a nuclear powered materials industry the answer to all our problems? Possibly, but other sectors are banking on nuclear as well. Our map of global energy flow in chapter 2 showed us that nuclear sources currently provide around 6% of global energy or, as it's all used for electricity generation, about 15% of global electricity. If all existing industry were to be powered by nuclear electricity now, that would require a 5 times increase in current capacity. We expect that demand for industrial output will double by 2050, so that increases our nuclear expansion to 10 times. But in addition, guess what the car industry is planning as its low carbon model for the future? Electric vehicles, which of course are only low carbon if the electricity comes from renewables, nuclear or CCS sources, so let's assume that all future vehicles are powered by nuclear electricity, and that their number doubles. And to crown that, our house builders are going to promote ground or air sourced heat pumps as the low carbon solution. In other words, not just all future electricity, but all future energy must come from nuclear power. So if demand doubles, we need to expand global nuclear installation by 32 times in the next 40 years. The world currently has around 422<sup>11</sup> reactors operating, so we need to anticipate about 13,400 reactors by 2050. That requires a building rate of about 320 new reactors per year (in addition to the conversion of all steel plant to new electrical technologies.) This is around 10 times the world's maximum historical construction rate<sup>12</sup>, so is technically feasible but difficult to believe.

So we're carrying on with this book because, although we can envisage a future materials industry powered solely by nuclear electricity, it seems to us unlikely that that will occur as there are so many other sectors competing for the same 'carbon free' electricity. So, let's keep looking for other answers, and when we assemble our forecasts of the future of materials processing in chapters 11 and 19, we'll return to our estimated need for nuclear power.

## Outlook: will these novel processes be adopted?

We've focused on technological possibilities in this chapter so far—to check what sort of brake we need to apply to the idea that incentives lead to innovations. So, now back to the incentives. Will the steel and aluminium industries adopt new processes, CCS or be electrified, and if electrified, will there be enough nuclear power? Can we expect the market to choose the best solution? History tells us that we can't; there are many examples of successful inferior technologies (the QWERTY keyboard on which we're typing this book being the most well known of them)<sup>13</sup>. Such technologies succeed because they get an early foothold in the market. As their market share increases they benefit from economies of scale, achieve cost reductions with experience, benefit from greater publicity and the development of auxiliary technology. These advantages (referred to by economists as increasing returns to scale) amplify the way chance events affect outcomes. In effect what this means is that no single technology can be considered to be best, it can be best only in a particular context but that context is itself affected by the technology chosen. This logic undermines the axioms of neo-classical economics and has motivated economists to turn to evolutionary theory to understand transition<sup>14</sup>. The role of government in this context is, in the words of Brian Arthur the father of complexity economics, “not a heavy hand, not an invisible hand, but a nudging hand”. The trouble is that evolution takes time and we don't have much time however big the nudge.

We've found several developments of novel processes in this chapter, but none offering a 'step-change' and none that are close to mass exploitation. A running theme in the chapter has been the separation of CO<sub>2</sub>, both from the processes of metal-making and from electricity generation. Separating and storing CO<sub>2</sub> is currently a popular option in discussions on responses to climate change. So having looked at separation in this chapter, we need to put on our black suits, turn the page, and set off to the funeral.



## Notes

1. We've done our best to find an original reference for this story, which we've found told in many different forms—always with Napoleon III, but with different visitors, and many different options for the table ware—plates, cutlery, serving dishes that were aluminium and not gold. Our earliest reference is an article in the February 1936 edition of "Popular Science" by Edwin Teale—who credits Napoleon with aluminium forks only, but with giving the King of Siam an aluminium watch fob as a gift. We've used plates, as the most commonly reported bit of tableware—and as our colleagues in the History department tell us that facts are far less important than the way you tell them, let it be plates from now on!

### Novel processes for steelmaking

2. On average we can harvest 1 kg of dry biomass per year for every square metre of land (Vitousek et al., 1986) and we need 10 kg of biomass to make 1 kg of charcoal (Tribal Energy and Environmental Information Clearinghouse, 2011). We've estimated that the UK's 'steel footprint' is around 30Mt and producing this requires 10Mt of coke. To make this coke we therefore need 100Mt of biomass, which is the average product of 100,000km<sup>2</sup>. This is about 40% of the UK, so it's not going to happen. Charcoal does not have the strength to support ore in the blast furnace, so can substitute no more than half our current use of coke. However 'biocoal', a new processed charcoal may have sufficient strength to allow complete substitution (IEA, 2009).
3. According to a recent review of the technical abatement potential in the UK steel sector "Hydrogen-based steelmaking is believed to be technically sound but there remains no sufficiently sized low/carbon free source. Nor does the industry think this likely even with a 2050 time horizon" (Adderley, 2011).
4. These estimates come from an overview of low CO<sub>2</sub> emission technologies for iron and steelmaking by Xu and Cang (2010).

### Novel processes for making aluminium

5. Wetting here refers to the interaction between a liquid and a solid surface. For example, a droplet of liquid on a non-wettable surface will remain as a perfect sphere, whilst a droplet of liquid on a wettable surface will spread out to form a thin layer, as shown in Figure 9.9. In wetted drained cathodes, new materials are used to make the surface of the cathode more wettable so that the liquid aluminium formed during electrolysis spreads more uniformly and so the anode-cathode distance can be reduced.

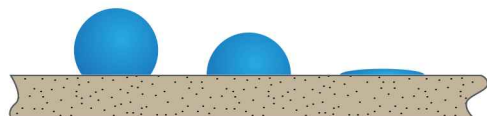


Figure 9.9—Wettability

6. Movement of the fluids and equipment within an electrolysis cell causes a wave to ripple through the liquid aluminium as it forms at the bottom of the cell. The distance between anode and cathode must therefore be sufficient that the wave of aluminium does

not cause a short circuit. The anode-tilt system aims to avoid this problem, by tilting the anode in phase with the wave in the liquid aluminium, as shown in Figure 9.10.

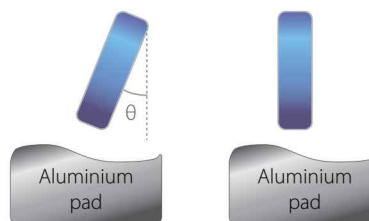


Figure 9.10—Anode tilt system

### Powering processes with 'clean' electricity

7. The current status of the Hlsarna pilot plant is described in a Tata news release (Tata, 2011b)
8. David MacKay's (2009) book, like ours, is published by UIT press, and also available on-line for free at [www.withouthotair.com](http://www.withouthotair.com).
9. This table comes from David MacKay's analysis on renewables (Table 25.1) (MacKay, 2009).
10. The power per unit area is equal to each country's energy use in 2008 from the U.S. Energy Information Administration (2011) divided by the land area as reported in Table 3 of the United Nations Statistics Division's Demographic Yearbook (2008). The electricity consumption of the countries in the table accounts for 70% of global electricity consumption.
11. The European Nuclear Society reports that as of 19th January 2011, there were 422 nuclear reactors in operation and 65 under construction.
12. David MacKay estimates that the world's maximum historical construction rate of nuclear reactors was in 1984, when 30GW of nuclear power was completed, or 30 1GW reactors. (MacKay, 2009) page 171.

### Outlook: with these novel processes be adopted

13. Other examples of successful inferior technologies quoted in Arthur (1989) include the alternating current, the narrow gauge of British railways and the programming language FORTRAN.
14. See Arthur (1999) for an explanation of complexity economics.
15. Parts of these graphics have been adapted from World Steel Association images