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October 2011

PROCESS WEST

Yara Belle Plaine

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Miracle material

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Our own Brave New World

This might not necessarily be the *Brave New World* that Aldous Huxley envisioned when he penned his iconic 1930s novel, but we are certainly living in the dawn of an era that will most certainly be characterized by tremendous technological change.

From power generation in the forestry industry to a "miracle material" that has the potential to revolutionize virtually every area of our lives, change is all around us.

It's a theme that plays very prominently in the October issue of *ProcessWest*.

Take **Ernest Granson's** insight on graphene, for example — a material "nominated by many scientists, engineers and entrepreneurs as the most promising substance this century — indeed, some say, even the last century."

Granson writes that this enigmatic material, a single layer of carbon atoms derived from the mineral graphite, exhibits exceptional conductivity, strength, flexibility and weight that could lead to a wide variety of uses, from super-fast transistors for microelectronic devices and circuits to building materials for aircraft, when combined with polymers.

There is such a strong belief in the potential of graphene, notes Granson, that this past spring, the European Commission approved a 10-year, $1-billion Euro research initiative to push for a technological breakthrough leading to large-scale commercialization.

"Graphene is usually described in superlatives; it's the strongest material known, the most lightweight, and mostly highly conductive. Its electrons move much faster than the semi conductors used in today's transistors," Dr. Tapash Chakraborty, professor of physics at the University of Manitoba and Canada Research Chair in Nanoscale Physics, tells Granson.

Western Canada's forestry industry, meanwhile, is not immune to its own forms of change, too.

As columnist **Tony Kryzanowski** points out, the sector "is drowning in potential bio-fuel sources capable of being incinerated directly to drive stream turbines or converted to fuels such as syngas and bio-diesel."

And the industry is starting to take action. From Weyerhaeuser to Al-Pac, Kryzanowski notes companies, often with considerable government backing, are making multi-million-dollar investments in plant upgrades that will generate, and even market, power to the grid.

Miller Western Forest Products, for example, is currently installing an anaerobic hybrid digester at its Whitecourt, Alta., pulp mill to pre-treat waste water and produce biogas, which will be used to generate electricity.

Daishowa-Marubeni International (DMI), meanwhile, is using more than $40 million in funding through the Pulp and Paper Green Transformation Program to increase its power-generating capacity by 650 per cent increase over previous export levels. That's enough energy to power 10,588 homes annually.

Technological advancements are further reshaping the agriculture industry, where fertilizer giant Yara Belle Plaine is introducing new technologies to Western Canadian farming practices.

In this issue's cover story, Yara Belle Plaine's Andrew Swenson discusses the company's new 'N' sensor, a tractor-mount mechanism that uses a light system that reflects off the leaves of the plants to detect how much nitrogen the plant is taking from the ground.

Heavily used in Europe, the sensor allows farmers to essentially map their fields – where they're deficient, where they're not.

In addition, Yara Belle Plaine has entered the micronutrient arena. From copper to zinc, and boron to magnesium, these add-ons will help make crops healthier, improve yields and protein content.

"We're trying to create efficiencies for the farmer," says Swenson.

* * *

The October issue of *ProcessWest* also marks the return of our annual survey.

Wrapped around the front cover, the survey, once completed, will allow us to get a better feel of our readers' western purchasing plans. Not only will this help us to shape our upcoming editorial content, but it will also give you an opportunity to win an iPad2 just for entering.

The survey can be filled out and faxed or mailed to the number and address provided. Or complete the survey online at www.processwest.ca/survey. The winner's name will be announced in the March 2012 issue.

* * *

Speaking of iPads, October marks a big milestone for *ProcessWest*, with the magazine's website, www.processwest.ca, now iPad optimized

It's a natural progression for our magazine given the staggering benefits that this revolutionary tablet offers — to both us and you.

Consider this. Smartphones and tablets are responsible for an estimated 6.8 per cent of all Internet traffic; and in the tablet world, the iPad accounts for 97 per cent of traffic.

And let's just admit it: everything looks better on an iPad. Maybe it's time to start running my photo then?

Jamie Zachary

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by Ernest Granson

Graphene: The miracle material

Can this single layer of atoms live up to its promise?

It has yet to be commercialized on a large scale, yet graphene has been nominated by many scientists, engineers and entrepreneurs as the most promising substance this century — indeed, some say, even the last century.

This enigmatic material, a single layer of carbon atoms derived from the mineral graphite, is the subject of research around the world, as well as countless publications and much serious contemplation by industry.

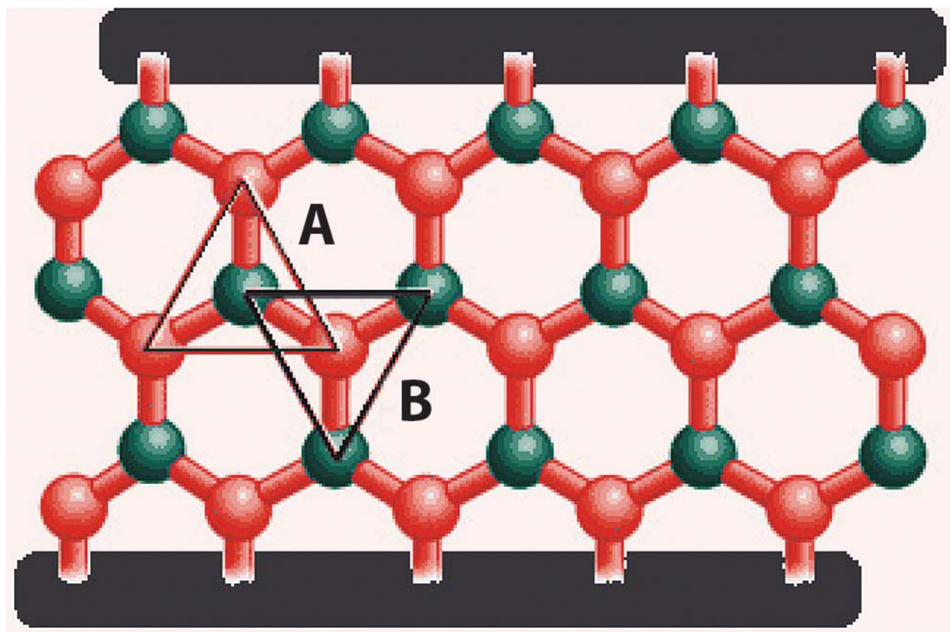
"Graphene is usually described in superlatives; it's the strongest material known, the most lightweight, and mostly highly conductive. Its electrons move much faster than the semi conductors used in today's transistors," says Dr. Tapash Chakraborty, professor of physics at the University of Manitoba and Canada Research Chair in Nanoscale Physics.

Graphene's exceptional conductivity, strength, flexibility and weight means it could have a wide variety of uses, from super-fast transistors for microelectronic devices and circuits to building materials for aircraft, when combined with polymers.

There is such a strong belief in the potential of graphene that this past spring, the European Commission approved a 10-year, $1-billion Euro research initiative to push for a technological breakthrough leading to large-scale commercialization.

It may not take 10 years for some graphene-based products to be brought to market though. Last year, IBM researchers demonstrated a 100-gigahertz graphene transistor, although the main researcher, Yu-Ming Lin, stressed that graphene in its current form wasn't capable of replacing silicon as the main component of circuits. However, this past spring, it seemed that IBM researchers had worked their way around a number of obstacles to build the first integrated circuit based on a graphene transistor.

Other near-future commercial possibilities include graphene film for use in flat-panel displays such as smart phones or tablets, technologies into which both Samsung and Nokia have placed significant investment for research. It's been suggested that those products could be ready for use in several years.



This diagram of a graphene lattice illustrates a unit cell containing two atoms – Atom A and Atom B. *Illustration courtesy Tapash Chakraborty.*

Graphene and the weirdness of quantum physics

For the non-physicist, it could be difficult to grasp the logic behind graphene's properties that make possible its seemingly limitless applications. But then again, logic is usually out the window when it comes to relativistic quantum physics, which happens to be the logic under which the graphene operates.

Technically speaking, electrons moving through the structure of graphene are subject to quantum electrodynamics (QED) as opposed to quantum mechanics. One phenomenon within QED theory called "perfect quantum tunneling" allows for objects, such as electrons, to pass through energy barriers without any resistance. This property, and also the conical-shaped bands in graphene that cause electrons to behave as if they are massless, moving at 1/300th the speed of light, accounts for the substance's super conductivity, Chakraborty says.

"The single layer of carbon atoms which forms graphene is made up of extremely tightly bound atoms which form a honeycomb or hexagonal lattice with two carbon atoms per unit cell where one carbon sits at each 120 degree corner," he says.

"That bonding explains why graphene is considered stronger than steel, while the flexibility is as a result of its single layer, two dimensional formation."

Graphene burst onto the physics scene in 2004 with the publication of the paper *Electric Field Effect in Atomically Thin Carbon Films* in the journal *Science*. Authors Andre K. Geim and Konstantin Novoselov, professors at the University of Manchester in England, along with fellow professors, described how they extracted graphene by mechanical exfoliation (repeated peeling) of small mesas of highly oriented pyrolytic graphite. In practical terms, a flake of carbon with a thickness of just one atom was obtained using regular adhesive tape. This came at a time when many believed it was impossible for such thin crystalline materials to be stable.

Geim, Novoselov and colleagues went on to explain the surprisingly high quality of electron transport they found for a film of such thickness, suggesting the properties of graphene would make it a more than ideal candidate as a metallic field-effect transistor, at least for in the future. For their research into this material, Geim and Novoselov were awarded the 2010 Nobel Prize in Physics.

While graphene, as a viable product has only come to the forefront in the last 10 years or so, graphite has long been considered as a useful mineral, going back to, at least, the Aztecs who used it as a marker. It wasn't known in Europe until the 1400s, but was thought be lead at the time. When a large, pure deposit of graphite was found in England in 1564, it became the main source for marking utensils which, at that time, were known as "lead" pencils.

In 1779, Swedish chemist K.W. Scheele, recognized for his major role in discovering oxygen, determined the mineral was not lead, but carbon after realizing that burning graphite resulted in carbon dioxide. The term graphite was given to the mineral in 1789 by well-known German scientist and geologist Abraham Gottlieb Werner.

Acute academic interest into graphite led to the discovery of several notable characteristics of graphene long before it became designated as an isolated substance.

It was a Canadian physicist conducting theoretical research into graphite to understand its electronic properties who pointed out a number of significant observations that still hold relevance to today's research.

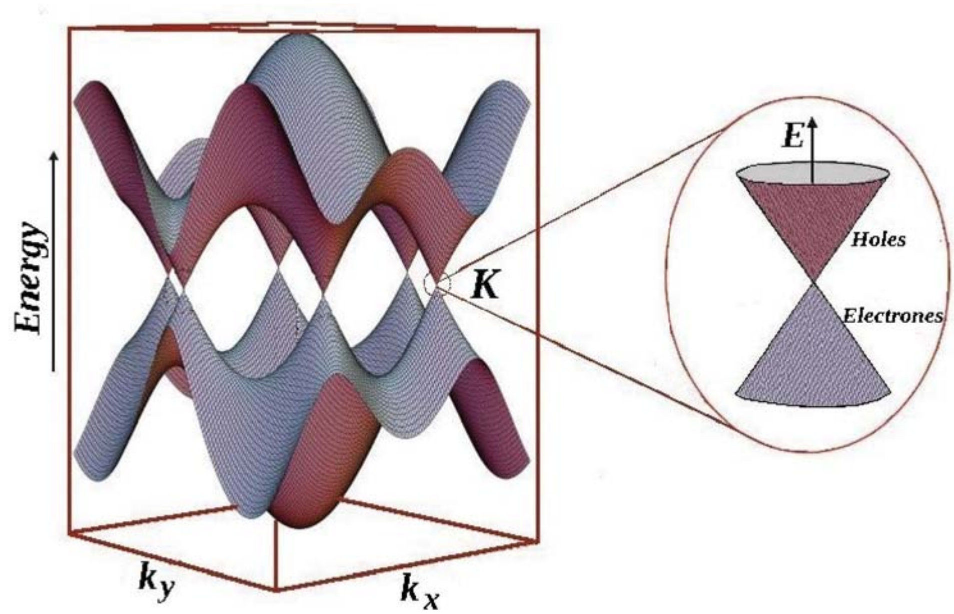
Philip R. Wallace, then with the National Research Council of Canada's Chalk River Laboratory at Chalk River, Ont., published his *Band Theory of Graphite* in 1947, in which he explained graphite's unique electronic energy band structure and, essentially, paved the way for the discovery of graphene.

German chemist Hanns-Peter Boehm is also considered a pioneer in the development of graphene. Using transmission electron microscopy and X-ray diffraction, Boehm and co-workers isolated and identified graphene sheets in 1961 — although there is some controversy about whether his results are technically considered isolation of layered graphene since what was actually produced were graphene flakes that were placed on thin nitrocellulose films for microscopic observation.

Boehm and his colleagues produced the graphene flakes by oxidizing bulk graphite with a potassium/sulfuric acid solution and using dilute sodium hydroxide to enlarge the resulting interlayer graphite spacing.

There is no dispute, however, Boehm's overall contribution toward graphite research. In 1994, as part of a committee and co-author of a paper for the International Union of Pure & Applied Chemistry, he helped officially name and describe the various graphite compounds, including the newly identified graphene.

Geim's work with graphene began in 2002 when he arrived at the University of Manchester from the University of Nijmegen in the Netherlands (and originally, from Moscow Physical-Technical University and the Institute of Solid State physics in Chernogolovka, Russia).



Energy dispersion relation of graphene (as derived by Philip Wallace). The lower band is completely filled and meets the totally empty band at the K point. ***Illustration courtesy Tapash Chakraborty.***

Becoming interested in variations of carbon nanotubes, which are also essentially graphite, he first attempted to create thin layers of graphite by using polishing equipment to reduce a piece of graphite,. He later reverted to the less hi-tech method of using Scotch tape to peel away the layers of graphite. The tape was dissolved and the layers were placed into solution.

Geim said the experiment didn't actually result in single-layer graphene, but in a substance about 10 layers thick; thin enough, however, to show promise of eventually obtaining a single layer.

"Now that the remarkable properties of graphene have been confirmed, the objective is to find other ways of controlled growth of the substance," says Chakraborty.

For instance the School of Physics at Georgia Tech has been working on the epitaxial technique where wafers of silicon carbide are heated to 1,000 C, evaporating the silicon, and leaving carbon layers, — in essence, graphene.

"There was some difficulty in achieving a single layer, but they are able to do this because, even if there several layers, when you grow the layers they rotate slightly and de-couple," says Chakraborty.

"So that's one controlled manner to grow graphene. This technique is being used by a number of research groups at companies such as IBM."

Another promising method is chemical vapor deposition, says Chakraborty. The Massachusetts Institute of Technology's Electrical and Computer Science Department, led by Jing Kong, as well as the SKKU Advanced Institute of Nanotechnology and Center for Human Interface Nano Technology, Sungkyunkwan University in Seoul, South Korea, have had considerable success with this method, in which methane gas is flowed onto a metal like nickel. It's cooled down, after which a layer of carbon is formed onto a graphene film. The film can then be transferred to a flexible polymer.

What's significant about this technology is it shows promise of larger-scale production, and the graphene maintains its important electronic properties even with the film being bent or twisted.

More recently, another team of MIT scientists injected compounds of bromine or chlorine into a fragment of graphite. The compounds penetrated in-between layers, pushing the layers slightly apart. When the graphite was dissolved, it naturally came apart where the added atoms were, forming graphene flakes two or three layers thick, and much larger in surface area. This resulting structure also produced the crucial band gap necessary to control electron flow, and allowing the graphene to act as a semi-conductor.

The lack of a band gap has been one of the major obstacles in the development of graphene material as a viable successor to silicon. It should be noted that numerous other research groups around the world are also zeroing in on removing this barrier.

Moving ahead with commercialization

While there is considerable effort taking place into graphene research, it's important to point out there are already numerous commercial efforts aimed at bringing graphene into full commercial production. Vorbeck Materials Corp., based in Jessup Md., produces graphene using a thermal exfoliation method patented by the Aksay research group at Princeton University.

Vorbeck CEO Kristen Silverberg, explains the Vorbeck process intentionally introduces "wrinkles" into the graphene sheets to prevent them from restacking.

"Much like a sheaf of paper, if the individual sheets of paper lie flat, it's easy to restack them," she says.

"If each individual sheet is slightly wrinkled, it prevents the stack from reforming."

The process used at Vorbeck has the advantage of cost-effectively producing commercial quantities of high-quality graphene using standard industrial equipment.

Some researchers have explored other exfoliation methods using bursts of energy or chemicals to produce graphene. Other researchers have attempted to produce graphene including by growing it epitaxially — that is, growing one crystal structure on top of another crystal structure.

Silverberg says Vorbeck is the only company authorized by the Environmental Protection Agency to produce graphene for use in commercial products. Vorbeck commissioned a ton-scale production plant in 2007. Two years later, it became the first company to launch a commercial product using graphene with the launch of the Vor-ink product line of graphene-based conductive inks for printed electronics. MeadWestvaco, a leading packaging company, is using Vor-ink in a new packaging product designed to deter theft.

In addition to its existing line of graphene-based conductive inks, Vorbeck expects to be the first company to sell graphene-based batteries. Last year, the company — in collaboration with the Pacific Northwest National Laboratory operated by Battelle Memorial Institute, a private, not-for-profit research organization, for the Department of Energy — announced a co-operative research and development agreement to develop Li-ion battery electrodes using Vorbeck's unique graphene material, Vor-x. These new battery materials could enable electronic devices and power tools that recharge in minutes rather than hours, or function as part of a hybrid battery system to extend the range of electric vehicles.

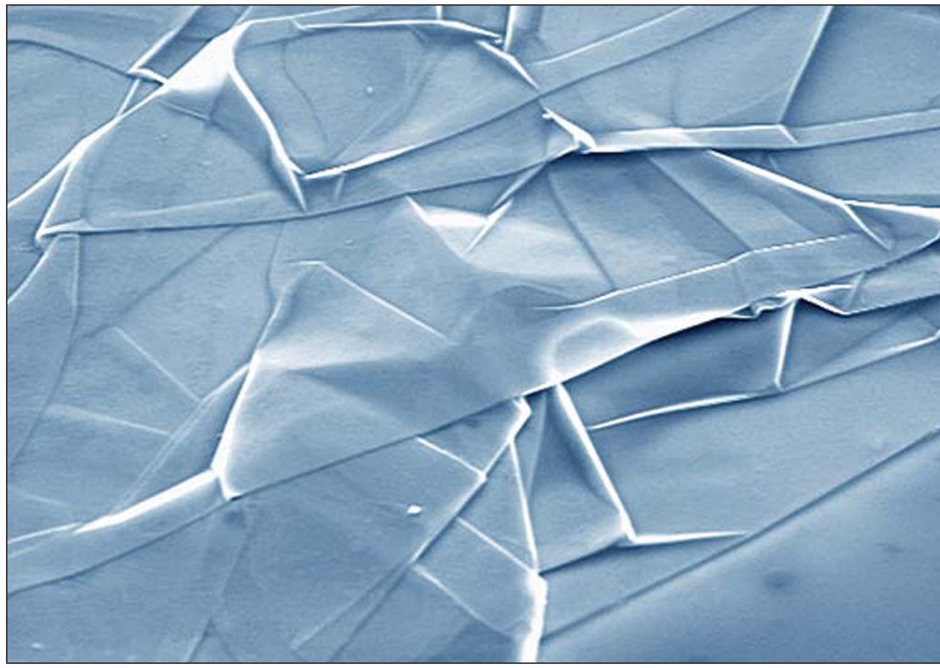
Vorbeck is also active in developing composite materials using graphene in partnership with several large companies, as well as the Army Research Lab.

"We believe graphene has enormous potential to transform a number of industries by enabling dramatic performance improvements at a low-cost," Silverberg says.

Graphene Energy Inc. of Austin, Tex., is also pursuing graphene's potential for efficient energy storage. However, this type of storage will be in the form of an ultracapacitor that can store and quickly deliver energy in a short amount of time compared to a battery.

Capacitors, from which ultracapacitors are derived, have been used for years to regulate and smooth out power output for electronic circuits in common appliances,. They are also used to temporarily maintain a power supply while a battery is being charged.

The energy stored in a capacitor, though, is generated electrostatically, as opposed to electrochemically as in a battery. The ultracapacitors utilize the storage based on (electrochemical) polarization of ions in an electrolyte which is still much faster than batteries. yet still an order of magnitude slower than electrolytic capacitors. Research into ultracapacitors began in the 1970s, but it's only been in the recent decade that their potential as a longer-term energy storage device has been recognized.



SEM micrograph of a strongly crumpled graphene sheet on a Si wafer. It looks like silk thrown over a surface. Lateral size of the image is 20 microns. Si wafer is at the bottom-right corner. ***Photo courtesy K. Novoselov, University of Manchester.***

Graphene Energy acting CEO Dr. Dileep Agnihotri says ultracapacitors, with their increased capacity for energy storage, have become possible alternatives to lead acid batteries for hybrid vehicles.

"We compared the energy generation capacity of traditional activated carbon based ultracapacitors of about five watt-hours per kilogram weight to that of lead acid batteries with 30 to 40 watt-hours per kilogram and to lithium batteries of more than 100 to 150 watt-hours per kilogram," says Agnihotri.

"We were aware of the growing use of ultracapacitors in use at train stations for stopping and starting trains, and with China's use of the device in buses. Given this data, we had to ask if there might be a role for this new material of graphene."

Based on research undertaken by researchers at the University of Texas in Austin — including well-known professor, Dr. Rodney Ruoff, who began studying graphene in the early 1990s and who leads the U of T's nanoscience and technology lab — the company began testing ultracapacitor cells that contained graphene electrodes. Agnihotri says they were surprised to learn the power capability and speed improve dramatically compared to electrodes made of activated carbon.

"Typically, there should be a discharge cycle of 0.5 Hz, which means every couple of seconds the capacitor discharges and then charges. The graphene-based cell tested to a range of five to 10 Hz, which means it can charge in one-quarter of a second or less."

Further testing, Agnihotri says, allowed researchers to project a cycle life of two million discharge/charge cycles before end of life, compared to a half to one million cycle life for a conventional ultracapacitor.

"These results were very exciting," he says. "And to get the graphene products into commercial production will not take any extreme reconfiguration of existing products. The current super and ultracapacitors are basically jelly-rolled cells ranging from coin size to large soda cans. The graphene products shouldn't be much different."

Just as importantly, Agnihotri says their cost analysis shows that, using graphene, overall production costs can be reduced by as much as 40 per cent.

"The cost per watt/hour stored is what matters most," he says. "On that metric, when we are in full scale production, it will cost two-and-a-half times less than the current technology.

"A major cost for ultracapacitors using activated carbons is quality control. However, with high-quality graphite as the raw material, that quality control is much easier to manage and therefore less expensive. Even the packing material will cost less since less is required to store same amount of energy."

The company is confident about its technology component, including current research and technology, and partnership talks are underway.

Its future steps are to set up a pilot project, with a timeline of about 12 to 18 months, and then to contract a third-party manufacturer for full-scale production.

About the Author: Ernest Granson is a Calgary-based writer and editor, and a regular contributor to PROCESSWest.