Region pins big economic hopes on little nanotubes

Nanotechnologies are a focus of competition between world economies. A race where coming second is not an option for States any more than regions. Among these is the Wallonia region of Belgium, which is wagering on nanotechnologies to help along its industrial redeployment. But the economic odds and health unknowns may make it a long shot.

Report by
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The reactor sitting in the huge production shed can produce up to 40 tonnes of carbon nanotubes a year, and yet occupies a bare thirty square metres of floor. The rest of the concrete expanse could easily hold other reactors, tangible evidence of the high hopes that this SME, Nanocyl, is putting in the growth of the nanomaterials industry. Where nanotechnologies are concerned, Nanocyl is both the spearhead and the pride of Wallonia, a French-speaking region in the south of Belgium. A product of Namur and Liège universities, the company has grown rapidly since being set up in 2002, and now ranks among the world's top carbon nanotube producers.

The fledgling business set up operations in Sambreville, between Namur and Charleroi, on land next to a factory run by Belgium's chemical industry giant, Solvay. Unlike its prestigious neighbour, Nanocyl has no swarms of workers or plumes of smoke billowing forth. Just a metal tube spewing out flames, the only visible evidence of manufacturing activity. The reason being that only one operator per machine is needed to keep production running smoothly. The nano industry here is as automated as it can be. The chemical reaction which converts gases into carbon nanotubes takes place in a completely closed system (see box). The nanotubes drop as black powder into huge clear plastic bags which are filled and sealed automatically. The operator then just has to load the bags into ordinary cardboard boxes and pallet them up.

A licence to print money?

Most of the Walloon company's output goes to Asian customers. "It's a cultural thing. Asia is more open to innovation than Europe", remarks Nanocyl's general manager, Francis Massin. The business boss did not wish to disclose his main customer's names, preferring instead to play up the qualities of his carbon nanotubes and the stupendous prospects for innovation they offer industrialists.

And the figures are literally mind-boggling: a carbon nanotube is 100 to 200 times stronger yet six times lighter than steel[1]. As well as the mechanical properties they confer on products that they are incorporated in, carbon nanotubes have thoroughly exceptional thermal and electrical conductivity[2]. As yet, we have barely scratched the surface of what can be done with these properties, which could revolutionize whole swathes of industry.

Carbon nanotubes (CNT) are a new form of crystalline carbon which resemble rolled-up strip of graphene sheets with one end capped. The basic shape of a CNT is a cylinder. These tiny tubes can have single or multiple concentric walls. Single-walled CBNT (SWCNT) have diameters of 0.4 to 2 nm (1 nm = 1 billionth of a metre), while multi-walled CNT (MWCNT) consist of multiple concentric cylinders of increasing diameter from 2 to 100 nm, depending on the number of walls, thus its structure is more complex.

1. Lafon, D, Roos, F et Ricaud, M 2008, Les nanotubes de carbone : quels risques, quelle prévention ?, *Hygiène et sécurité du travail. Cahiers de notes documentaires*, 1st quarter, No. 210, INRS.

2. CNT can carry current densities close to 10^{10} A/cm^2 - at least two orders of magnitude higher than metals. They have a thermal conductivity higher than that of silver, copper and diamond. Lafon, *op.cit.*

Impression of a carbon nanotube. The price of carbon nanotubes has fallen from 500 euros/ gramme in the year 2000 to under 250 euros/ kilo today.
Image: © Nanocyl, Th. Strickaert

Nanocyl is wagering on innovation to give it a lead on its rivals. "Our success will depend on our ability to deliver added-value products", muses Francis Massin. Aware that in the long term it could be up against unbeatable competition when emerging economies launch into manufacturing nanoparticles, the Walloon SME has embarked on a real race against time to develop high added value finished products. Some of the carbon nanopowders stay in the Sambreville plant to be turned into plastic granules for the electronics industry. They go into making tubs used in the production of computer chips and hard drives. The anti-static properties that nanotubes give these plastic tubs significantly reduces the risk of damage to the chips. Car-making is another growth market, for parts manufacture from injection systems to dashboards.

The plant also produces silicone paints with CNT mixed in, which could be of value to the shipbuilding industry. "Tests have shown that barnacles cannot cling to the hull of ships painted with our paint, so it could replace the paints in use today that are highly toxic for the marine environment", forecasts Francis Massin.

Nanocyl has received a total of nearly one and a half million euros in EU funding for different R&D projects. The Walloon firm is currently coordinating the Inteltex project to develop smart textiles that react in specific ways, such as to temperature changes[3]. Potential applications include firefighting clothing that can detect carbon monoxide, or medical clothing that monitors body temperature. The company manager also foresees a huge market in the construction industry, with CNT-added concrete or fire retardant electric cable shielding. "These cables have already been lab tested, and when subjected to fire have been shown not to burn or give off toxic fumes".

Although the undeniable standard-bearer, Nanocyl is not the only nanotechnology concern in Wallonia. Nanopôle is a very young company based on a public-private partnership to develop the nanopowder industry in Wallonia. The company receives funding under the Marshall Plan, a huge public investment programme to kick-start Wallonia's economic recovery. The money has enabled the company to buy an impressive piece of kit that can produce twelve different types of nanopowders.

The business goal is to eventually get to the position of selling nanopowders to industrial customers and to market nanopowder production lines. Adding tiny amounts of nanopowders to traditional materials like glass or plastic enhances their mechanical strength and heat resistance. The scope is vast, ranging from the traditional metalworking industry to aerospace.

"For the time being, we're turning all requests down", says Guy Fryns talking about

How are CNT produced?

The method commonly used is catalytic vapour phase deposition (or chemical vapour deposition – CVD); a solid reagent (the catalyst) is placed in a tube furnace (the reactor), and a hydrocarbon (e.g., acetylene or methane) is passed through it. This is then heated to a certain temperature, when contact with the catalyst causes a gas-decomposition reaction to occur, and the carbon contained in the gas deposits in the form of nanotubes. This is the prototype for the reactor, which Nanocyl has exclusive rights to exploit under patents licensed to it by the University of Liège.

demands from potential customers. Strange words from a company boss, but they exemplify the still very experimental nature of the nanomaterials industry. "We produced our first firm powders this June", says the delighted Nanopôle manager. The nanoparticles industry is quality-obsessed, so the laboratory is never very far from the reactor. In one lab, a young woman is doing things with a tube containing a trace amount of silicon carbide[4]. A score of lidded plastic containers are laid out on a stainless steel table. Their precious contents will be analyzed by electron microscopy to determine their particle size distribution among other things.

The physical properties of nanoparticles are just as significant as their chemical properties. The smaller the particle size, the greater its surface-to-mass ratio. This means that a collection of nanoparticles has a bigger surface area than a material in its normal form, which can give it greater reactivity[5]. And this raises toxicity and safety issues. Leaving aside the increased reactivity, the atom-scale nanoparticles would easily be able to pass through the mucous membrane barriers of the nose and bronchial tubes to deposit in the deep lungs (alveoli). Some studies have found that carbon nanotubes caused significant pulmonary lesions in rodents comparable in some cases to those resulting from inhaling asbestos particles (see interview, p. 31).

3. www.inteltex.eu.

4. A ceramic compound of silicon and carbon. Its high mechanical strength and heat resistance makes it ideal for electronic applications for military use, and the aerospace and carmaking industries.

5. Ross, P 2007, " Nanotoxines" , *Technology Review*, No.1, April-May, p. 41.

6. *Assessing the risks in nanotechnology: Commission's Scientific Committee adopts opinion*, Press release <http://ec.europa.eu/health/ph_risk/news/news_en.htm>.

Region seeks to calm toxicity fears

The scientific press' reporting of the worrying findings of animal experiments prompted a flurry of questions, not just in academic circles, but also from European politicians and trade unionists. Are those who produce and consume goods containing nanoparticles unwittingly courting a health disaster? While the health effects of nanomaterials may not get anything like the media focus put on genetically modified food or mobile phone use, they are something the European authorities are starting to take very seriously indeed.

In February 2009, the European Commission's Scientific Committee on Emerging and Newly Identified Health Risks gave an Opinion on nanomaterials in which it acknowledges that the methods available to assess the hazards of human exposure to nanomaterials are insufficient, and for lack of a general approach, recommends that a risk assessment be done on a case-by-case basis for each nanomaterial. The Committee cites the example of carbon nanotubes and the findings of laboratory studies that some carbon nanotubes resemble asbestos fibres[6]. In April, the European Parliament said the lack of provisions and specific tests for nanomaterials was regrettable. A month later, the Commission announced a public consultation exercise on the potential risks of nanotechnologies.

The European institutions are not alone in their concerns about the health consequences of these new materials and the impact that public opposition could have in the race for world leadership in nanotechnologies. The Walloon Region is going all-out to redeploy its industrial manufacturing industry base towards state-of-the-art technologies (computing, pharmaceuticals, etc.). As well as backing projects by smaller nano industry firms, the regional government has anted up 5 million euros investment in the Nanotoxico project to develop appropriate toxicity testing models for the three types of nanoparticles produced in the region (carbon nanotubes, silicon and titanium carbides). The project is being run by the University of Namur, one of the co-founders of Nanocyl.

The Nanotoxico project has already produced a prototype to generate a carbon nanotube-enriched atmosphere. Inhalation experiments on rats will start in early 2010. The team, headed by cellular biology specialist and project coordinator Dr. Olivier Toussaint, has high hopes of this model, which will enable animal experimentation under human exposure-like conditions. Most animal toxicity tests to date have been done by directly injecting carbon nanotubes into the animal's body – a million miles away from realistic work exposure scenarios where the main risk is from inhaling nanoparticles. Nanotoxico's promoters also hope to develop *in vitro* ways for producers to test their nanoparticles, which could prove invaluable under the new REACH regime - the new EU rules that require producers to assess the toxicity of their products before putting them on the market.

"Hopefully, the findings from our experiments will help support producers to fulfil their risk assessment and prevention obligations. The ultimate aim is to feed into the establishment of occupational exposure limits at European level", explains Olivier Toussaint.

By investing so heavily, the Walloon authorities are hoping to be certain that the technologies they are supporting will not precipitate a health scandal twenty or thirty years down the line. They are also wanting to reassure the public and avoid a genetically modified food-type scenario[7].

"Nanotech development projects in Wallonia are publicly-funded, so they have to be directed towards the public interest. Should carbon nanotubes be found to be highly toxic, we would obviously stop supporting a sector which in any event would no longer be of economic interest", insists Baudouin Jambe of the Walloon Region's Department for the Economy, Employment and Research.

But the Walloon authorities have no plans to pull out of nanotech development at present. Their focus is more on risk control than on the intrinsic toxicity of nanoparticles, which is known to vary dramatically according to their size, size distribution, chemical properties, method of manufacture, etc. "We have to be sure that what is produced meets the maximum safety requirements both for the workers who make them and users. We want to know in what situations nanomaterials are dangerous so we can do everything possible to avoid the health risks."

As tends to happen in any debate on nanotechnologies, there are ultimately more questions than clear-cut answers. Like all its "rivals", the Walloon Region has accepted this measure of uncertainty, hoping that if science cannot make nanomaterials non-toxic it will at least be able to offer ways of getting the most from them at least risk.

7. Referring to widespread public opposition to GMOs in the EU, the former Walloon Minister for Research and Technologies said at the Nanotoxico project launch, "the development of nanotechnologies must not be held back by the same attitude, if it is not based on scientific studies." Speech (in French) <www.fundp.ac.be/universite/services/relext/presse>.

BASF recommends the most stringent precautions

The world chemical industry leader, the German group BASF, published the results of a study on the toxicity of carbon nanotubes in July this year.

Rats were made to inhale variable concentrations (from 0.1 to 2.5 milligrams per m^3) of multi-wall carbon nanotubes produced by the Belgian firm Nanocyl for 90 days. The study's authors observed lung inflammation at the lowest concentration (0.1 mg/m^3), which made it impossible to define a No Observed Adverse Effect Concentration. Inflammation was also observed in the nasal cavities, larynx and trachea.

The study's authors therefore recommend "the strictest industrial hygiene measures for handling these MWCNT".

See: "Inhalation toxicity of multi-wall carbon nanotubes in rats exposed for 3 months", *Toxicological Sciences*, 7 July 2009. Abstract downloadable from http://toxsci.oxfordjournals.org/cgi/content/abstract/kfp146v1.