



Nickel Use in Emerging Technologies

Introduction

While the dominant use of nickel is in stainless steel and alloys, where output is measured in thousands of tonnes, nickel is also finding uses where the amount of nickel involved is calculated in parts per million. This Insight report, the 24th in the series of INSG Insight briefing reports, provides members with information on areas where nickel is active at the molecular level. The first part of the report looks at how the unique characteristics of nickel can be used to produce hydrogen utilizing nanoscale interactions in energy systems. The second part of the report provides information on plants which bio-accumulate nickel. This report is intended to contribute to a better understanding by member countries of issues surrounding nickel and the environment and to provide information on new and emerging uses for nickel.

Using Nickel to Produce Hydrogen

Several research teams have been working to produce hydrogen with methods that rely on nickel. Hydrogen is a potential fuel which could be used to power fuel cells in zero-emissions vehicles or to generate electricity. It could also offer a way of storing energy from renewable energy projects based on wind or photo-voltaic generation. Electricity could be used to convert water into hydrogen which in turn can be stored or transported and converted back to electricity in fuel cells. One advantage of using hydrogen in fuel cells to produce electricity is that there are no CO₂ emissions.

In August 2014 a report was published by a team at Stanford University in the United States who have developed a relatively cheap, emissions-free method to split water molecules and obtain hydrogen. The team employed nanoscale nickel oxide/nickel heterostructures formed on carbon nanotube sidewalls as electrocatalysts. The scientists used the electrocatalysts in a device that passes electric current through two electrodes and splits liquid water into hydrogen and oxygen gas. While other water splitters use precious-metal catalysts such as platinum, the electrodes in this case are made of nickel and iron. Using these electrocatalysts the system is active enough to split water at room temperature using a 1.5-volt battery. The research team found a nickel-metal/nickel-oxide structure that is more active than pure nickel metal or pure nickel oxide alone. Since the use of the nickel/nickel-oxide catalyst significantly lowers the voltage required to split water, it could eventually save hydrogen producers billions of dollars in electricity costs. Further information can be found at <http://news.stanford.edu/news/2014/august/splitter-clean-fuel-082014.html>

In April 2014 a team at the University of Delaware in the United States reported that they have demonstrated that nickel nanostructures in the form of hollow spheres can catalyze the water-splitting reaction under conditions that compare favorably to using a much more expensive ruthenium or iridium catalysts. Further details can be found at <http://pubs.acs.org/doi/abs/10.1021/ja502128j>

Nickel in Artificial Photosynthesis

Nickel also plays a role in a different system developed to produce hydrogen by means of artificial photosynthesis. A team of researchers at the University of Rochester in the United States has developed a photochemical hydrogen-generating system which utilizes cadmium–selenide (CdSe) quantum dots, nickel salt catalysts and ascorbic acid (vitamin C). The system has a quantum efficiency of 36% – for every 100 photons absorbed, 36 hydrogen molecules are produced. If the surrounding solution is a mix of water and ethanol, this efficiency increases to 66%. One limiting factor is that the vitamin C gets used up and regularly needs to be replenished during each hydrogen production cycle.

The researchers say that their nickel containing nanocrystal catalysts are better than previous artificial photosynthesis nanoparticle systems as they are more stable in sunlight, but they do not yet know why this is the case. Further information can be found at

<http://physicsworld.com/cws/article/news/2012/nov/09/nanocrystals-produce-hydrogen-using-sunlight>

Nickel Accumulation in Plants

In May 2014 a report was published describing the discovery by scientists from the University of the Philippines of a plant, *Rinorea niccolifera*, which accumulates nickel at very high levels. The shrub reportedly was found to accumulate over 18,000 parts per million (ppm) of nickel and not be poisoned by the metal. (The report was published on line at <http://www.pensoft.net/news.php?n=384>)

It has been known for many years that certain species of plants accumulate metals in their leaves, stems and roots. Plant species have been identified which accumulate copper, cobalt, nickel, lead, zinc, cadmium and other metals. One definition of a hyper-accumulator is a plant that accumulates at least 1,000 mg/g⁻¹ (0.1% dry weight) of copper, chromium, lead or cobalt, or at least 10,000 mg/g-1 (1% dry weight) of manganese or nickel.

While the fact that plants can accumulate and concentrate metals, including nickel, is not new, recent advances in gene technology may open the way for this biological fact to be used in a number of ways. Dr Augustine Doronila of the School of Chemistry, University of Melbourne, a co-author of the report on *Rinorea niccolifera*, noted that "Hyperaccumulator plants have great potential for the development of green technologies, for example, 'phytoremediation' and 'phytomining'". Phytoremediation refers to the use of plants to remove metals from contaminated soils, while phytomining is the use of plants in metal containing sites to recover metals.

At least 300 species have been identified which hyper-accumulate nickel. The hyper-accumulation of nickel appears to provide plants with protection against

fungal and insect attack. A partial list of some of these species with the highest rates of accumulation is included at the end of this Insight report.

There are several ways in which hyper-accumulating plants may be used.

Phytoremediation offers a means to use plants to mitigate environmental contamination without the need to excavate the contaminant material and dispose of it elsewhere. Phytoremediation can be applied to contaminated soils or water by fostering the growth of plants which accumulate and concentrate metals. One advantage of this approach is that contaminated soils may be treated in situ. It does, however, require a long-term commitment, as the process is dependent on the rate of plant growth.

A second potential application of metal accumulation by plants is prospecting for new mineral deposits making use of the accumulation of metal in leaves and bark of plants. In regions with hills or mountains samples can be taken from plants and the concentration of metal mapped according to elevation. If it is found that metal accumulation rises sharply below a particular elevation, further survey work and drilling can be done at the point where the change is detected.

Another application of hyper-accumulating plants is phytomining. Selected species can be grown on a target area and then harvested and processed to remove the metal. After sufficient plant growth and metal accumulation, the above-ground portions of the plant are harvested and removed.

In the past, the fact that some plants accumulate nickel has been more of a scientific curiosity than a useful tool. However, with new knowledge of genetics and advances in the ability to identify and activate specific genes responsible for hyper-accumulation, it may be possible to select plants for specific situations. It is also possible to transfer the genes from one species to another and to thereby design plants for the purpose of hyper-accumulating metals including nickel.

Outlook for Nickel in New Technologies

Nickel and nickel compounds are increasingly finding novel uses in nanoscale engineering of materials. Currently, much of the world's supply of hydrogen gas is made via reactions with methane and steam at high temperatures, releasing greenhouse gas carbon dioxide in the process. Using electricity from renewable sources to split water by electrolysis is at present too expensive to compete with methane derived hydrogen. But the use of nickel-containing catalysts may lower the cost and offer less-polluting sources of hydrogen for hydrogen-based energy systems.

Green technologies such as phytoremediation and phytomining may be increasingly used in the future. Research on nickel accumulating plants may help to better understand how to best use these natural characteristics for specific purposes.

Member countries are encouraged to contact the INSG secretariat with questions or suggestions for further work on this topic.

Comments or Questions - Please contact Curtis Stewart at the INSG Secretariat. Email: curtis_stewart@ilzsg.org or telephone +351 21 359 2423

Selected Plants Which Hyper-Accumulate Nickel

Accumulation rates of nickel (in mg/kg of dry weight)	<i>Latin name</i>	Notes
29400	<i>Alyssum argenteum</i> All. (<i>Brassica</i>)	Distrib. Italy
34400	<i>Peltaria emarginata</i> (Boiss.) Hausskn. (<i>Brassica</i>)	Distrib. Greece
14,900 to 27,700, up to 32,000	<i>Psychotria douarrei</i>	Origin New Caledonia; 372 records of plants. Ni contents in leaves of <i>P. douarrei</i> vary considerably due to leaf age.
H-up to 26% in xylem	<i>Sebertia acuminata</i>	Origin Caledonia
21,500	<i>Stackhousia tryonii</i> Bailey (<i>Stackhousiaceae</i>)	Origin western Australia
14800	<i>Streptanthus polygaloides</i> Gray (<i>Brassica</i>)	Ni-hyperaccumulation protects <i>S. polygaloides</i> against fungal and bacterial pathogens.
16200	<i>Thlaspi caerulescens</i>	phytoextraction.
52120	<i>Thlaspi cypricum</i> Brnm. (<i>Brassica</i>)	Distrib. Cyprus
35600	<i>Thlaspi oxyceras</i> (Boiss.) Hedge (<i>Brassica</i>)	distrib. Turkey, Syria

Source: Majeti Narasimha Vara Prasad, *Nickelophilous plants and their significance in phytotechnologies*. *Braz. J. Plant Physiol.* Vol.17 no.1 Londrina Jan./Mar. 2005