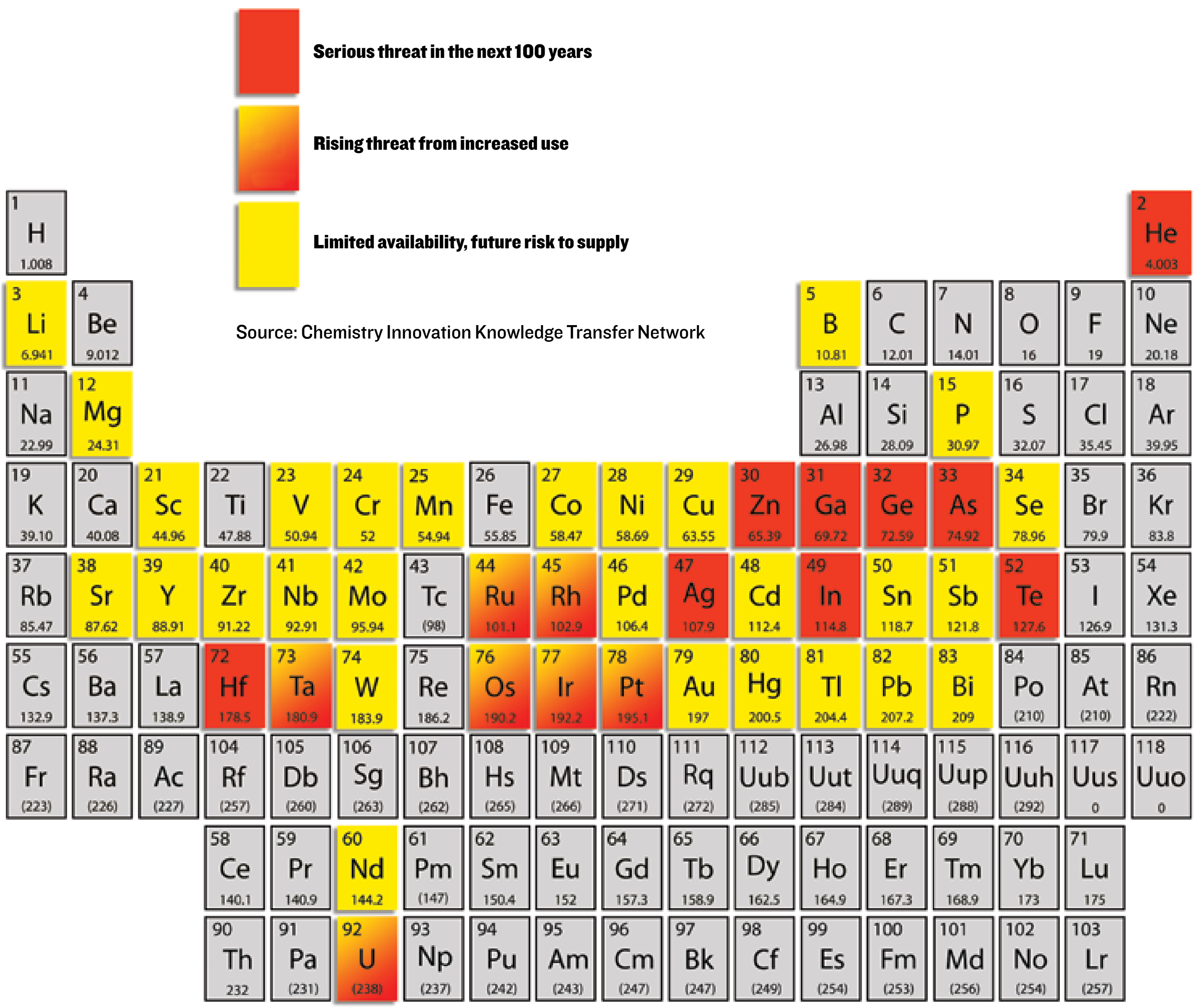
**Endangered elements**

# Critical thinking

As our supply of some essential elements dries up, it's time to start urban mining. Emma Davies reports





Last October, China started building the world's biggest off-shore wind farm in Bohai Bay, a few hours from Beijing. The country is constructing wind farms on an unprecedented scale – surely good news given its insatiable appetite for coal. But each megawatt of power a wind turbine generates requires up to one tonne of rare earth permanent magnets. The elements used in the magnets – neodymium, dysprosium and terbium – are in short supply and the west is in danger of losing access to them as China's domestic needs soar.

Unfortunately, the green future of the UK and much of Europe also relies heavily on wind turbines rich in rare earths. And it's not just green technology that is under threat – many of our everyday electronic items, from iPhones to LCD televisions, depend on the same critical elements.

Rare earths are not the only elements causing supply concerns – elements such as helium (see Balloon about to burst? p53), phosphorus (see Taking the P, p54) and copper are beginning to slip from our grasp.

'The periodic table is a thing of real beauty to chemists but we are staring at the possibility of not being able to access parts of it,' says Mike Pitts, of the UK's Chemistry Innovation Knowledge Transfer Network.

Pitts and his colleagues have compiled an 'endangered element' periodic table where red elements are under 'serious threat' of becoming unavailable in less than a century (see facing page). Helium is marked red, as are the semiconductor staples gallium and indium. Meanwhile, the rare earth metals rank near the top of most 'critical' lists.

## Action stations

Western governments are awakening slowly to the threat of losing access to key elements and expert panels in the EU and US have published lengthy reports. *Critical raw materials for the EU,* published in 2010, identified 14 raw materials and metal groups, including all of the rare earth and platinum group metals, as well as antimony, beryllium, cobalt, fluorspar, gallium, germanium, graphite, indium, magnesium, niobium, tantalum, and tungsten. The expert group that compiled the report would like to see 'policy actions' to make recycling more efficient and is keen to promote research into recycling 'technically challenging' products.

'There's currently an imbalance between the rate at which we're using materials and recycling,' says Pitts. 'We are making the elements economically unrecoverable. You get concentrations of metals in waste streams that are higher than the ores they are coming from.'

## Magnetic attraction

The rare earth elements (REEs) – the fifteen lanthanides, plus scandium and yttrium – are being consumed at alarming rates, partly to feed our obsession with the latest must-have technology. 'The real gift of the rare earths has been miniaturisation,' says Jack Lifton, who runs a US consultancy called Technology Metals Research. Rare earths like neodymium and dysprosium are used to make small, lightweight, and incredibly strong magnets. From military high-tech gadgets to headphones, magnetic jewellery clasps and magnetic toys, the rare earths have brought huge benefits.

Many green technologies are heavily dependent on the REEs, especially wind turbines and hybrid cars; each Toyota Prius hybrid car is reported to contain as much as 1kg of neodymium in its motor and 10–15kg of lanthanum in its battery.

Although the metals are not all that rare, they are only found – lumped together – in particular

### In short

- **Supply of several elements, including helium, phosphorus, indium and gallium is predicted to exceed demand in the near future**
- **Rare earths used in magnets and electronics are not scarce, but are difficult to separate and purify**
- **The west relies on China to supply rare earths, but as China's domestic demand grows, alternatives are desperately required.**
- **Recycling and alternative sources are being explored, but they may not arrive quickly enough to plug the short term demand gap**


**A monument in a field of wind turbines in Damao, China. The inscription reads: 'The home of rare earths welcomes you'**

REUTERS

## The screen

'Indium is one of the most critical elements because of the way that we use it,' says Mike Pitts, from the UK's Chemistry Innovation Knowledge Transfer Network. For example, every liquid crystal display screen contains indium components.

About 45 per cent of all indium extracted is used for the indium tin oxide that lines solar cells and flat panel displays.

The Earth's crust contains roughly three times as much indium as silver, although silver can be mined far more efficiently. In 2007 the US Geological Survey estimated that we will run out of indium for extraction in less than two decades, although the indium industry tends to dispute such figures.

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Apparently identical screens can be different inside, making recycling more difficult

'There is more indium and gallium in use than in proven possible reserves,' says Roger Morton from UK recycling specialists Axion Consulting. 'So it's more interesting to mine stuff around you than mine it out of the ground,' he says.

Recycling the indium from spent technology holds an obvious appeal but industry is reluctant to invest. C-Tech innovation, a UK technology development company, was part of a recent project to recycle flat screens and recover liquid crystals, glass, and indium using an acid-leaching process. 'We have the technology which will work to recover the indium from screens, but at the moment it's not economically viable,' says Ian Holmes, project manager at C-Tech. 'The price of indium is less than half of what it was when we started the project three years ago,' he says. The project highlighted several recycling issues, not least the differing internal makeup of seemingly identical devices. 'There's a long list of issues to be addressed,' says Holmes.

In the past couple of years, Axion has had interest from some major Asian electronics manufacturers looking to set up segregated EU recycling schemes for their branded products, says Morton. The idea is that the companies would stay in touch with those who had bought their technology and after a few years offer a deal on a new model in exchange for the old. Although such schemes would boost sales of new products, the 'prime driver is to get the resource back,' says Morton. 'It's much easier to recycle a stream of identical computers of a single brand.'

regions of the Earth's crust. Their similar chemical properties make them difficult and expensive to separate from one another. Not only are they becoming harder to mine but the few nations that do mine them are clutching their precious resources ever tighter.

China has 37 per cent of the world's accessible reserves, according to the British Geological Survey (BGS), followed by the former Soviet Republics that make up the Commonwealth of Independent States, then the US and Australia. But China supplies about 96 per cent of the world's REEs, according to the BGS. In recent years it has started to cut rare earth exports and is expected to limit exports to finished products, according to the US Government Accountability Office (GAO).

Lifton is alarmed by the slow pace with which western governments are dealing with the supply situation. 'These metals are not used for their structural value – they are used for their unique electrical and magnetic properties and there is no substitute for them,' he says.

### Heavy heart

Demand is predicted to outpace supply for the so-called heavy rare earths dysprosium and terbium in little more than a decade, perhaps less. Not only are the elements harder to extract than the light REEs, but all of the world's heavy rare earths are mined in China.

Dysprosium and terbium are 'miracle ingredients of green energy products,' says Lifton. Very small amounts of dysprosium give magnets that are up to 90 per cent lighter, while terbium can cut the electricity consumption of lights by up to 80 per cent. Alloying neodymium with terbium and dysprosium preserves the magnetic properties at the high temperatures of hybrid car engines and wind turbines. The high temperature magnets need considerably more dysprosium relative to neodymium

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## Balloon about to burst?

Helium may be the second most abundant element in the universe, but here on earth this noble gas is rare and precious. The only element to remain liquid at absolute zero, its two stable isotopes, helium-4 and helium-3, are essential and irreplaceable mainstays of cryogenics. $^{4}$He can supercool magnets down to about 1.8K, and $^{3}$He goes really low – down to below 1K. For years, US government stockpiles have created the illusion of an abundant supply of $^{4}$He and an adequate supply of $^{3}$He, but recently growing worldwide demand and short-sighted management have shattered the illusion.

Global demand for $^{4}$He is climbing as emerging powers such as China and India step up helium-hungry activities. Yet, despite the small supply and the growing demand, helium is cheap – a helium filled party balloon costs just a few dollars, for example. This is because the US government, which controls the Fort Knox of helium – the US National Helium Reserve near Amarillo, Texas – has been selling it off at bargain basement prices.

The cheap price means that this precious resource has been squandered, according to Nobel laureate Robert Richardson, who discovered liquid helium's superfluid properties. At the current rates, 'the world would run out in 25 years, plus or minus five years,' he told a gathering of Nobel laureates in August of this year.

$^{4}$He can be recycled, but with prices so low, there is little incentive. The price needs to rise by 20- to 50-fold to make recycling worth while, according to Richardson, who says that a helium-filled balloon should cost \$100. Spurred on by recent National Research Council recommendations to sell $^{4}$He at market prices, the US government announced in August that prices will increase by 15 per cent in 2011.


**Artificially cheap prices and poor resource management could spell the end of the party balloon**

$^{3}$He is critical for European Organisation for Nuclear Research (CERN) in Switzerland, and other neutron scattering facilities. The isotope has also revolutionised lung imaging, and it is used in oil and gas exploration. $^{3}$He is a byproduct of the radioactive decay of tritium, the heavy-hydrogen used in thermonuclear warheads. Thanks to the cold war arms race, the US has had a steady and adequate supply.

But after the terrorist attacks on 11 September 2001, US national security agencies began using $^{3}$He in nuclear detectors that were installed by the thousands at airports, shipyards and border crossings. These scanners now account for 80 per cent of US consumption of the gas.

*Rebecca Renner*

than is found in the ores.

The Chinese think they are running out of dysprosium and terbium, explains Lifton. China currently produces about 900 tonnes of dysprosium per year and estimates that it can mine a further 13 500 tonnes. So at the current consumption rate, the country could run out of the element in 15 years. But given the soaring demand, reserves could be exhausted even sooner.

'If we want electric cars, we had better start producing some dysprosium, because the Chinese won't keep supplying it to us,' adds Lifton. 'My guess is we're going to be short of dysprosium before anyone gets a solution rolling.' The US GAO has reported that it may take up to 15 years to rebuild a rare earth supply chain in the US. Industry is onto the problem but time is running out.

Countries with reserves are scrambling to open mines. In July 2010 US company Ucore Rare Metals started drilling at its rare earth mine in southeast Alaska, which could produce significant amounts of dysprosium. Canada has several mines under development. The problem with all of these is that the start-up costs are high but the mines are small, with limited revenues, says Lifton. 'So either you subsidise them or you get the end-user industry to put the money in and develop them.'

Mountain Pass in California, US, was once the largest rare earth mine in the world – but ceased production in 2002, partly because of Chinese businesses undercutting prices. Now US company Molycorp is set to reopen the mine in 2011, and by 2012 expects to be mining and separating cerium, lanthanum, praseodymium, and neodymium oxides at full capacity. The mine will do much to ease the current pressure on neodymium supplies.

Yet Mountain Pass will not initially be able to refine the rare earth oxides into raw materials and will probably have to ship them to China. Refined rare earths are

## Taking the P

Modern agriculture depends on phosphorus, which is mostly obtained from mined phosphate rock. Phosphorus is typically combined with sulfuric acid, nitrogen and potassium in fertilisers. Scientists with the Global Phosphorus Research Initiative estimate that within 30 to 40 years there won't be enough phosphorus from mining to meet agricultural demand, and predict a global peak in 30 years.

BRYCE RICHTER, UNIVERSITY OF WISCONSIN-MADISON, US

**Phosphorus can be reclaimed from wastewater**

Yet phosphorus is relatively easy to recover from water systems. Every year the global population excretes around three million tonnes of phosphorus in urine and faeces and highly populated cities have been described as phosphorus hotspots. If urine can be kept separate from the rest of the sewage, it can be applied straight to the fields. In some parts of Sweden, all new toilets must be able to divert urine for storage and use by local farmers.

UK water company Thames Water is building a 'nutrient recovery facility' to remove a compound called struvite, which contains phosphorus and ammonia, from sewage at its works in Slough. The plant is scheduled to begin operations in mid-2011.

The phosphorus extracted from Slough's wastewater is predicted to form 150 tonnes of phosphate fertiliser pellets per year which can be spread directly onto soil.

The struvite blocks pipes and causes water companies real headaches. 'This project is a classic win-win,' says Piers Clark, Thames Water's director of asset management. 'We solve a costly problem and in so doing provide a renewable form of phosphate.'

currently only available from China and US industry officials have told the GAO that it would take at least two years to develop a pilot plant that could refine the oxides to metals.

### There is a light

So far, so gloomy. Yet Pitts sees the situation as a 'huge opportunity' for chemists to help recover the elements. 'We should be scared but equally excited about the opportunities,' he says. There are projects to reduce and recycle rare earths. When computers are discarded the hard drives are dismantled so as to destroy any data. Andy Williams's team at the University of Birmingham, UK, has found a neat way to turn their neodymium magnets into powder, simply by exposing them to hydrogen gas at atmospheric pressure. 'Hydrogen goes into the spaces between the neodymium atoms and causes the structure to swell,' explains Williams. 'The surface swells but the inside doesn't, creating stresses that cause the material to break apart.'

Williams has managed to make new magnets by pressing the resulting powder together and heating it. The magnets are not top-spec but can be used in motors. 'We can also add extra neodymium and dysprosium and change it to a different grade of material,' explains Williams. 'We want to take it to the next step where we're actually collecting scrap and reprocessing it into magnets.'

Meanwhile, researchers at the University of Leeds, UK, have found a way to reclaim rare earth oxides cheaply from the waste stream from refining titanium dioxide. The titanium dioxide industry 'hates' the rare earths that contaminate their feedstock, explains project leader Animesh Jha.

Rare earth chlorides have extremely high boiling points, thanks to strong nuclear forces. Working with UK company Millennium Chemicals (now Cristal Global), Jha's team set about trying to purify lower grade titanium tetrachloride feedstock. The process that they came up with involves roasting aluminate materials with alkali. 'During roasting the dispersed rare earth minerals flocculate in the highly alkaline medium,' explains Jha. The metal oxides – of neodymium, cerium, lanthanum and praseodymium – form a separate layer that floats despite its high density, thanks to repulsion between the OH groups surrounding the metals. 'Our titanium dioxide process has a very low carbon footprint compared to the standard acid leaching process,' says Jha.

Jha is currently seeking funding for the next project stage – separating out the component rare earth oxides. The rare earth oxides all have very similar properties and Jha has a difficult task in store.

We all have a difficult time ahead and it is hard to see how short-term shortages of rare earth elements will be addressed. Let's hope that the wind of change will blow across the West and give scientists the intellectual and financial boost needed for a recycling revolution.

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**Praseodymium, cerium, lanthanum, neodymium, samarium and gadolinium oxides – their similar properties make them difficult to separate**

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