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**Environmental Chemistry Group** 

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# **Bulletin**





#### In this issue

The Diamond Light Source in South Oxfordshire on the Harwell Science and Innovation Campus is the largest UK-funded scientific facility to be built for over 30 years. The machine is a third generation synchrotron, combining three particle accelerators which accelerate electrons up to close to the speed of -rays generated by the Diamond light inside a storage ring (pictured courtesy of Diamond Light Source Ltd ) - over 560 metres in circumference. Accelerator-based synchrotron light was seen for the first time in 1947. By the 1960s, the exceptional properties of synchrotron

light, which can be produced over the entire range of the electromagnetic spectrum, were recognised. At the Harwell facility, these properties are being used to study a range of materials from proteins to engineering components. On pp 3-10 of this issue, **Imad Ahmed** explains how X Light Source are used to unravel the pathways for the formation of a highly reactive and potentially useful environmental material, green rust.

#### **Also**

Professor James Harrison, the ECG Distinguished Guest Lecturer for 2010, describes the impact of new coal technologies on efficiency savings in ironmaking and in energy production. And Royal Society of **Chemistry** initiatives in promoting the role of the chemical sciences in solar fuel and in energy storage technologies are reported.



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# **Environmental Chemistry Group**

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The RSC's Environmental Chemistry Group (ECG) considers all aspects of the complex relationships between chemistry and the environment. The ECG aims to understand the behaviour of chemical species in the water, soil and atmospheric environments; exploring their sources, reactions, transport and in particular their effects on each of these environments.

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### In situ studies of green rust formation using synchrotron-based X-ray scattering. Helping to develop a new range of environmental materials

The natural environment is rich in nanoparticulate mineral phases, such as iron and manganese oxides and oxyhydroxides, with unique chemical properties. Some of these minerals, for example Green Rusts, have the potential to be developed into a new generation of environmental remediation materials which could be utilized to clean up contaminated land. Advances in X-ray technologies at third -generation synchrotron sources (e.g. the Diamond Light Source) have helped to characterise the formation and crystallisation of highly reactive nanoparticles under simulated environmental conditions. In this article, Dr. Imad Ahmed, Dr. Sam Shaw, Ms. Gabriella Kakonyi and Prof. Liane G. Benning, describe how stateof-the-art in situ time-resolved synchrotron-based scattering and diffraction methods are used to determine the mechanisms and kinetics of green rust nanoparticle formation and growth.

#### Introduction

exploited in a number of remediation technologies including tion (~80%) in trichloroethene (TCE) groundwater concen-

zero valent iron (ZVI) Permeable Reactive Barriers (PRB). In these systems, ZVI is used as a barrier where a large The remediation of contaminated land often requires the use trench is dug at the edge of a contaminated land site to interof technologies (e.g. permeable reactive barriers or soil cept contaminated groundwater moving from the site. Redox washing techniques (BHANDARI et al., 2007)) to clean up -active contaminants such as U<sup>6+</sup> and Cr<sup>6+</sup> are reduced as pollution caused by the legacy historical industrial activities they interact with the Fe<sup>0</sup> into less soluble and bioavailable (e.g. mining, chemical manufacturing etc.). The bioavailabil- forms (e.g.  $UO_2^{2+}$  to  $UO_{2(s)}$ ). In recent years, a large amount ity and toxicity of many contaminants in the environment are of research has also focused on the use of nanoparticulate controlled by their redox state. For example,  $CrO_4^{2-}$  (i.e. remediation strategies, where the materials (e.g. nano-ZVI) Cr<sup>6+</sup>) is highly soluble and poses a significant threat to the are injected into a polluted subsurface aquifer (Figure 1) environment, whereas Cr3+ is highly insoluble and poses a then move into the contamination plume and reductively much reduced hazard. The reduction of redox-active inor- decontaminate the groundwater (ZHANG, 2003). For examganic and organic species for decontamination purposes is ple, field trials in Florida (USA) reported significant reductrations upon the injection of nano-ZVI (QUINN et al., 2005). The development of nanoparticles based remediation techutilized in the environment.

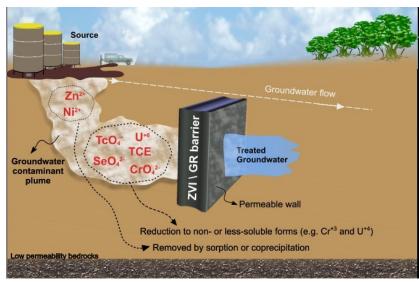


Figure 1: Permeable Reactive Barrier System: ZVI/GR to remove inorganic and organic contaminants from groundwater.

#### What is green rust?

The Green Rust (GR) family of compounds have been suggested (RUBY et al., 2006b) as potential materials for use in reductive remediation technologies. The name green rust relates to their colour and formation from corroding iron. GR's are mixed Fe<sup>2+</sup>/Fe<sup>3+</sup> solid compounds with a Layered Double Hydroxide (LDH) structure. Each layer in the GR crystal is positively charged and composed of edge-sharing octahedrally coordinated Fe<sup>2+</sup> and Fe<sup>3+</sup> forming hydroxide sheets, which are intercalated with negatively charged anions and water molecules (Figure 2). GR's have the general chemical formula:

$$\left[\operatorname{Fe}_{(1-x)}^{2+}\operatorname{Fe}_{x}^{3+}(\operatorname{OH})_{2}\right]^{x+}.\left[(x/n)A^{n-}).m\operatorname{H}_{2}\operatorname{O}\right]^{x-}$$

nologies relies on the manufacture of materials which have where  $x = Fe^{3+}/Fe_{total}$ ,  $A^{n-}$  denotes interlayer anions whose suitable chemical and physical properties which allow them charge is n, and m is moles of intercalated water molecules. to adequately disperse within the contaminated plume and Various types of anionic species can be intercalated in the effectively remediate the contamination. Here we present GR structure including SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, formate, and lacresearch into green rust nanoparticles which have the potentate (DRISSI et al., 1995; REFAIT and GÉNIN, 1993; SABOT et tial to be utilized for environmental cleanup. However, their al., 2007; SUMOONDUR et al., 2009). Sulphate- and carbonhighly reactive nature makes them difficult to study using ate-containing GR (GRSO<sub>4</sub> and GRCO<sub>3</sub>, respectively) are conventional techniques. Therefore we have developed a among the most studied forms, and have been found to occur new synchrotron-based approach to studying the formation in a number of natural (e.g. hydromorphic soils) and engiand stability of green rusts under the conditions they may be neered environments (e.g. corrosion of steel in seawater, OLOWE and GENIN, 1991). In these environments, green

> rusts (also known by its mineral name 'fougerite', GÉNIN et al., 2001) tend to form at the interface between the oxic and anoxic zones where both Fe2+ and Fe3+ can coexist leading to the formation of mixed oxidation state compounds.

Recent research has shown that the presence of highly reactive Fe2+ within the GR structure gives these materials a large capacity to reduce a variety of mobile inorganic and organic contaminants (LEGRAND et al., 2004; MYNENI et al., 1997; O'LOUGH-LIN et al., 2003). The reduction of inorganic species leads, in many cases, to the formation of highly insoluble

phases that are non-mobile and less bioavailable in the environment. For example, GR has been shown to reduce the soluble uranyl ions (UO22+ ) into insoluble UO2(s) nanoparticles (O'LOUGHLIN et al., 2003). Also, the reductive transformation of chlorinated hydrocarbons (e.g. TCE and DCM) leads to dechlorination and breakdown of these toxic pollutants (O'LOUGHLIN and BURRIS, 2004). Other examples pertaining to the reductive potential of GR materials are summarised in Figure 3. These unique redox properties make GR a potential candidate for use as a 'reactive redox barrier' material for environmental prevention and cleanup technologies such as PRB systems.

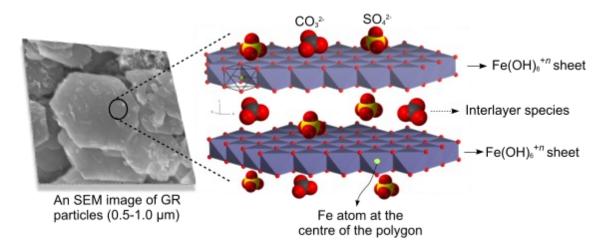


Figure 2: Scanning Electron Microscopy (SEM) photomicrograph of GR particles and schematic drawing for the layered structure of GR with interlayer containing water and anionic species such as carbonate, sulphate and chloride.

Due to their high Fe2+ content, GR's are highly reactive re- crystalline and usually highly sensitive to physicochemical great difficulties in handling, sampling and characterizing mation and transformation of GR. these phases. Similar to other highly redox-reactive phases such as mackinawite (nominally "FeS"), characterization of GR using conventional ex situ techniques such as X-ray powder diffraction (XRD) and infrared spectroscopy requires sample pre-treatment procedures (e.g. drying, freeze-drying and washing)  $CO_{2(s)}$ is difficult. We found that GRSO4 can oxidize during ageing for several days in an H<sub>2</sub>/N<sub>2</sub>-

-sensitive GR via conventional ex situ techniques challenging, time consuming and in some cases inaccurate. In addition, identification of short-lived (minutes to hours) precursors or intermediate phases in any reaction is even more challenging using traditional ex situ methods. This is often because the precursors/ intermediates are either amorphous or semi-

glove box with an O₂ content as low as ≤

0.005%. This makes studying the formation,

transformation pathways and the stability of air

ductants, but this also means that they transform into ferric changes in the reacting solution (e.g. pH, redox potential or phases (e.g. goethite) within minutes of exposure to air. This mixing rates). In the next section, we describe a novel in situ reactivity caused GR's to go unnoticed in many natural and approach for studying the formation and transformation of geo-environmental systems for many years, and leads to highly reactive phases, and its use in characterising the for-

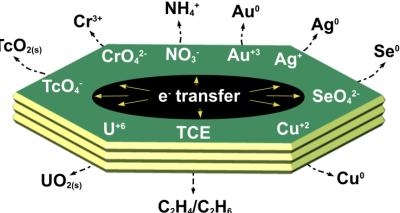
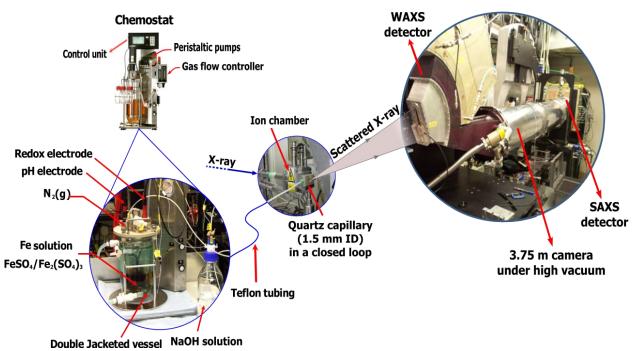


Figure 3: Schematic drawing summarizing reactions in which GR acts as a reductant for redox-reactive contaminants. The contaminants are transformed into less mobile (or soluble) and less toxic forms while GR oxidizes into ferric solid phases (e.g. goethite).

# Characterisation of GR using *in situ* X- tions. The solutions or dilute suspensions were constantly circulated through a closed loop consisting of a quartz capillary (1.5 mm ID, 10 mm well) connected to the reaction were

To overcome the difficulties of studying GR, we developed a synchrotron-based in situ approach for characterizing the formation of air sensitive nanoparticles. This approach makes use of a chemostat reactor combined with in situ time resolved X-ray scattering measurements. The Small- and Wide angle X-ray Scattering (SAXS/WAXS) experiments were carried out on beamline station MPW6.2 of the Synchrotron Radiation Source (SRS), Daresbury Laboratory, UK and beamline I22 of the Diamond Light Source (DLS), Oxford, UK. The WAXS measurements collected at scattering angles > 5° provides data on the intramolecular and interatomic correlations for crystalline or semi-crystalline structures. The SAXS (scattering angle  $< 5^{\circ}$ ) data provides information on larger features (as large as ~ 200 nm) in solid samples and thus it is a useful technique in studying ordering on the meso- and nano-length scales, such as particle size and morphology. Figure 4 shows a schematic diagram of the experimental setup. A chemostat system, which allowed precise control and measurement of pH and redox potential (Eh) was used to synthesise the GR under anaerobic condi-

tions. The solutions or dilute suspensions were constantly circulated through a closed loop consisting of a quartz capillary (1.5 mm ID, 10  $\mu$ m wall) connected to the reaction vessel via Teflon tubing. The quartz capillary was aligned with the synchrotron X-ray beam ( $\lambda = 1.0$  Å) allowing collection of time-resolved WAXS and SAXS data at selected time interval (typically 120 sec), for up to 18 hours. This was done simultaneous with the time resolved monitoring of the chemical data (i.e. pH, redox potential (Eh) and volume of reactants added, which were recorded via an automated control unit attached to the chemostat system. As shown in **Figure 4**, the WAXS detector was positioned to cover a wide angular range of  $5-65^{\circ}$  from normal to the X-ray beam. The SAXS detector positioned to collect data at  $\leq 5^{\circ}$  and was positioned at the end of a 3-8 meter camera under vacuum.



**Figure 4:** Schematic diagram of the experimental setup used for the synthesis of GR and the simultaneous collection of electrochemical and WAXS/SAXS data. The contents of the double jacketed reaction vessel were constantly circulated through a quartz capillary mounted in-line with the incident synchrotron X-ray beam.

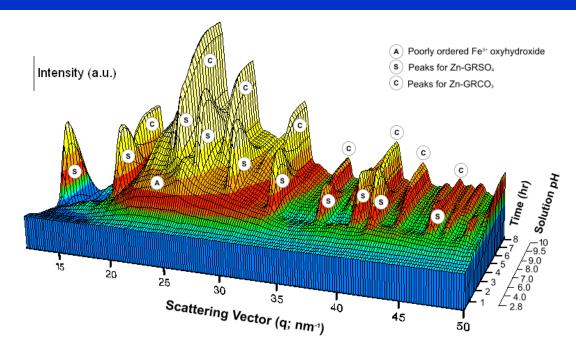


Figure 5: Time resolved Wide Angle X-ray Scattering data showing the formation of Zn-containing GR. Characteristic peaks of Zn-GRSO<sub>4</sub> appear at pH 6.9 and these are completely replaced by Zn-GRCO<sub>3</sub> peaks at pH > 9.5. After Ahmed et al., (2008).

#### Formation of green rust

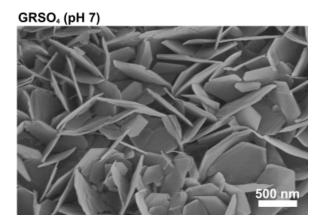
Green rust was synthesised by induced hydrolysis under strict anoxic conditions. The reaction was initiated by the progressive addition of a basic solution to a solution containing dissolved Fe<sup>2+</sup> and Fe<sup>3+</sup>. Different GR forms can be synthesised using this approach. For example, GRSO<sub>4</sub> was synthesised by mixing Fe<sup>2+</sup> and Fe<sup>3+</sup> sulphate and adding NaOH. If Na<sub>2</sub>CO<sub>3</sub> was used instead of NaOH, GRSO<sub>4</sub> formed at pH < 8.5, and was transformed completely into GRCO<sub>3</sub> at pH above 9.

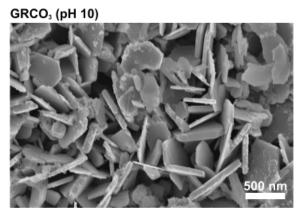
Zn-containing GRSO<sub>4</sub> (Zn-GRSO<sub>4</sub>) and GRCO<sub>3</sub> (Znoxyhydroxysulphate; Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>4.5</sub>(SO<sub>4</sub>)<sub>1.75</sub>) was a precursor nanoparticles. This initiates an electron transfer between the

of Zn-GRSO<sub>4</sub>, which formed at pH 6.9 - 9.5 (Figure 5). Beyond pH ~8.3, HCO<sub>3</sub><sup>-</sup> (from the addition of Na<sub>2</sub>CO<sub>3</sub>) dissociated into CO32- and exchanged for the intercalated SO<sub>4</sub><sup>2-</sup> in the interlayer of Zn-GRSO<sub>4</sub>, leading to the formation of Zn-GRCO<sub>3</sub>.

As shown in Figure 6, both GRSO<sub>4</sub> and GRCO<sub>3</sub> (freshly synthesised by coprecipitation) exhibit hexagonal plate-like particle morphologies with an average edge length of ~250 nm. However, GRCO<sub>3</sub> possesses almost three times the thickness (~ 80 nm) of GRSO<sub>4</sub> (AHMED et al., 2008).

GRCO<sub>3</sub>) phases were synthesised by coprecipitation follow- In a more recent paper (AHMED et al., 2010), we demoning the method described by Ahmed et al., (2008). A 3D strated that schwertmannite (~ 5 nm) and nanogoethite (< 50 representation of the time-resolved WAXS patterns from the nm) precede the formation of GRSO<sub>4</sub>. Schwertmannite experiment forming Zn-GR is shown in Figure 5. Analyz- formed at pH 2.8 – 4.5 by the hydrolysis of Fe<sup>3+</sup> and then ing these data vs reaction time allowed the quantification of transformed within  $\sim 1$  h into nanogoethite at pH 5.5 – 6. The the complex reaction sequences that are controlled by the transformation reaction of schwertmannite into goethite in changes in the solution chemistry (e.g. pH). In this way, GR most environmental systems is known to be very slow and formation and transformation pathways as well as the requires several months to complete. We have suggested that mechanisms for each reaction step were derived. In Ahmed in the presence of Fe<sup>2+</sup> this reaction is catalysed via the suret al., (2008), we have shown that schwertmannite (an Fe<sup>3+</sup> face adsorption of Fe<sup>2+</sup> ions onto the schwertmannite





**Figure 6:** SEM micrographs illustrating the hexagonal plate-like morphology and the different dimensions of GRSO₄ and GRCO₃ particles.

Fe<sup>3+</sup> in the solid phase and the surface-bound Fe<sup>2+</sup> ions. This reaction decreases the stability of the schwertmannite crystal leading to structural re-arrangements and finally formation of the more stable goethite phase. With increasing pH the goethite transforms gradually into GRSO<sub>4</sub>. At pH > 7, the solubility of Fe<sup>2+</sup> decreases which leads to the incorporation of Fe<sup>2+</sup> ions in oxyhydroxide structure and the gradual formation of mixed Fe<sup>2+</sup>/Fe<sup>3+</sup> octahedral sheets (primary building units of GR) whose excess positive charge is stabilised by the adsorption of sulphate ions. As Fe<sup>2+</sup> hydrolysis continues to occur, the formation and growth of these Fe<sup>2+</sup>/Fe<sup>3+</sup> sheets continue until GR crystals are well formed. The GR crystals continue to grow in the a,b crystallographic direction with increasing pH up to 10. These processes are summarised schematically in **Figure 7**.

#### **Outlook**

Similar to ZVI, GR oxidizes quickly when in contact with chemical species carrying electron-deficient centres (e.g. O<sub>2</sub> and NO<sub>3</sub><sup>-</sup>) which limit the longevity of the redox barrier. However, more can be done to extend the longevity of GR-containing barrier. For example, it has been demonstrated that the presence of trace amounts of dissolved phosphate or silicate increased the GR stability towards oxidative transformations. This was explained by the adsorption of these species at the lateral faces of GR (Ruby *et al.*, 2006a). It is also known that the type of intercalated anions is critical to defining the chemical stability, particle size and shape of the GR material. For example, chloride GR is less stable than the corresponding sulphate and carbonate forms of GR and its formation/stability in the natural environment seems unlikely.

We are currently testing a range of GR compounds in the

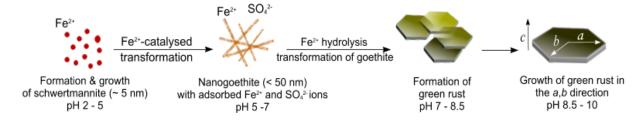


Figure 7: Schematic illustration for the formation and transformation processes involved in the formation of GRSO<sub>4</sub>. After (AHMED et al., 2010).

laboratory to characterise their effectiveness at reducing a (II)-Fe(III) hydroxide-carbonate (Green Rust 1): Pourbaix range of contaminates including  $CrO_4^{2-}$ ,  $SeO_4^{2-}$  and  $UO_2^{2+}$ . Our aim is to understand whether any of the GR compounds Corrosion Science 37, 2025-2041. we have synthesised will be suitable for decontaminating a range of industrial effluents. This includes studies of the GRclean up of simulated radionuclides waste streams to determine if these materials could be used to immobilise redox sensitive radionuclides (e.g. U) in these polluted effluents.

#### **Acknowledgments**

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#### Web links

#### Mineral databases:

http://www.mindat.org/index.php

http://www.galleries.com/minerals/by-name.htm

Diamond Light Source: http://www.diamond.ac.uk/

Lightsources.org: News, information, and educational materials about the world's synchrotron and free electron laser light source facilities http:// www.lightsources.org/cms/

A 'review of third and next generation synchrotron light sources' by D. H. Bilderback et al. was published in Journal of Physics B: Atomic, Molecular and Optical Physics, 2005, 38, S773-S797 as part of a 'Special Issue: Atoms, Quanta and Relativity – A Century after Einstein's Miraculous Year'. The review discusses the origins of synchrotron radiation, the link to equations developed by Maxwell, Lorentz and Albert Einstein, and in particular the role of Einstein's special theory of relativity in the realisation of synchrotron light as an experimental tool. The significance of terms such as 'third generation' and 'brilliance', which are commonly in use in this area of research are also explained.

# Technology and the use of coal

**Professor James Harrison** Chairman of the British Coal Utilisation Association and formerly Director of the Coal Research Establishment for British Coal presented this year's **ECG Distinguished Guest Lecture**, which took place at Burlington House on March 24th 2010.

#### Introduction

Utilisation of coal. The Industrial Revolution was based on coal. But it was a matter of serious concern in the UK in the mid-nineteenth century that the production of coal from the known reserves would not be able to sustain the increasing demands of industry. By the year 2000 it was predicted, the country would need 2000 tons of coal a year if the rate of increase in demand continued. It was recognised that coal was being used ever more efficiently, but that increased efficiency brought with it increased demand – a message that the present government planners might heed! There was debate at the time as to the extent that the improvements in utilisation that the practical engineers were achieving would be helped by the more scientific approach of the developing understanding of thermodynamics. At least, it was said, the theories defined the limits of what could be achieved. The interplay of pragmatic improvements versus science continues as the technology of the use of coal has progressed and continues to progress.

Although coal is no longer the main energy provider in the UK, it supplies about 45% of electricity generation. Worldwide, coal provides about 27% of world energy consumption and about 62% of electricity generation.

**Environmental impact.** From the earliest times there have been problems with the adverse effects of dust and smoke and the other emissions arising from inefficient combustion in poorly designed plant. The efficiency of the open fire was only about 25% and steam locomotives only about 7% overall. However, it was not until recently that the extent of the effects on the environment has been fully appreciated.

Smoke and dust emissions were the first problems to be faced, by improving the efficiency of combustion, so that their reduction paid for itself by reducing consumption. Acid rain and carbon dioxide emissions have called for much more radical and expensive modifications to the technology of coal utilisation.

Coal technologies. These advances have depended on a much fuller understanding of the underlying science of coal conversion and combustion. This has led to the introduction of many new technologies, but traditional technology has also benefited and has not stopped still. In the large-scale uses of coal, particularly iron-making and electricity generation, the newer technologies, designed to offer step-change improvements, are continually challenged by the more gradual advances made in the design and operation of established process plant. An improved version of the familiar is more acceptable, and less risky, than a radical new approach, as yet unproven.

#### **Ironmaking**

The use of coal for ironmaking is a good example of the interplay of science and practice. For thousands of years charcoal had been used to reduce iron ore, but when the charcoal supply dried up, ironmakers turned to coal as a substitute. The early methods of making coke imitated the process for producing charcoal from wood. Coal was allowed to smoulder in beehive ovens until the volatile matter had been driven off, leaving, when the right quality of coal was available, a residue which was hard, strong and porous and suitable for use in the larger furnaces that were being

developed. Beehive ovens were still operating in Durham in One consequence of this great improvement has been to ing process.

But although the larger furnaces and the new methods of making coke brought about benefits of scale, there was still much more art than science about the overall ironmaking process. How was coal converted into coke? What were the properties of an ideal coke? Was there a 'coking principle'

that could be added to coal to ensure a good product? Could furnaces ever be run on scientific principles or was there an art that had to be handed down from generation to generation? As more was understood of the behaviour of different coals under different heating regimes and, in particular the interaction of competing chemical processes of decomposition and recombination was studied in the laboratory, the production of coke was put on a base, allowing firmer

the 1950's, but by then the much larger by-product coke reduce the claimed advantages of alternative ironmaking ovens had largely taken over. These could produce coke of processes - direct reduction of iron ore from coal or natural uniform quality from a wider range of coal and also made gas. These processes are of particular interest where there is use of the gas and volatile material released during the cok- a lack of suitable coal for cokemaking and for smaller scale applications. They contribute about 5% of the world's iron production. Attention is increasingly being given to the need to reduce emissions of CO<sub>2</sub> from ironmaking plant. One method under development by Corus involves the use of oxygen to replace air to avoid the introduction of nitrogen, recycling the offgas to the base of the furnace and the strip-

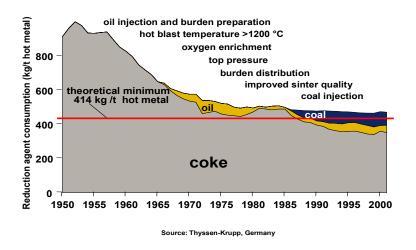


Figure 1: Carbon usage in blast furnace ironmaking over the last 50 years. (Illustration: ThyssenKrupp and Corus)

increased flexibility in the blending of the feed material and more control over the properties of the resulting coke.

At the same time, the chemistry of the blast furnace was being better understood, so that the desirable properties of the coke and other ingredients could be better defined. This better understanding has led to great improvements in the overall performance of blast furnaces. A hundred years ago the production of a ton of iron in a blast furnace required the consumption of four tons of coal. In most recent practice this has been reduced to about half a ton of coal per ton of iron (Figure 1).

ping of CO<sub>2</sub>

#### Combustion, domestic and industrial

Although the world consumption of coal for ironmaking is about three-quarters of a billion tonnes a year, the demand for coal for combustion is far greater. In the UK some coal is still used for home heating, some in industry, but the greatest use is for power production. The transition from small scale uses to the large central plant has been brought about by a variety of factors, but the prime driver has been the environment. The first problem to be tackled was that of smoke more effectively and without producing smoke. The princi- UK). ples applied to these appliances are those that are still used for domestic and small industrial applications. However, in the UK domestic market coal was taken over by gas, first from oil and later by natural gas. Coal is better handled and more efficiently combusted on larger plant.

The concerns about the contribution of coal combustion to acid rain gave an extra impetus to the development of fluidised bed boilers, because limestone could be added to the

from inefficient domestic and industrial boilers. The first bed to capture sulphur compounds without the need for addiapproach was the development of smokeless fuels in the tional flue gas clean up as was needed in conventional pf form of reactive coke and smokeless briquettes. A range of plant. The lower temperature of combustion in fluidised beds smokeless solid fuel was introduced in the 1950s and 1960s also meant that the production of oxides of nitrogen was aimed at allowing the continued use of open fires, but with lower. There was a major research project at Grimethorpe higher efficiency and no smoke. The other approach was to which proved the concept of pressurised combustion. This develop a domestic appliance that could burn coal itself, but has been the basis of full scale plant abroad (but not in the

#### **Coal for Power Plant**

In conventional power plant, the need to reduce emissions of sulphur oxides required the installation of considerable plant to clean up the flue gases. Emissions of oxides of nitrogen, NO<sub>x</sub>, also had to be addressed. The extent to which nitrogen in the combustion air is converted to oxides, is reduced at lower temperatures. Combustion temperatures have been

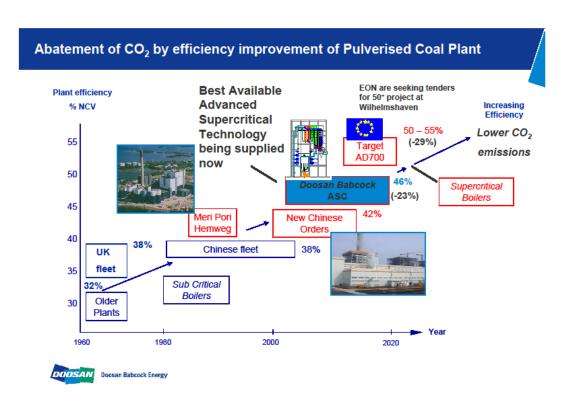


Figure 2: Technology-driven improvements to coal-based power plant generation. (Illustration: Doosan Babcock, BCURA Coal Science Lecture 2008 http://www.bcura.org/ csl08.pdf)

lowered by developing burners in which air is introduced in pulverised coal with oxygen and steam; in a suspension in straints of installed equipment.

These developments and the improvement of materials of construction have enabled the use of higher steam temperatures. The most recent plant, using superheated steam, can have overall efficiencies approaching 50%, compared with developments will take efficiencies even higher. Figure 2 is illustrative.

However, if CO<sub>2</sub> is captured for transport and storage, the overall efficiency of a pf (pulverised fuel) plant using supercritical steam would be reduced to some 25%. This drastic reduction in efficiency has increased the interest in alternative coal-fired systems.

There are two main contenders Oxyburn - the use of oxygen instead of air for combustion in an otherwise conventional design - and systems based on gasification with oxygen using gas turbines and steam turbines in combined cycles. In both these routes CO2 does not have to be separated from nitrogen and in the gasification system it is captured at high pressure, ready for transport and storage.

Oxyburn is currently at the small demonstration scale. It is being promoted in several projects, for example at Didcot where the development of computer models enables studies to be made of different configurations and different operating procedures before they are tried out on full scale plant. This means that many more options can be explored than would be feasible on the plant itself.

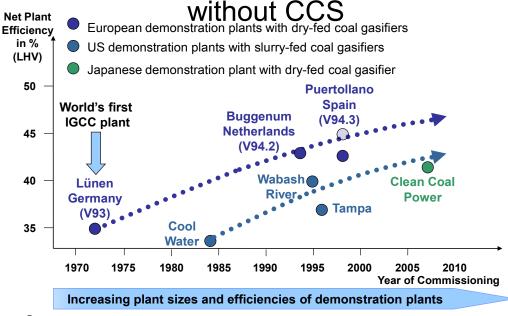
There are several gasifiers that have operated for many years at the commercial scale. They differ in the method of feed -

stages, and by recirculation of flue gas, staging the introduc- water, or as a lump solid. The resulting gases may be cooled tion of air into the combustion space of the boiler. NO<sub>x</sub> can in a heat recovery system or by direct quenching with water. be reduced in this way, but a negative effect is that it is more They are finally treated in a variety of cleaning processes. difficult to achieve complete combustion. This is shown by The process gas may be used directly or modified by shift the increase in the amount of carbon in the ash residue. A reactions to adjust the ratio of CO to hydrogen. There are recent development is to identify the optimum combination therefore several options in the choice of gasification system of operating conditions at a plant, to minimise NO<sub>x</sub> and car- to meet the needs of individual sites and for particular applibon in ash by computational fluid dynamics, taking into cations. The first gasification combined cycle plant was built account the science of combustion and the practical re- in Germany in the 1970s. Since then a series of plants have been built with increasing efficiencies and more are under construction, for example in China. In Britain the project at Hatfield has received European support. Current progress in the efficiencies of power plants based on oxygengasification technologies is summarised in Figure 3.

the 38% of plant with standard steam conditions. Further In considering the merits of the different options for future power plant, the need to cater for the capture of CO<sub>2</sub>, has become one of the most important criteria. Many studies have been made of the merits of the options for power generation, pre-combustion with its large efficiency penalty or post combustion with high capital costs. These studies indicate that in general there is little to choose between the overall economics, so the final choice will depend on the different conditions at different sites which may favour a particular option.

> Although all the components of the various options for CO<sub>2</sub> capture and storage have been operated on the large scale separately, there is the need to demonstrate their robustness in power generation. These issues are the heart of the Government's competitions, which are intended to demonstrate carbon capture and storage in four projects using different systems. In order to reduce the duplication of CO2 handling facilities, it would it be desirable for the Government to promote a national scheme for transport and long term storage, taking into account problems of ownership and responsibility for health and safety aspects. Progress is needed rapidly, not only because of the urgent need for new plant in the UK, but also because solutions are needed for application to plants abroad, as in China and India, where new coal-fired plant is being brought into operation almost daily.

# Development of IGCC net plant efficiencies for coal-based IGCC plants



O Puertollano plant efficiency for ISO conditions and high quality coal

**Figure 3:** Efficiencies in coal-based integrated gasification combined cycle plants (IGCC) without carbon capture sequestration (CCS).

#### Coal for transport fuel

In the UK, the need to clean up fuel for transport is likely to further require demand for electricity for road and rail transport and/ or for the production of hydrogen, if that becomes the preferred solution. As long as any fossil fuel is used for electricity, any renewable electricity will be most effectively used as electricity, rather than converted into hydrogen. This means that hydrogen would continue to rely on fossil sources, which in practice means coal, as supplies of natural gas become increasingly difficult to maintain.

Established gasification processes can be used, and there is much activity in current R&D programmes aimed at refining the conventional route from coal and in developing new ones. For example, studies of conventional gasification followed by cryogenic or membrane separation indicate that

hydrogen costs could be lowered considerably and coproduction of hydrogen and electric power might lower costs further. The proposed gasification plant at Hatfield is considering the merits of such a combined objective. In the longer term more novel routes from coal to hydrogen are being developed, for example those based on chemical-looping cycles

#### **Underground gasification**

There are many reserves of coal worldwide that are uneconomic or impossible to recover by conventional mining for reasons of quality, accessibility or depth. Many trials have been carried out in the attempt to recover the energy in the form of gas produced by the introduction of air or oxygen with steam directly into the coal seams. There are formidable problems to overcome in controlling the combustion/ gasification reactions, in managing the strata in which the coal occurs, in preventing leakage between workings and to the surface and in obtaining a consistent and long-term product gas. Although short term success has sometimes been obtained, no project has been operated on a commercial basis. The technology is being re-assessed in many parts of the world at the present time, taking into account the advances that have been made in drilling and linking technology in the oil industry. There are several pilot projects, but little information has been released from them. The rewards of success would be considerable.

#### Conclusion

Coal will continue to have an important role in contributing to the supply of energy in the UK, as in many other parts of the world. For this to be compatible with the reduction of emissions of carbon dioxide, there is urgent need to demonstrate carbon capture, transport and storage. The components are operating on the large scale in different applications around the world. There is no reason to doubt that they can operate successfully together, but this needs to be proved by the demonstration of total systems operating on a power plant. There is a case in the UK for the Government to promote a national pipeline grid with designated storage sites with appropriate monitoring provisions for the long term. There is also the need for assurance from the government that the investment in the additional plant would be economic, for example by a guaranteed price for carbon.

#### Professor JAMES HARRISON, FRSC, FREng.

March 2010

#### Web links

British Coal Utilisation Association http://www.bcura.org/

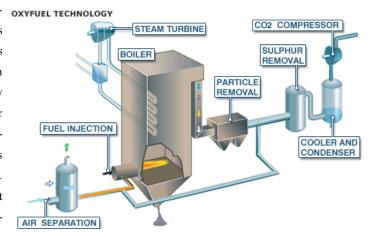
Carbon Capture Journal http://www.carboncapturejournal.com/index.php

Control and Minimisation of Coal-fired Power Plant Emissions (Report by the Working Party on Fossil Fuels International Agency) http://www.iea.org/ papers/2003/Coal\_Fired\_Fossil\_Fuels.pdf

The Association for Iron & Steel Technology (A USA-based organisation) http://www.aist.org/

The Coalmining History Resource Centre http://www.cmhrc.co.uk/site/home/

The Grimethorpe Pressurised Fluidised-Bed Combustion Project http://www.brad.ac.uk/library/special/grime.php



#### Royal Society to publish new guide to the science of climate change

The Royal Society is to publish a new guide to the science of climate change to help the public gain a better understanding of the issue. The guide is due to be published in the summer of 2010.

Martin Rees, President of the Royal Society said: "Climate change is a hugely important issue but the public debate has all too often been clouded by exaggeration and misleading information. We aim to provide the public with a clear indication of what is known about the climate system, what we think we know about it and, just as importantly, the aspects we still do not understand very well."

The document will be prepared by experts from within the Fellowship and, as with all policy statements and reports published by the society, will be subject to review by other Fellows with a broad range of views and expertise. The final document will be agreed by the Council of the Society.

# Storing our energy:

#### Summary document of a Royal Society of **Chemistry Steering Group**

#### Introduction

Developing viable means to store energy is becoming an everincreasing priority. Innovations for generating renewable energy for the resources [reference 2]. The UK national grid will require improved ways to store the electricity that is produced. Alongside this, reducing the emissions of greenhouse gases from transport will also rely on methods to store alternative energy sources.

In light of these challenges, the Royal Society of Chemistry has formed a European-wide steering group on electrochemical energy storage chaired by Professor Peter Bruce, from the University of St Andrews. The group has cross-European members from both academia and industry who have been reviewing the best practice to support research and development into electrochemical energy storage devices. The steering group has produced a document to communicate their discussions, and they are now planning activities towards implementing their recommendations.

#### Ambitious targets

Governments across the world are setting targets to reduce anthropogenic greenhouse gas emissions, especially carbon dioxide (CO<sub>2</sub>), by increasing the use of electricity generated by renewable technologies. The EU is aiming to cut CO<sub>2</sub> emissions by 20% from 1990 levels by 2020 [reference1] and to generate 20% of overall energy by renewable has now ratified the EU renewable target goals, which equates to a seven-fold increase in UK renewable energy production from 2008 levels. In addition the UK's own Climate Change Act requires a reduction of greenhouse gas emissions in the UK, of at least 80% by 2050, and reductions in CO2 of 26% by 2020 against a 1990 baseline [reference 3].

#### Renewable electricity generation

Around 25% of all CO2 emissions in the UK and EU come from electricity generation, and predominantly coal- and gas-fired power stations [reference 4]. The demand for electricity varies widely depending on the season, day of the week and time of day. Countries like the UK, which have a fully interconnected national grid, usually have a baseload of available electricity, with flexible generating facilities able to come on line at short notice.

The UK Renewable Energy Strategy aims to derive 30-40% of the UK's electricity from renewable sources (mainly onshore and offshore wind) by 2020. This is problematic for the national grid because wind energy is intermittent and solar energy is subject to the regular diurnal patterns of supply.

To sustain a continuous supply of electricity, there will either need to be sufficient back-up in the form of a flexible power plant (such as coal or gas) or energy will need to be stored at times of high generation for release at times of high demand.

#### **Transport**

CO<sub>2</sub> emissions from all transport makes up roughly one third of all global greenhouse gas emissions. The King Review [reference 5] has identified energy storage as one of the enabling technologies for low emission electric and hybrid vehicles, with the aim to reduce CO2 emissions per kilometre by 30% by 2030 and 90% by 2050. A lowemission vehicle which runs on hydrogen from sustainable resources, and has a 200+ mile range, is also one of the definitive aims identified by the 2007 RSC report, Fuelling the Future [reference 6].

However, there are still significant technological challenges in battery, hydrogen storage and fuel cell development, which need to be addressed.

In addition to decarbonising private transport, it is important that other transport sectors are also included, such as the electrification of the entire rail network, along with a move to electric or hydrogen buses and heavy-goods vehicles.

#### **Consumer electronics**

The manufacture of energy storage devices for consumer electronics is a growth industry. It is driven by the huge increase in sales of portable electronic devices that require battery power (such as laptops, mobile telephones and digital cameras) and of mains-connected devices that require and use batteries for memory back-up.

The development of ever more sophisticated and powerful electronic equipment will require greater amounts of stored energy, most probably at levels that are well beyond the capabilities of conventional batteries. Fuel cells, advanced batteries and other storage technologies have huge potential, however, more research will be required to solve power output and recharge challenges.

# Types of energy storage

#### **Batteries**

A battery is a device for the chemical storage of electrical energy for subsequent use as direct-current electricity [reference 7].

Conventional batteries are cheap to produce, have a commercially proven technology and are likely to continue to be used for energy storage, despite the following intrinsic limitations:

- They contain toxic lead and cadmium components and therefore cannot be safely scaled up.
- The amount of energy that may be stored or transported, in a given amount of mass, is low.
- They have high self-discharge, meaning that internal chemical reactions reduce the charge stored in the battery over time, thereby decreasing their lifetime.

The following alternatives have potential applications in large-scale static electricity storage:

- sodium-sulphur;
- zebra batteries: already used in transportation;
- redox flow-cell batteries.

However, further research and development is required to resolve problems relating to lifetime, reliability and cost.

Lithium-ion batteries are the dominant energy storage technology for portable electronic devices and have potential to be a key energy source in a number of applications, including electric vehicles.

The voltage, capacity, life-time, and safety of a lithium-ion battery could be improved dramatically depending on the material for the electrodes and electrolyte. Funding for materials research is therefore vital. Upscaling is required for lithium-ion batteries to be used in vehicles and considerable investments of both time and money are therefore required.

Future research and development ing the voltage of the capacitors. into batteries is extremely important: Surface chemistry and materials,

Methods of recycling raw materi-

als or replacing rare and expensive metals will have to be found.

- Improved battery performance may be achieved by developing new materials (including nanomaterials) and methods of their synthesis.
- Improved safety could be realised by using novel electrodes and electrolytes.

#### **Supercapacitors**

Supercapacitors differ from conventional electrostatic capacitors in that they store electrostatic charge in the form of ions on the surface of materials with very high surface area.

Supercapacitors are predominantly used in consumer electronics. They can be charged and discharged quickly and are thus used when a large amount of power is required quickly. Examples of uses include:

- a camera flash;
- an emergency door on an aircraft;
- use in hybrid vehicles for start-up and regenerative breaking systems

Carbon-hybrid supercapacitors have huge potential because they have higher energy storage capacity than carbon-only supercapacitors, however the lifetime is shorter. More research is needed to realise their full potential.

Future research and development into supercapacitors is extremely important to address the challenges in improving cycle life and increasing the voltage of the capacitors. Surface chemistry and materials, such as nanoporous electrode materials, will be key to their develop-

ment. To successfully introduce supercapacitors to the hybrid vehicle market, production costs also need to be reduced.

#### Fuel cells

A fuel cell is a means of converting a fuel (e.g. hydrogen and methanol) into electricity. Fuel cells are already used in niche markets and have good potential for further use in:

- · vehicles:
- portable electronics;
- static applications.

However, fundamental problems remain in the development of commercially viable fuel cells, such as their lifetime, reliability and production costs.

In particular, improvements need to be made in:

- water-free membranes which promote proton transfer to improve their efficiency;
- increasing the porosity of electrode materials:
- the efficiency, life-time and durability of catalysts and finding cheaper alternatives;
- hydrogen infrastructure, including hydrogen storage;
- the purity of the fuels used.

#### Funding mechanisms

#### **Basic research**

Research into new and improved electrochemical energy storage technologies requires an understanding of the basic science relating to the materials used. This calls for knowledge in a diverse range of disciplines – from electrochemistry, to chemical catalysis and corrosion processes, to fundamental electron transfer processes. It is essential that fundamental, as well as applied research, continues to be funded to promote the expansion of relevant scientific knowledge.

Training the next generation of chemists must also remain a priority.

#### **Cross-European R&D**

Electrochemical energy storage poses long-term challenges that require a sustained investment. European coordination will therefore be essential, especially if we are to remain competitive in the face of the large funding actions seen today in Japan and America. It would be appropriate to have a Europeanwide agency or institution for energy storage, in the same way as the nuclear fusion or airbus collaboration is organised. A joint institution would also ensure that research is not duplicated and serve as a platform for technology transfer. It could be based mainly on publicly funded research activities to maintain independence; however, it should also allow "buy-in" from industry to help tackle specific problems and enable knowledge transfer.

The independence of the funding process supporting the development of a variety of energy storage solutions must be key. It is vital not to pick early winners in the future funding process for this type of research. Experience has shown that market pull should decide which technology is the most practicable

and economically viable.

## Knowledge and technology transfer

Encouraging innovation requires the transfer of knowledge and skills from academia into industry. Initiatives set up by the Technology Strategy Board, such as the Knowledge Transfer Networks (KTNs), are intended to facilitate this transfer, and it is essential that this work continues to be supported.

The RSC is working with the nano-KTN, who are working on nanoenabled energy storage, with the aim of bridging networks and educating government on the issues.

Small and spin-off companies often play a vital role in bringing new emerging technologies from research into development. In the UK, they play a vital role in employing a large proportion of skilled workers and contributing to regional economies. It is essential that these small companies are supported as they are much more vulnerable to market fluctuations, and that they are given access to available European funding

#### A vision for the future European Centres of Excellence

There is a need to focus and strengthen efforts in European research in the development of energy storage devices. As part of this effort, it is necessary to establish (virtual) European Centres of Excellence for energy storage technologies, including batteries, fuel cells and supercapacitors. These would bring together the best people in

Europe, and should have an independent testing facility for each energy storage technology. Such a centre would focus on medium- to long-term challenges, and would receive sustained long-term funding. The centre would also serve to promote technology transfer, ensure that research is not duplicated, and allow independent and comparative quality assessment of energy storage devices.

It is key that the centre is independent, truly European (with no particular country overpowering the institution) and that bureaucracy is kept to a minimum. CERN or ILL Grenoble could be taken as examples of good joint European scientific ventures.

#### Collaboration through SusChem

It is essential to gain the support of the European Union in setting up a Centre of Excellence for energy storage technologies. SusChem

[http://www.suschem.org/] promotes renewable sources, COM, 2008 sustainable chemistry research in Europe and is well placed to take these proposals forward to the European Commission, and to influence the direction of European funding calls.

A network for energy storage, leading to a Centre of Excellence, would help strengthen the research base in Europe. Currently, the USA and Japan are the unchallenged leaders in this arena. If Europe wishes to stay independent and be competitive in the future, it is vital that a European research base is fostered now.

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### **Driving solar fuels:**

# Summary of a Royal Society of Chemistry workshop

#### Introduction

Solar fuels are chemical fuels produced by harnessing energy from the sun. As it becomes increasingly necessary to investigate alternative renewable sources of energy, it is important to understand the current position of solar fuels research within the UK.

The RSC policy document, Chemistry for Tomorrow's World, is a roadmap that highlights solar fuels research as an important opportunity for the chemical sciences. In order to scope the current position of this research, and determine how to drive the development of solar fuels technology, the RSC held a workshop in December 2009 at the Chemistry Centre in London, which was chaired by Professor James Durrant, Imperial College, London. This article summarises the opinions of the expert group that took part in these discussions.

#### **Key drivers**

The development of solar fuels technologies has several key drivers, including the following societal drivers:

 The supply of energy to the UK has historically been through fossil fuels, which are a finite resource.

- Production of clean fuel is of global importance; there are major concerns regarding the use of fossil fuels as a predominant energy supply, namely pollution and growing CO<sub>2</sub> emissions.
- There is a need to develop a globally scalable strategy for CO<sub>2</sub> -neutral synthesis and use of fuels for transport.
- Security of supply the UK

   (along with many other countries)
   currently needs to buy its liquid
   fuels and so is subject to price
   fluctuations and dependent on
   good international relations.
- Renewable energy storage strategies to address the intermittency limitations of current UK renewable energy are currently based almost entirely on producing electricity.
- For the chemical industry to be sustainable, chemical feedstocks will need to shift from oil to alternatives.
- The use of CO<sub>2</sub> as a large scale chemical feedstock for fuel synthesis would provide an alternative to CO<sub>2</sub> sequestration.

Alongside these societal and commercial pressures, recent scientific advances are additional drivers for the timeliness of a solar fuel initiative. These include advances in the design, synthesis and characterisation of nanomaterials, in our understanding of biological multielectron catalysis, and in rapid advances in the development of catalysts for electrochemical and photochemical fuel synthesis.

# Solar fuels research strategies

Solar energy represents the largest renewable energy resource available globally. Research into solar fuels began during the oil price spike in the 1970s, and has now gained global momentum. The US recently announced a \$250m solar fuels hub initiative, and solar fuels are gradually moving up the European agenda, for example the Dutch €35m Biosolar programme.

At present, a range of strategies can be envisaged for solar fuel synthesis. These strategies range from the use of photovoltaics to drive water electrolysis through to the direct photochemical reduction of CO<sub>2</sub>. Common features of all of these strategies are that they rely on solar energy and that they use multielectron catalysis to drive molecular fuel synthesis, often em-

ploying bio-inspired materials design and development.

### Solar fuels research within the UK

It is vital that the UK engage in the rapidly developing field of solar fuels, if we are to ensure that we establish a sound base on which to develop a leading research and development programme. This will allow commercial exploitation by UK plc, in an area which has the potential to grow in the medium and long term to be a major component of global energy supply.

The UK already has significant strengths in many relevant areas of research that support solar fuels technologies, including world leading research in materials chemistry, catalysis chemistry, electrochemistry, molecular processes of photosynthesis, and organic and dye sensitized photovoltaics. There are several academic programmes within the UK which are directly focused upon solar fuel strategies, for example the SolarCAP project between the Universities of York, Nottingham, Manchester and UEA, which targets the development of photoelectrochemical nanoscale systems for CO2 fixation and alkane oxygenation. A collaboration between University College London (UCL) and University of Strathclyde is targeting nanocrystalline photochemical diodes for water splitting or CO<sub>2</sub> fixation and alkane oxygenation, while scientists at Imperial College are investigating solar driven renewable hydrogen generation.

In addition, three new projects targeting CO<sub>2</sub> reduction, based at Imperial College, UCL and University of Bath, are starting in May 2010 and have been funded under the Engineering and Physical Sciences

Research Council's (EPSRC) Nanotechnology Grand Challenge programme.

There is significant value in further enhancing the strong research areas associated with solar fuels, as successful products in the solar fuels supply chain will be in high demand throughout the world. It is possible that research in this area will be viewed as being of high risk, due to the long time scales; they are technically highly challenging, and it may take several years to advance technologically enough to create products which are ready to market. However, the financial and societal gains have potential to be very large when the technology comes to frui-

## Meeting solar fuels research challenges

### Basic research and training

Within this relatively recent field of research, there are many significant fundamental questions that must still be answered, and on this basis, the expansion of relevant scientific knowledge will depend on both applied and basic research.

The most important foundation for the future of solar fuels research is the strong chemistry education required to develop a thorough knowledge base. Training the next generation of chemists should exist in a supportive environment; it should be stimulating and informative in order to retain skilled scientists in chemistry. The competent teaching of science and especially of chemistry is essential throughout all stages of schooling, through to undergraduate and postgraduate studies in wellequipped and well-funded universities.

#### **Funding**

In order for the UK to benefit from the opportunities offered by the growth of a solar fuels industry, participants of the RSC workshop proposed that the following funding strategies should be presented to the relevant funding bodies:

- A coherent solar fuels programme needs to be established. This requires a strategy that incorporates funding from BBSRC (Biotechnology and Biological Sciences Research Council) and EPSRC in order to cover all areas of solar fuels research. It has been acknowledged by researchers within the field that a specific "centre of excellence" is not required.
- A managed programme will be required to accelerate the research in the most efficient way.
- In order to capitalise on investment in solar fuels research there needs to be a long term research programme.
- The UK should follow the lead of other countries where the funding duration is extended for projects that are long term and offer significant potential societal gain.

#### Raising awareness

There is currently very little general knowledge, outside its core research base, about solar fuels technologies, and it is increasingly important to provide more substantial information for the general public, for industry and for government, in order that the potential of solar fuels can be understood. The RSC is well placed to communicate this potential to relevant stakeholders to ensure that it is fully appreciated.

If the UK energy and chemical industries become more exposed to the idea of producing fuels and chemical feedstocks from solar energy, and to the science behind it, then the UK could be in a very strong position to develop this area.

#### **Key stakeholders**

Industry is cautious about getting involved with solar fuels research due to the associated high risk and long timescales. The industrial partners that could see the most benefit from investing in solar fuels research would be those who are currently involved in the relevant materials and catalysis synthesis as well as in the energy and utilities sectors.

Small and medium enterprises (SMEs) and spin-off companies often play a vital role in bringing new emerging technologies from research into commercial development. In the UK, such companies employ a large proportion of skilled workers and greatly enhance regional economies. It is essential that they are properly supported, and given access to as wide a branch of funding as possible, as they are much more vulnerable to market fluctuations than larger organisations.

Given the increased focus within Europe, it will be hugely beneficial for the UK to position itself strongly alongside European researchers in order to be part of large scale solar fuels programmes commissioned in Europe. In this regard, it is felt by attendees of the workshop that the lack of engagement of the EPSRC in a recent European Science Foundation (ESF) call was a significant opportunity to have missed.

Encouraging innovation in the solar fuels sector requires the transfer of

knowledge and skills across the supply chain and from academia into industry. Initiatives set up by the Technology Strategy Board, such as the Knowledge Transfer Networks (KTNs), are intended to facilitate this transfer and it is essential that this continues to be supported. The RSC works closely with the Chemistry Innovation KTN, which acts as a link to the other KTNs and instigates connections with a wider industry base. Other organisations, for example the Society of Chemical Industry (SCI), the Institution of Chemical Engineers (IChemE) and the Institute of Materials, Minerals and Mining (IOM3) should also be engaged as they represent industrialists and engineers.

In order to increase the awareness of solar fuels technology in the community it is important to engage with the wider bracket of national policy makers and funders. In the first instance this will include the Department of Energy and Climate Change and Department of Business, Innovation and Skills in central government and the relevant lead technologists in the Technology Strategy Board (who could disperse information to the regions through the Regional Development Agencies).

With suitable buy-in from funding bodies, government, and industry, solar fuels has the potential to be a viable solution to a huge global challenge.

#### Summary

 The RSC determined solar fuels to be a clean technology that could potentially be employed to provide sustainable energy and held a workshop to scope the current position and determine how to drive development in the UK.

- This opportunity is one that is very heavily routed in fundamental chemistry, where there is currently relatively little focus from the public sector and industry in the UK.
- The RSC is well placed to provide a significant impact in driving forward work in this area.
- 4. The RSC solar fuels workshop group would like to take steps towards raising awareness of solar fuels as a clean technology to get it on to the national energy/sustainability agendas.
- The group recommends promoting early investment, and long term funding, in both fundamental and applied research in areas relevant to solar fuels, enabling a strong UK position.

#### Web link



Chemistry for Tomorrow's World http:// www.rsc.org/ ScienceAnd-Technology/ roadmap/ index.asp

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#### **Meeting report**

# 2010 Environmental Chemistry Group Distinguished Guest Lecture and Symposium

# King Coal: future prospects for growth, use and clean technologies

The Environmental Chemistry Group held its Thirtyseventh Annual General Meeting and Distinguished Guest Lecture Symposium on Wednesday March 24th 2010 in The Library, which is part of the RSC Chemistry Centre at Burlington House. Around 50 delegates attended the Symposium which took the theme "King Coal: future prospects for growth, use and clean technologies", and the 2010 Distinguished Guest Lecturer was Professor James Sumner Harrison.

The speakers covered several aspects of coal use. The most salient theme to emerge from the day's proceedings was a link between the international aspects of coal supply (chiefly Australia (29%), Indonesia (22%) and Russia (11%)) with rising coal consumption (China and India) and the prospects for CCS (Carbon Capture and Storage) as means of ameliorating carbon dioxide emissions.

Douglas Parr (Chief Scientist and Policy Director, Greenpeace) talked on "The Role of Coal in a Climate-threatened World". His presentation emphasised that coal combustion is acknowledged as the largest global carbon dioxide emitter. If there were a focus on the energy efficient use of a combination of energy sources [solar, biomass, wind etc. and properly managed other sources (gas, coal etc.)], then there would "... be little or no need for large scale investment in conventional technology in the period up to 2020". If coal

use were to increase after that time, then a combination of mandatory Emissions Performance Standard (EPS) requirements for new plants (330g CO<sub>2</sub>/kWh) and the use of CCS are necessary to ensure that the UK meets its carbon emissions targets. Two points emerged from this. First, the UK is responsible for only about 2% of global carbon dioxide emissions and second, the importance of the 2020 date. Both these points were developed by subsequent speakers.

Nigel Yaxley (Managing Director, Association of Coal Importers) explained that coal was the world's fastest growing energy source (50% growth by 2030) and that China dwarfs other producers. Indonesia is the world's biggest exporter of steam coal – most of which goes into the Asian market. The world's biggest coal consumers are China (2000 million tonnes of coal equivalent), the US (750) and the EU (400; mostly in Poland). The US, China,

India, Russia and Australia lead in proven coal reserves. Coal is also used for steel production - coking coal demand in 2009 was around 800 million tonnes (e.g. in China coking coal is 8% of total use).

Although most coal demand is met by indigenous supplies, 15% of coal is traded and the nature of this trade is changing. For example in the UK, in 1990, 90 million tonnes of demand was met indigenously, but in 2009 only 18 million tonnes out of a demand for 40 million tonnes was produced internally. The picture emerges of economies in the countries such as India and China being driven by coal (chiefly for energy but also for steel production) and significant change in world coal markets being consequent on this alignment. The impact of these changes on carbon dioxide emissions is profound and "demonstrates the imperatives for CCS". The IEA CCS roadmap "envisions 100 CCS projects globally by 2020 and over 3000 by 2050" and the EU has agreed twelve CCS demonstrations by 2015 (including Hatfield). The UK has offered financial support for up to four commercial scale CCS demonstrations with an expectation that CCS will be a proven technology by 2020 and that CCS will be retrofitted to coal power sources by 2025.

Concurring with the previous speaker, Nigel Yaxley emphasised that the increased use of coal was only compatible with internationally agreed targets for carbon dioxide emissions - if serious money and political resolve are to be invested in the speedy development of feasible CCS technologies. However, progress in the UK is relentlessly slow and an opportunity for the development of a scientifically expert

industrial base in these technologies is being wasted.

Stuart Haszeldine (Professor of Geology, Edinburgh) continued and developed the themes of the previous speakers with his presentation "CCS: silver bullet or broken bridge?" He pointed out that the six year trend for carbon dioxide emissions globally is faster than the worst IPCC projection and that fossil fuels will still provide most of world energy to 2050. If CCS is seen as part of a solution to the increased carbon dioxide emissions associated with (still) increasing fossil fuel use, then there are diffisolve before that can be confirmed.

The post-combustion carbon dioxide capture method (flue gases are captured (e.g. in aqueous monoethanolamine)) has only been demonstrated for a 10% pilot scale. Currently all commercial carbon dioxide capture plants use similar processes. The CCS Oxyfuel process (currently used in 5 MWe experimental burners) involves oxygen (from air) being injected into flue gases and (after water removal) 100% carbon dioxide being produced. Pre-combustion capture (IGCC: Integrated Gasification Combined Cycle) has been piloted at 30% scale; basically coal is reacted with steam to produce carbon monoxide and hydrogen and the hydrogen is used as the fuel (the water-gas and shift reactions).

For each of these processes a carbon capture penalty exists in terms of efficiency and this penalty increases as the demands for the percentage of emitted carbon captured become higher. Having captured the carbon dioxide it needs to be transported to the storage site and stored. The use of carbon diox-

ide in oil fields for Enhanced Oil Recovery (EOR) and storage in saline aquifers or depleted gas fields are possibilities for storage. Currently ubiquitous deep saline formations (e.g. brine-filled sandstone) formations offer the best volumes for the geological storage of carbon dioxide. Such formations need to be porous and permeable so large volumes of supercritical carbon dioxide can be injected into them. An impermeable seal must also exist.

Like the two earlier speakers, Professor Haszeldine emphasised the need for accelerated CCS investcult policy and technical problems to ment. The first UK plant is expected in 2014, three more by 2018 and commercial plant from 2020, with an annual cost increase from UK CCS technology estimated as £28 per household in the UK for electricity. However, progress is slow. Although some legislative and regulatory processes have been agreed (e.g. ownership of pore space), the UK policy has yet to be ratified (e.g. OSPAR Convention) or is still under discussion (e.g. licensing of storage) or is still being debated (e.g. EPS). CCS installation requires an unprecedented rate of growth to be operating in 2020/2025 but world activity is currently too slow to achieve this, hence CCS is currently . . . 'a rope bridge not a highway.'

#### **Professor James Harrison**

(Chairman of the British Coal Utilisation Association) focused his Distinguished Guest Lecture on "Advances in the technology of the use of coal". His theme gave insight into the technical improvements which had occurred in relation to blast furnace operations over the past 50 years and more, and emphasised the salience of the water gas reaction sequence. Economic forces within the steel industry itself have seen significant progress towards maximising the efficiency of coal use. From 1950 to 2000 the consumption of coke (kg/tonne hot metal produced) had decreased from 1000 kg/tonne to the theoretical minimum of 414 kg/tonne. And industry has responded to environmental concerns about the emissions of gases (e.g. sulphur oxide) and particulates – albeit as a consequence of the Clean Air Act and subsequent legislation.

Currently the technology of choice is the Advanced Supercritical Pulverised Coal Boiler/Steam Turbine for plants in the 350-1000 MW range, which provides efficiencies of 46/47% and can be designed to incorporate CCS technology. Again there is an expectation that 2020 will be the year in which CCS plant becomes commercially available.

In summary, the lectures in the Symposium delineated:

 the pathway which exists between climate change scenarios

- the connection of global coal use to those scenarios
- the embryonic technological solutions extant in the coal industry which are pertinent to achieving the policy targets set by governments
- the need for coherent international action in relation to CCS
- the difficulties of implementing CCS-oriented solutions in mature industries such as power generation and steel making
- and, above all, the need to engender the political will for rapidity, investment and an urgent response to an opportunity for the development of international leadership by the UK scientific and engineering community . . . before it is lost.

#### Dr LEO SALTER

Cornwall College, Pool,

Redruth, Cornwall

March 2010



#### Web link

The PowerPoint slides from the 2010 DGL and accompanying

symposium may be seen on the RSC ECG Web pages at http:// www.rsc.org/Membership/ Networking/InterestGroups/ Environmental/ DistinguishedGuestLecture.asp





# Issues in Environmental Science and Technology

A recent addition to the RSC Series

#### **Ecosystem Services**

Series Editors: R. M. Harrison and R. E. Hester. Publisher: Royal Society of Chemistry, Cambridge UK, 2010. ISBN: 978-1-84973-018-1, 192 pp, £59.95

As human populations grow, so do the resource demands imposed on ecosystems, and the impacts of anthropogenic use and abuse are becoming ever more apparent. This has led to the development of the concept of ecosystem services, which describes the beneficial functions provided by ecosystems for human society.

Ecosystem services are limited and hence threatened by over-exploitation, and there is an urgent imperative to evaluate trade-offs between immediate and long-term human needs and to take action to protect biodiversity, which is a key factor in delivering ecosystem services. To help inform decision-makers, economic value is increasingly being associated with many ecosystem services and is often

based on the replacement with anthropogenic alternatives. The ongoing challenges of maintaining sustainable ecosystems and prescribing economic value to nature is prompting multi-disciplinary shifts in how we recognise and manage the environment.

This volume brings together emerging topics in environmental science, making an excellent source for policy makers and environmental consultants working in the field or related areas. *Ecosystem Services* also serves as a concise and referenced primer for advanced students and researchers in environmental science and management.

#### **Meeting report**

# ECG Atmospheric & Environmental Chemistry Forum 2010

The second ECG Forum event for PhD students and early career post-doctoral researchers was held at Burlington House on the 4<sup>th</sup> June 2010. The Forum's remit was expanded somewhat from the Atmospheric Chemistry Forum organised in April 2009 to include environmental as well as atmospheric chemistry.

Every attending delegate delivered a talk or a poster presentation introducing their research area and showcasing elements of their own work. **Prof Dudley Shallcross** (Bristol University) gave wideranging overview of atmospheric chemistry's impacts in the Forum's Invited Lecture: "From the urban to the global scale: what we know and the challenges ahead".

The Forum's presentations and scientific discussion broadly spanned the following six areas:

- Laboratory studies of aerosol particles' growth and light scattering properties;
- Laboratory studies of gas phase chemical reactions;
- Environmental chemistry trace metals in lake sediments, the removal of dyes from aqueous waste;

- Atmospheric field measurements and their interpretation – hydrogen and carbon monoxide, halocarbons, Antarctic ozone, street canyon dynamics, and new instrumentation;
- Hydrocarbons and biofuels their atmospheric chemistry and their effects on the atmosphere's oxidising capacity; and, further afield:
- The atmospheric chemistry of Mars.

The Forum's final session was a discussion on careers where an invited panel – **Mathew Evans** (Leeds University), **Helen Walker** (AEA Technology) and **Charlie Ashley-Roberts** (RSC careers advisor) – described their career paths to date – had they followed a carefully crafted career plan *or* simply been in the right place at the right time? The panel then fielded a range of questions from the floor, many of which will have a resonance with us all:

- Is it best to remain in the same research area (where one has developed skills and expertise), or to diversify into new areas?
- How can we manoeuvre ourselves into the job/institution of choice?
   What are the pros and cons of

- going to work abroad? How easy is it to return to the UK and find employment afterwards? Is an overseas postdoctoral position a pre-requisite for getting a UK academic position?
- How can we most effectively communicate our science to inform policy makers; to have politicians listen; to convince a sometimes sceptical public that atmospheric and environmental issues require action (e.g. climate change)?

The organisers gratefully acknowledge the award of an RSC Travel Grant for the participants of this event. We hope to publish a selection of talk and poster abstracts from this Forum in the next issue (January 2011) of the ECG *Bulletin*.

#### STEPHEN BALL and WILLIAM BLOSS

Atmospheric Chemistry Representatives on the EGC Committee





The atmospheres of Mars (top) and the Antarctic (bottom)

#### Forthcoming symposium

# Geochemical speciation & bioavailability of trace elements: progress, challenges & future trends

Date: 7 – 8<sup>th</sup> September 2010

Venue: Lancaster University, UK.

**Sponsors:** Environmental Mineralogy Group and the RSC Environmental Chemistry Group

Elemental speciation analysis is increasingly recognised as key to understanding the behaviour of pollutants in aquatic and terrestrial environments. Models that are able to predict elemental reactivity, bioavailability and transport are needed to better assess short and long-term risks from trace elements in the environment. As yet, geochemical models are limited in the extent to which they incorporate the formation kinetics and transport properties of metal and radionuclide complexes, and colloidal associations, in a fully mechanistic way.

This two-day conference aims to bring together geochemists, aquatic chemists, mineralogists, biologists, toxicologists and engineers to discuss recent progress in this field and identify avenues for future research and collaboration. Thus, it gives us great pleasure to invite scientists, technologists, students, legislators, government officials, and all those who are interested in studying and predicting the speciation and bioavailability of key trace elements in the environment to participate in this conference.

The conference comprises plenary poster sessions and nine keynote lectures by experts in the field:

- Dr. Jon Petter Gustafsson (Royal Institute of Technology, Sweden)
- 2. Prof. **Erik Smolders** (Leuven University, Belgium)
- 3. Dr. **Dmitrii Kulik** (Paul Scherrer Institute, Switzerland)
- Prof. Willem Van Riemsdijk (Wageningen University, Netherlands)
- 5. Prof. **Herman Van Leeuwen** (Wageningen University)
- 6. Dr. **Scott Young** (Nottingham University)
- 7. Prof. **Stan Van den Berg** (Liverpool University)
- 8. Dr. **Hao Zhang** (Lancaster University)
- Dr. Steve Lofts (Centre of Ecology and Hydrology, Lancaster).

#### Registration & payment

Participation is *limited to 70 delegates* due to space restrictions thus, pre-registration is encouraged. Registration will be £110 with a student rate of £75. Registration includes refreshments, lunches, con-

ference dinner, car parking, book of abstracts etc. B&B accommodation will be at the University campus, with en suite rooms at £46 per night. *Deadline for abstract submission for poster presentations is 30<sup>th</sup> July 2010*. Abstracts should be emailed to l.ahmed@lancaster.ac.u.

Registration and further information may be found at

#### http://minersoc-emg.org/events/ GeoSpec2010.htm

The Environmental Mineralogy Group (EMG) is a Special Interest Group of the Mineralogical Society of Great Britain and Ireland.

#### **Contact details**

Conference organisers: **Dr Imad Ahmed** (Lancaster University; email: I.ahmed@lancaster.ac.uk) and **Dr. Elizabeth Bailey** (Nottingham University; email: liz.bailey@nottingham.ac.uk).



**Lancaster University campus** 

#### **Forthcoming Symposium**

# Contaminated land: chemistry and toxicology aspects of chemical risk

# RSC Environmental Chemistry Group and RSC Toxicology Group

28th September 2010

Royal Society of Chemistry, Burlington House, Piccadilly, London

"Exploring the science applied in models used to assess the risk to long-term human health from contaminants in soil."

#### **Programme**

09:30 Registration and coffee

#### Session 1 Oral Pathways

10:00 **Dr Sohel Saikat,** Health Protection Agency: *Oral bioaccessibility data: missing the point in exposure assessment of soil-borne chemicals* 

10:35 **Dr Chris Collins**, University of Reading: *Modelling* plant uptake of organic chemicals – current status and future needs

11:10 Alan Dowding, Food Standards Agency: The Food Standards Agency's approach to assessing uptake of chemicals by crops from contaminated soil

11:45 - 12:45 Lunch

#### Session 2 Inhalation Pathways

12:50 **Katy Baker,** Arcadis: Vapour Intrusion in the UK – Where do we go next?

13:25 To be confirmed

14:00 **Simon Firth**, Firth Consultants: *Chemical exposure* via *inhalation of soil derived dust – modelling versus measurement* 

14:35 - 15:05 Coffee and tea

#### Session 3 Dermal Pathways

15:10 **Alison Mckay**, Mckay Environmental Ltd: *The dermal pathway* – *A touchy subject!* 

15:45 **Tayo Adedeji**, Atkins : Dermal Exposures to soil: metabolism, toxicity and acute duration exposures

16:20 Discussion and questions to speakers

17:00 Meeting close

#### Fee per delegate:

£150 Non-environmental Chemistry Group (ECG) or non-Toxicology Group (TOX) member £120 ECG/TOX member

£50 RSC student member

#### The registration closing date is 27th August 2010

Admission is by ticket only and places are limited so please contact Kate Jones (toxicology@rsc.org) initially to notify your interest in registering for the event. If places are still available, then details of where to send the registration slip below and cheque payment (or BACs) will be provided. If you wish to pay by credit card you will need to use the online registration procedure (details available from Kate Jones, toxicology@rsc.org). For RSC members please provide your membership number in any correspondence.

Upon receipt of the registration slip and payment, delegates will become registered for the event. Cancellations received before the cancellation deadline, 27th August 2010, will be subject to an administration charge of 25% of the total fees. It is not possible to offer refunds on cancellations received after this date, although a change in attending delegate is possible.

This event has been organised by James Lymer, Kate Jones and Mike Quint on behalf of the RSC's Environmental Chemistry and Toxicology Groups. The event is also supported by the RSC Environment, Sustainability and Energy Forum.

#### RSC ENVIRONMENTAL CHEMISTRY GROUP & RSC TOXICOLOGY GROUP

# Contaminated Land: Chemistry and Toxicology Aspects of Chemical Risk Assessment

Please complete all the details below:
Full name:
Employment Address:
Email address:
Daytime telephone:
Do you have any medical, access or dietary requirements? Yes/No (delete as appropriate)
If 'Yes', please provide details:
I enclose payment for (please tick the box as appropriate):
RSC Student Member (£50)
RSC ECG and/or TOX Member (£120)
☐ Non-member (£150)
RSC Membership number (if applicable):
Please indicate whether you wish to pay by Cheque or by BACS*
*delete as appropriate
Please make cheques payable to: RSC Toxicology Trust
For details of direct BACS Payments, please contact Kate Jones (toxicology@rsc.org)
To details of direct broot ayments, please contact react solies (toxicology@fsc.org)

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#### **Advertisement**





# Training opportunities in Air Quality and Carbon Management

With the recent multitude of changes to the Local Air Quality Management process and the increasing predominance of climate change on the political agenda, now is the time for employers and staff to ensure that they are in command of all the facts.

The University of the West of England's Air Quality Management Resource Centre (AQMRC) has developed a range of training and development opportunities to build skills and understanding in the fields of air quality and carbon management. Whether you are a recent graduate or needing to update your skills in an existing role, this training will give you the opportunity to focus your development in a way that is specific to your needs and requirements.

A series of seven different one-day courses are on offer here at UWE, Bristol, through 2010 and 2011, focusing on specific aspects of Air Quality and Carbon Management (see course list below). Each day's course comprises of four topic presentations with materials available online for up to three months.

These courses are designed to provide an overview of Air Quality and Carbon Management in the UK, and are aimed primarily at professionals in these, and related, fields in local government and environmental consultancies

Accredited by the Institute of Air Quality Management and the Institution of Environmental Science, each one-day course is equivalent to five hours Continuing Professional Development (CPD) with an additional 12 CPD hours available for further work online.

Course fees are £285 per attendee (including lunch and refreshments). Full details and a programme are available on registration. To register your interest for any of the courses below, please email agmrc@uwe.ac.uk.

#### One-day training courses

- Introduction to Air Pollution
- Introduction to Carbon Management
- Introduction Local Air Quality Management
- LAQM: Monitoring and modelling
- LAQM: Review and Assessment
- LAQM: Action Planning
- LAQM for Planners

N.B. Courses require a minimum of six attendees to run. UWE reserve the right to withdraw/amend advertised courses without prior notice; registered attendees will be notified.

In addition to the courses described above, a flexible package of CPD (including additional modules) is available for delivery at your location or at UWE. For more information about training opportunities and to discuss your specific needs, please contact aqmrc@uwe.ac.uk.

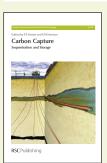
### **Issues in Environmental Science and Technology**

#### **Series Editors**

R E Hester, University of York, UK | R M Harrison, University of Birmingham, UK

This comprehensive series from RSC Publishing has been devised to tackle important environmental topics in response to the rapid growth of interest in this area and the need for authoritative reviews of such topics. Issue are published twice a year with each volume addressing a specific topic.

Written by world experts in their specialised fields, the series presents a multidisciplinary approach to pollution and environmental science and, in addition to covering the chemistry of environmental processes, focuses on broader issues; notably economic, legal and political considerations.



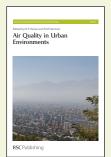
**Title:** Carbon Capture **ISBN:** 9781847559173

**Price:** £54.95

Publication date: 22/12/2009

Description: Reports on methods of capturing and storing CO<sub>2</sub> from major sources to reduce the levels

emitted to the atmosphere by human activities.



Title: Air Quality in Urban Environments

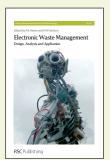
ISBN: 9781847559074

Price: £54.95

Publication date: 31/07/2009

**Description:** Provides comprehensive coverage of urban air pollution from sources through atmospheric

processes, to human exposure and effects on health and the policy response.



**Title:** Electronic Waste Management

ISBN: 9780854041121

**Price:** £49.95

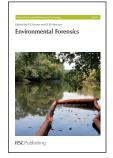
Publication date: 03/12/2008

**Description:** This volume presents an up-to-date review of the scale of the electronic waste problem, the impact of recent legislation, current

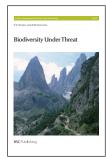
and future methods for treatment, recycling and disposal.



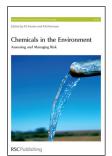
#### Other volumes available



"...this is a very useful book and gives an excellent position statement on the application of the techniques and of their limitations in environmental forensics." Reviewed in Chemistry World.



"The present book provides a very valuable introduction into environmental science and technology in general..." Reviewed in Chemistry World.



A bang up-to-date account of current and near-future legislation governing the assessment of risk and the management of chemicals in the environment. Reviewed in *ScienceDirect*.