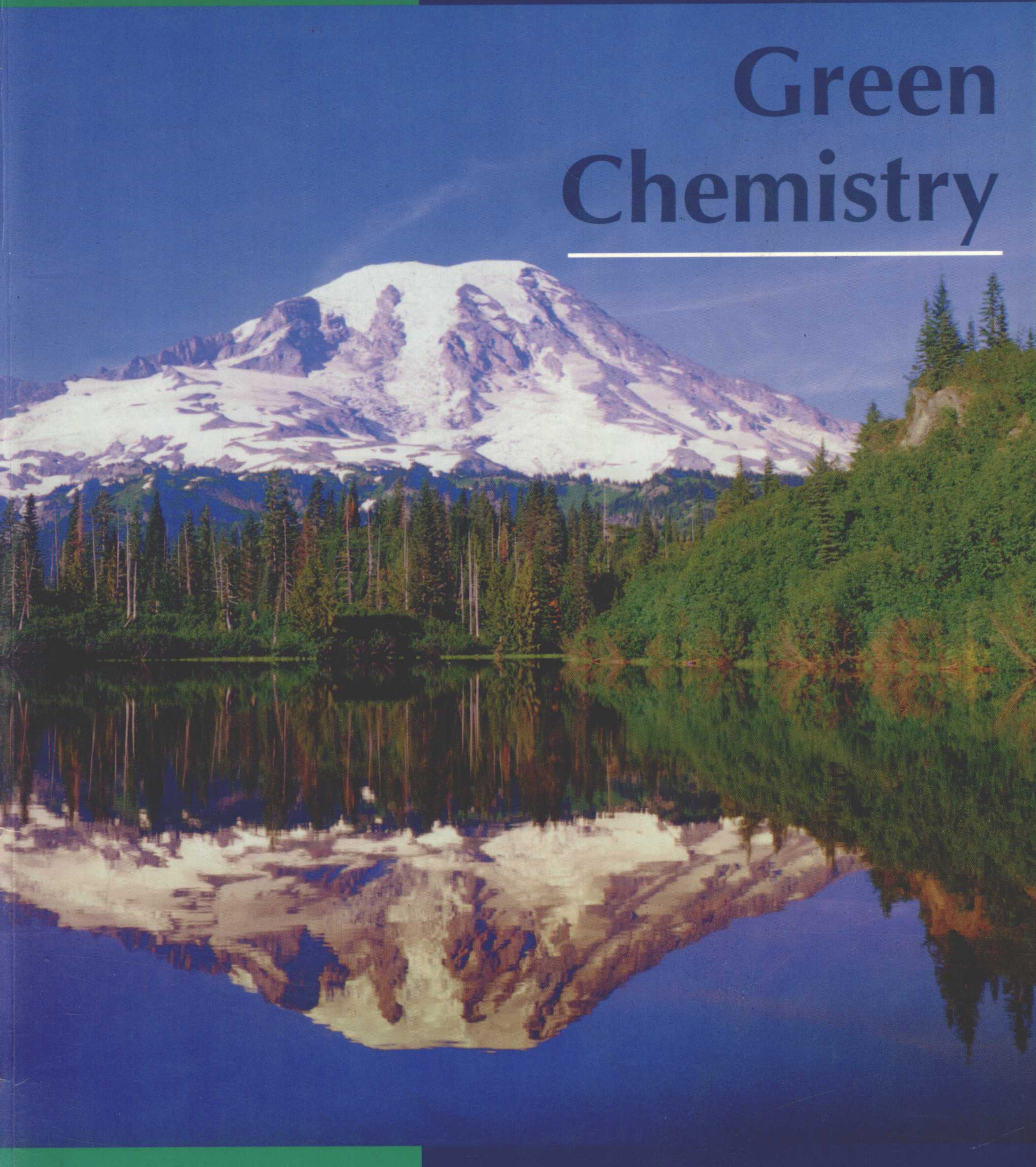
Green Chemistry



This resource outlines areas for the teaching of green and environmental chemistry and sustainable development for 11-19 year old students.

Dorothy Warren

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ROYAL SOCIETY OF CHEMISTRY

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Written by Dorothy Warren
RSC School Teacher Fellow 1999–2000

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Written by Dorothy Warren

Edited by Colin Osborne and Maria Pack

Designed by Imogen Bertin

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Robert Turner Eaton

This resource was produced with the help of a donation from the estate of Robert Turner Eaton, CChem FRSC, a member of the Royal Society of Chemistry since 1936.

Robert Eaton started his working life with British Celanese in Derby and studied for his degree at night school. He gained a BSc in Chemical Engineering as a London University external student through Nottingham University.

He spent most of his working life with the Royal Ordnance Factories (now part of BAe Systems) at various sites throughout the country manufacturing explosives, weapons and ammunition, and, after the war, concrete railway sleepers.

After a spell with the Ministry of Defence in London he finished his working life as HM Second Inspector of Explosives.

He would have appreciated this resource as he took a great interest in education, taking his daughter with him to chemistry lectures as well as continuing to give his firework safety lecture to children at a local Junior School even in his 86th year.

Elizabeth Eaton
David Eaton

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Foreword

In recent years there have been dramatic improvements in the processes used in the chemical and pharmaceutical industries to reflect both society's concern for the environment and the increased regulatory pressure placed on the industries. These improvements have not been reflected in the science curriculum taught to young people in schools and colleges and consequently the image of the industries is not what it might be. The Royal Society of Chemistry and the Green Chemistry Network at the University of York are concerned to provide a balanced view of the successes and failures of the chemical and pharmaceutical industry. Thus the Society is delighted to be able to provide the up-to-date information for teachers and students contained in this resource. The processes included are those commonly taught at GCSE and Standard grade and it is hoped that the material will enable teachers to show students that chemists are continually searching for ways to make the materials society needs in a more environmentally friendly way.

Professor James Clark CChem FRSC
Director, Green Chemistry Network, University of York

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Using this publication on the web

The student worksheets may be downloaded from

http://www.chemsoc.org/networks/LearnNet/green-chem.htm

as .pdf files and as Word files that can be adapted by teachers.

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Green Chemistry and sustainable development

Introduction

Education for sustainable development is about the learning needed to maintain and improve our quality of life and the quality of life for future generations. It is also about educating students and the general public so that future generations have a world to live in that can provide the required material resources. So minimising the use of raw materials by recycling is encouraged. It is also about making sure that the environment is not polluted and learning about the social and economic issues this involves. Education for sustainable development is now part of the school curriculum and can it be delivered across several subject areas.

Green Chemistry is chemistry for the environment. It was first defined by the US Environmental Protection Agency as 'the utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products'. In other words, Green Chemistry is really a philosophy and way of thinking that can help chemists in research and production to develop more eco-friendly and efficient products and processes. The phrase 'Green Chemistry' is now accepted internationally and it should be pointed out that it has nothing to do with politics. For some chemists in European countries this has been a sticking point.

If Green Chemistry is to succeed then it is important that the principles are known, understood and implemented in industry. Therefore, we must start teaching the basis of the principles of Green Chemistry at school. A large section of the teachers' notes contain background information about Green Chemistry and indicate where it can be included in the curriculum. Several of the reactions taught in post-16 courses have now been 'greened', and in practice the original processes are no longer carried out in industry. Under sources of information there is a list of journals and websites which contain up to date articles on Green Chemistry.

The student activities **Aluminium extraction** and **Investigating the life cycle of poly(ethene)** are designed to be integrated into current schemes of work, rather than to be used out of context. The Green energy activities will help the students to focus on alternative sources of energy and sustainability. The third set of student activities is based around air pollution and offers the opportunity to carry out practical and Internet investigations. The final activity involves finding a suitable fuel for future cars, which will be both environmentally friendly and economical to produce.

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Green Chemistry

Teachers' notes

Objectives

- To know the principles of Green Chemistry and be able to apply them to industrial processes.
- To understand why Green Chemistry is important in modern day life.

Outline

This resource contains the following sections:

- Background information on Green Chemistry that will enable teachers to update their own knowledge.
- A life cycle analysis study of poly(ethene). The students must decide upon the 'greenest' cycle.
- A problem solving exercise: How to extract the fictitious metal, tabbium, from its ore, tabcite. This follows a study of aluminium extraction.

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Background information

The Twelve Principles of Green Chemistry[1]

1. **Prevention**
   It is better to prevent waste than to treat or clean up waste after it has been created.

2. **Atom economy**
   Synthetic methods should be designed to maximise the incorporation of all materials used in the process into the final product.

3. **Less hazardous chemical synthesis**
   Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to people or the environment.

4. **Designing safer chemicals**
   Chemical products should be designed to effect their desired function while minimising their toxicity.

5. **Safer solvents and auxiliaries**
   The use of auxiliary substances (*eg* solvents or separation agents) should be made unnecessary whenever possible and innocuous when used.

6. **Design for energy efficiency**
   Energy requirements of chemical processes should be recognised for their environmental and economic impacts and should be minimised. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. **Use of renewable feedstocks**
   A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. **Reduce derivatives**
   Unnecessary derivatization (use of blocking groups, protection/de-protection, and temporary modification of physical/chemical processes) should be minimised or avoided if possible, because such steps require additional reagents and can generate waste.

9. **Catalysis**
   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. **Design for degradation**
    Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. **Real-time analysis for pollution prevention**
    Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. **Inherently safer chemistry for accident prevention**
    Substances and the form of a substance used in a chemical process should be chosen to minimise the potential for chemical accidents, including releases, explosions, and fires.

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The twelve principles of Green Chemistry are listed above and cover such concepts as:

- the design of processes to maximise the amount of raw material that ends up in the product;
- the use of safe, environmentally-benign solvents where possible;
- the design of energy efficient processes; and
- the best form of waste disposal – aiming not to create waste in the first place.

Much of this seems like common sense, but when you look at many recent industrial processes or academic research, you will see that until very recently many of these things were principles that were not really considered. However, there is now a move towards clean technology and part of the driving force towards this goal is through social and legislative pressure. Chemists are also now realising that many green processes are actually cheaper than other methods because of reduced waste disposal. Green Chemistry does not necessarily mean expensive chemistry.

The principles of Green Chemistry have been explained and illustrated in an article by Mike Lancaster[2], which is reproduced at the end of this section. Some of the examples quoted, such as the Friedel-Crafts reaction and the nitration of aromatic components appear in many post-16 courses.

For further information visit the Green Chemistry website
http://www.chemsoc.org/networks/gcn/ (accessed March 2001)

You can join the Green Chemistry Network, which is based at the University of York, via the website. The Green Chemistry journal, which contains articles of general interest as well as academic papers, can be accessed online.

The most important principle is that of prevention. If toxic waste is not made in the first place, then it will not have to be cleaned up. It should be noted that 'recycling' is not really a Green Chemistry principle, as it assumes that there is waste. So, for example, recycling of plastics, aluminium or steel is not Green Chemistry, but sustainable living. However, the recycling of waste compounds at the end of a synthesis, instead of them being thrown away, would be classified as Green Chemistry.

In 1989, the Chemical Industries Association (CIA) set up the Responsible Care Programme, which is the industry's commitment to continual improvement in health, safety and environmental performance and openness in communication about its activities. The emphasis is on safety and environmental performance, because these issues are important to employees, neighbours and the wider public. The public's perception of the industry is largely based upon environmental issues. There are now 46 countries signed up to Responsible Care, which accounts for 86% of the world's production of chemicals.

The Responsible Care Programme is built around eight specific elements, which include Product Stewardship, Confidence in Chemicals and Partnerships down the supply chain. The programme is managed from the top downwards, which means that the guiding principles of having a rigorous health, safety and environmental policy are implemented as well as the company's commitment to sustainable development.

Product Stewardship addresses the challenge of managing the risks of existing products and developing new products with even lower environmental impact. The process requires a structured approach to hazard and risk assessment. Confidence in Chemicals is concerned about the control and use of some chemicals. There is growing pressure to impose tighter restrictions on the use of some substances and in some cases even the call to ban them. Partnerships down the supply chain means a commitment to health

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and safety and communication, for example with product distributors and all those involved with the chemical industry. It means that the work done at one level will not be undone at another level.

Teaching Green Chemistry in schools and colleges

By the time many students reach secondary education, they will already have formed an image about science and the chemical industry. For many that the image is not a good one. For some students the chemical industry will only be seen as a major polluter and producer of toxic waste. This perception and the portrayal of the industry in the media may have contributed to the decline in the percentage of undergraduates taking chemistry degrees over the past decade. Green Chemistry promotes an opportunity to readdress some of those images. It offers an education for sustainable development, which now has a place in the school curriculum. For chemistry to be an attractive subject in the 21st century we should give a balanced view by discussing the following issues at school and with the public in general:

- Chemistry plays an integral part of our lives. Chemistry in all around us in the clothes we wear, the food we eat and the buildings we live in *etc.*
- Chemistry is here to stay, whether we like it or not.
- We need well-qualified and creative chemists to maintain and develop our quality of life.
- In the future non-renewable hydrocarbon feedstocks will be depleted, so chemists need to find new renewable feedstocks, such as plants. Chemists are working to find new and cleaner methods of making many products such as plastics and pharmaceuticals.
- In the past, chemistry has caused many environmental problems.
- The chemical industry is now trying to address some of these issues by applying The Twelve Principles of Green Chemistry.
- The consumer market place often drives the chemical industry by buying certain products. If a product doesn't sell then it is discontinued; if it sells well then more is produced.
- As consumers we have a choice as to which products to buy. This in turn will have an influence on the chemical industry. Often people complain, for example, that 'environmentally friendly detergents' are expensive. If more people bought the product then production would go up and the price would go down.
- The success or failure of the Green Chemistry industry will be decided by industry and so it is important to teach people about the principles. Legislation of international agreements have their part to play as well, as has social pressure. It should be pointed out that Green Chemistry is apolitical.

Green Chemistry in the curriculum

At first it may appear that there is not much room in the curriculum for Green Chemistry, mainly because the phrase is not mentioned. However, on closer examination there are many opportunities to introduce the principles. Listed below are some suggested examples as to how some of the principles could be introduced:

- Metal extraction processes – aluminium, iron
- Industries that burn coal
- Preventing acid rain

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- Production of ammonia
- Manufacture of chlorine
- Polymerisation
- Waste management

Metal extraction processes

Energy efficiency improvements have been important for the extraction of both aluminium and iron from their ores.

Aluminium

Many aluminium extraction plants have been placed next to cheap hydroelectric power (HEP) sources in countries such as Norway. As well as greening the process, it makes economic sense. The process is greener, because HEP is a renewable energy source, and does not emit any carbon dioxide into the atmosphere. Carbon dioxide is, of course, a greenhouse gas and plays a key role in global warming. Under the Kyoto agreement, Box 1, developed nations must find ways of reducing CO_2 emissions. However, not all aluminium extraction plants use renewable energy supplies. Some plants continue to buy electricity made from fossil fuels, because they find it is more convenient and essentially the same price as buying from renewable sources.

The Kyoto agreement **Box 1**

'The Kyoto agreement represents a historic and unprecedented step to reduce the threat of global warming in an environmentally strong and economically sound way. It involves 160 nations, and recognizes the crucial importance of specific steps to address climate change.'

The agreement was the result of continuing talks between the participating nations during the period 1992–1997. Discussions are still going on as the agreement is examined and loopholes are discovered.

The target for the UK is to reduce the 1990 levels of CO_2 emission by 12% by 2010, although the government would like to see it reduced by 20%. Also by 2010, 10% of the energy supplied to European countries will have to come from renewable sources. This is part of the non-fossil fuel obligation. The driving force for this agreement is not only the threat of global warming, but also the recognition that fossil fuel feed-stocks will soon become depleted if consumption continues at current rates.

When Hans Christian Oersted first extracted aluminium in 1824, he used potassium amalgam to reduce aluminium chloride. Only a small amount of the impure metal was produced. Over the next thirty years various scientists worked hard to find a better way of extracting the metal. The reduction method developed as potassium amalgam was replaced by pure potassium, which was subsequently replaced by sodium. The quality and quantity of aluminium produced improved with each method. At this time aluminium metal was thought of as a very precious metal. It was not economically viable to produce aluminium on an industrial scale using these methods, which also had various known risks and hazards associated with them. Pure potassium, sodium, potassium amalgam and chlorine (used in the production of aluminium chloride) all can cause harm to human health and the environment. During the experiments the risk of explosion or of laboratory equipment catching fire was high. It was in 1886 that aluminium was first extracted by electrolysis by Charles Hall of the USA and Paul Heroult of France. Independently of each other, they both discovered that you could obtain a solution of aluminium oxide by dissolving it in molten cryolite (sodium hexafluoroaluminate(III)) at 700 °C. Then, by passing electricity through the solution, aluminium was made. The Hall-Heroult cell is still used today. Aluminium extraction

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by electrolysis brought a safe and easy way of producing good quality aluminium. Aluminium production was still relatively expensive because of the high temperatures involved but because aluminium possessed some attractive properties such as low density, high tensile strength and resistance to corrosion, there was a market for aluminium metal. The high demand for aluminium meant that production levels grew creating a large and successful industry.

The history of aluminium production[3] can be used to illustrate some of the Green Chemistry principles, such as prevention, less hazardous chemical synthesis, reduced derivatives, real-time analysis for pollution prevention, inherently safer chemistry for accident prevention and more recently design for energy efficiency and, in some plants, use of renewable feedstocks of energy supply. However, it must be pointed out that in the 19th century, people were not concerned about the effect of the extraction method upon the environment, but rather the quality and quantity of aluminium and its production cost. It just happens that in this case, the method of extraction became greener as it developed. Green Chemistry was not the driving force for adopting the electrolysis method of extraction in favour of the reduction method.

The student activity, **Aluminium extraction**, presents students with the history of aluminium extraction as it happened. The students are then encouraged to discuss the environmental issues surrounding the development of the method.

Iron

The extraction of iron has seen many improvements to reduce energy consumption. Such measures include oxygen enrichment and preheating of the blast, use of hydrocarbons as auxiliary fuels, operating the furnace at a higher pressure, minimising the use of limestone and preparation of the raw materials to improve their chemical, physical and metallurgical properties so that the chemical process can take place more rapidly in the furnace, with the least amount of fuel. In the production of steel the move from casting in ingots to continuous casting has provided a significant saving in energy (up to 3.0 kJ/tonne of finished product). In the UK 88% of steel is continuously cast and world production of continuously cast iron is running at about 78%.

Over the last thirty years Corus (formally British Steel) has taken measures to reduce emissions, lowering air pollution.

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Box 2

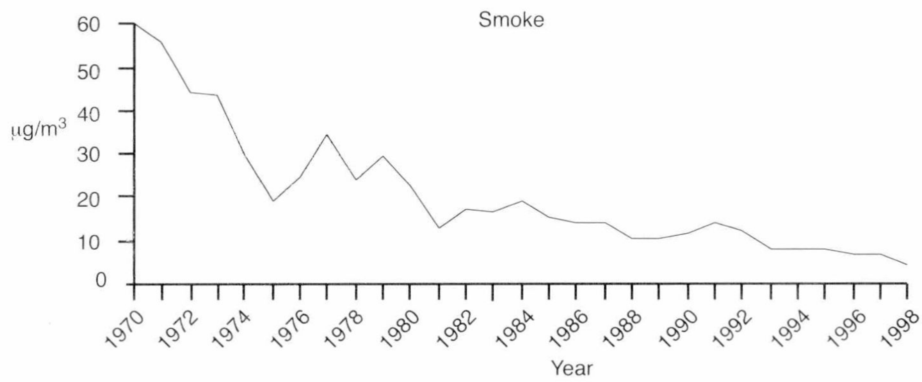

Figure 1 Smoke measurements at Scunthorpe Works perimeter (© Corus UK Limited, 2000)

The level of smoke pollution has been cut by more than 50% since 1970. This is mainly due to the introduction of new methodology and a new coal charging system. The apertures on the ovens are automatically cleaned and sealed thus preventing air pollution.

Box 3

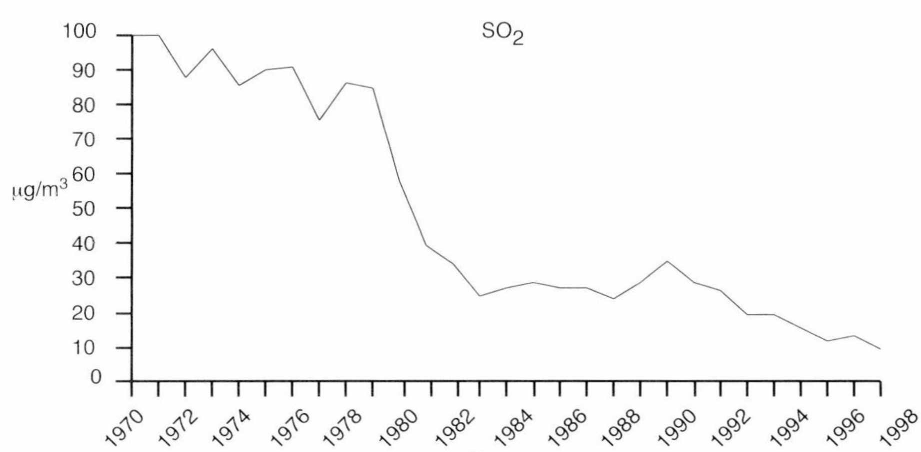

Figure 2 Sulfur dioxide (SO_2) measurements at Scunthorpe Works perimeter (© Corus UK Limited, 2000)

Low sulfur dioxide levels at Scunthorpe have contributed to long term reduction in atmospheric concentration. Like coal-fired power stations, the steel industry has had to find ways of reducing their sulfur dioxide emissions.

Both aluminium and steel are recycled on a large scale, which not only saves raw materials and energy used in the extraction process, but reduces waste, which otherwise may end up in landfill. Only 5% of the energy required to extract aluminium from bauxite is needed to recycle aluminium and only 1.1% of aluminium goes to landfill. Recycling steel saves 50% of the energy consumed in the extraction of iron and also cuts down on greenhouse emissions. About 41% of the world

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production of steel comes from recycled materials. During the recycling of steel food cans the layer of tin is removed, separated and reused.

Industries that burn coal and desulfurisation

Coal-fired power stations and other industries that burn coal have had to take measures to control sulfur dioxide emissions.[4] All coal contains some sulfur, as coal was formed from living things. Even coal with the lowest levels of sulfur (less than 1%) still produces significant amounts of sulfur dioxide *eg* burning 1000 tonnes of coal in an hour will produce up to 20 tonnes of sulfur dioxide an hour.

It is not practical to remove sulfur from the coal before it is burnt so the other options are to remove sulfur dioxide as it is formed and to remove sulfur during combustion. Technologies to achieve the latter have been developed, but few have achieved wide commercial application, partly because the success of the technology is still not yet proven. They include Fluidised Bed Combustion (FBC) and the Integrated Gasification Combined Cycle (IGCC).

Flue gas desulfurisation is widely used and this can remove about 90% of the sulfur dioxide. There are several different methods for removing sulfur dioxide, but it should be pointed out that sometimes when one problem is solved another one is formed. All factors need to be considered and taken into account. The solution is not always straightforward. Often reasons for choosing a particular method maybe be determined by economics or the position of the industrial site.

a) Reaction with calcium carbonate (limestone)
to produce calcium sulfate(IV) which is then oxidised to calcium sulfate(VI) (gypsum) and used in the production of cement and plaster.

$$2CaCO_3 + 2SO_2 + H_2O \rightarrow (CaSO_3)_2.H_2O + 2CO_2$$

$$(CaSO_3)_2.H_2O + O_2 + H_2O \rightarrow 2CaSO_4.2H_2O$$

The problem with this method is that it produces more carbon dioxide, which is another gas that needs to be controlled and it uses large quantities of another raw material, namely calcium carbonate (limestone). However, if there was a nearby market for the gypsum then it could be quite profitable.

b) Reaction with calcium hydroxide (slaked lime)
is known as 'spray dry absorption' because the flue gases are mixed with a spray of calcium hydroxide and water. The alkaline droplets absorb the acidic gas and the water is evaporated.

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$$

$$CaSO_3 + {}^1/_2\,O_2 \rightarrow CaSO_4$$

The gypsum produced by this reaction is not as pure as that produced by the previous reaction; therefore it is not as marketable. Much of it is buried in landfill sites. Carbon dioxide is still a problem because the calcium hydroxide (slaked lime) is produced from calcium carbonate (limestone) by heating and adding water.