Commercialization of Cryptomelane-type Manganese Oxide (OMS-2) Nanowire Paper Oil Sorbent

by

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ABSTRACT

Cryptomelane-type Manganese oxide (OMS-2, a group of Octahedral Molecular Sieves) nanowire paper exhibits interesting properties: reversible wettability, oleophilic while being hydrophobic, and high thermal stability. These properties open up possible markets for commercialization. This thesis reviews the market potential of each of these properties and explores the competitiveness of the nanowire paper in the proposed markets.

The proposed values of this technology are in its high selective absorbency towards oil, high performance over cost metric and its high thermal stability. Its thermal stability enables a thermal desorption type process to regenerate and recycle the sorbent for reuse. This translates into further differentiation and provides greater value for the users.

Thesis Supervisor: Francesco Stellacci
Title: Assistant Professor of Materials Science and Engineering

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- Shelby Hull, Stormwater Consultant, Contech Stormwater Solutions, Inc

Introduction

Self-assembly of ordered structures from simple systems has been of great interest in the material science field[1]. These structures can be used in many different fields—as catalysts, sensors, templates for other processes and in photoelectronics and separation processes.

Here, one of such structures showed interesting wetting behavior that opened up a multitude of application potentials. The Cryptomelane-type Manganese oxide (OMS-2, a group of Octahedral Molecular Sieves) nanowire paper was self-assembled through a thermal process with precursors. The Manganese Oxide (MnO_2) Nanowire paper is reversibly superhydrophobic and hydrophilic, has high oil absorbency in its hydrophobic state and also has high thermal stability.

This evaluation aims to find the best commercialization path (if any) for this technology. First, the technology is evaluated and its differentiating points listed out. An understanding of the maturity of the technology field was also undertaken to better identify its market potential. Secondly, possible markets were identified and commercialization opportunity discussed. Thirdly, an evaluation of the markets and competition was undertaken. Fourthly, an intellectual property analysis was done. Next, a cost analysis was presented together with a value proposition for the technology with regards to the chosen markets. Finally, a conclusion was made on how to proceed.

The terms sorbent and absorbent are used interchangeably throughout the thesis.

Technology

The MnO_2 nanowire paper is prepared through mixing stoichiometric mixture of potassium sulfate, potassium persulfate, and manganese sulfate monohydrate in 3:3:2

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[1] Jikang Yuan, Kate Laubernds, Josanlet Villegas, Sinue Gomez, and Steven L. Suib, Spontaneous Formation of Inorganic Paper-Link Materials

ratio dissolved in 70ml distilled and deionized water (DDW). The mixture was heated in an oven in a sealed Teflon vessel for four days at 250°C. Next, the rigid solid was re-suspended in 800ml DDW and stirred overnight to produce a wool-like suspension. The water was then removed and the paper-like membrane was cast on a Teflon substrate and heated for 24 hours at 85°C. The nanowire paper can then be peeled off.

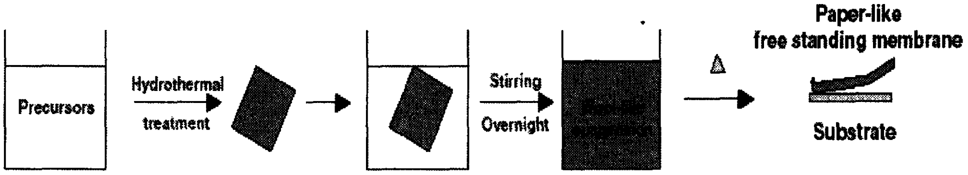

Figure 1: Schematic representation of the synthesis procedure of MnO_2 Nanowire paper [2]

The fabrication procedure is relatively simple and has a 50% yield. It is also highly scalable in terms of the size of the nanowire paper. The long processing time may be a problem in an industrial process, but batch processing could be used to overcome this.

The paper-like membrane consists of layers of cryptomelane-type manganese oxide (OMS-2) fibers. These fibers are made out of self-assembled nanowire bundles several hundreds of micrometers long and interpenetrate within the membrane to form a porous network. This porous network provides the high surface area for its superabsorbency property.

Transmission Electron Microscopy (TEM) image of a single nanowire showed a diameter of 19nm (Figure 3).

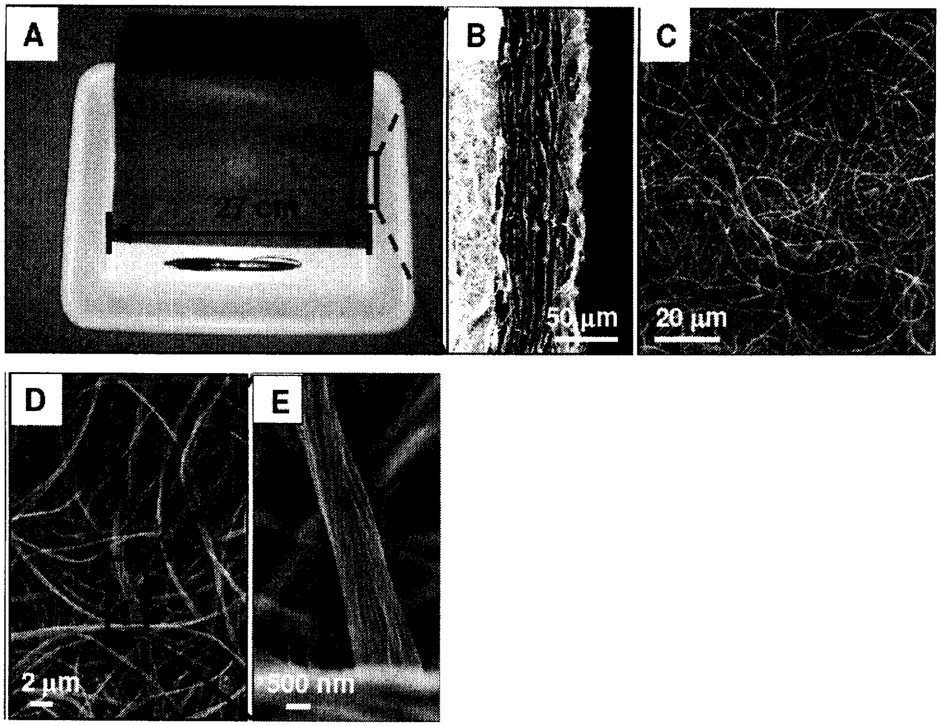

Figure 2: Nanowire paper structure (SEM image at different magnifications) [2]

Figure 3: Nanowire paper structure (TEM image of a single MnO_2 nanowire)

The MnO_2 nanowire paper has some differentiating properties:

1) Reversible wettability (superhydrophobic and superhydrophilic)
2) Superhydrophobicity and oleophilicity
3) High thermal stability
4) Simple fabrication

1. Reversible wettability

The paper is superhydrophilic in its as-fabricated state. The wetting time of 0.05s is reproducible until the saturation point is reached at a particular location (Figure 4).

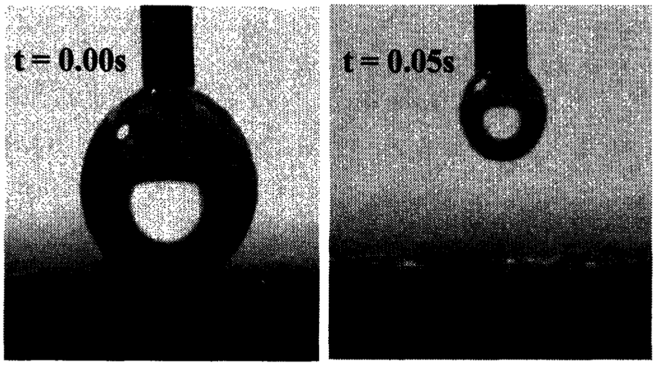

Figure 4: Water droplet absorbed into the paper [2]

To convert it to a superhydrophobic material, the paper is coated with silane at 230°C through Chemical Vapor Deposition (CVD). The modified nanowire paper becomes superhydrophobic with high contact angle of 172 ±1° (Figure 5).

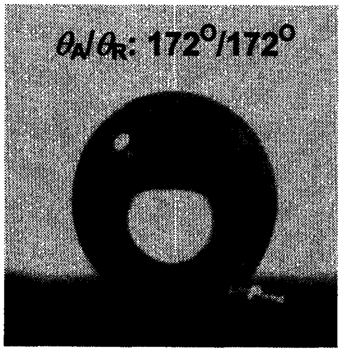

Figure 5: High contact angle showing superhydrophobicity [2]

This process is reversible as the hydrophobic coating can be removed by heating the paper at 390°C. This reversible process was tested up to 8 times (Figure 7) and showed good repeatability. The high wettability change is highly desirable in applications that will be discussed below. However, the way at which this is achieved limits its applicability

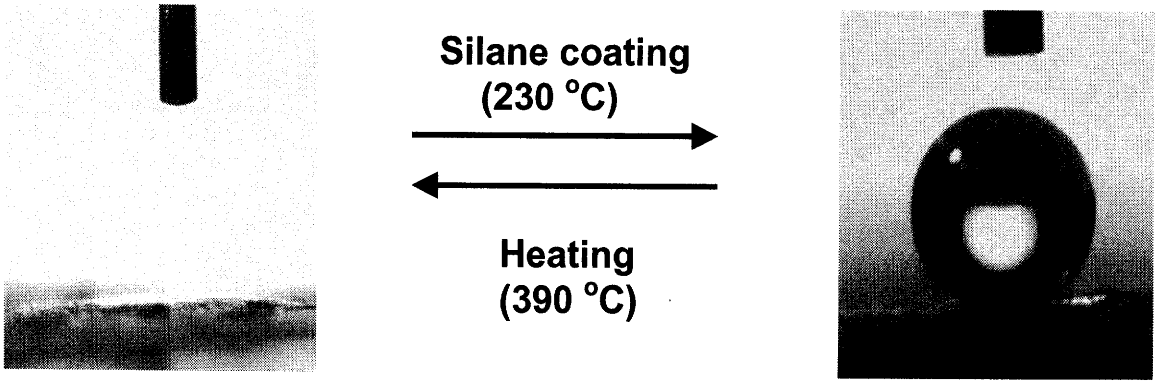

Figure 6: Reversible wettability [2]

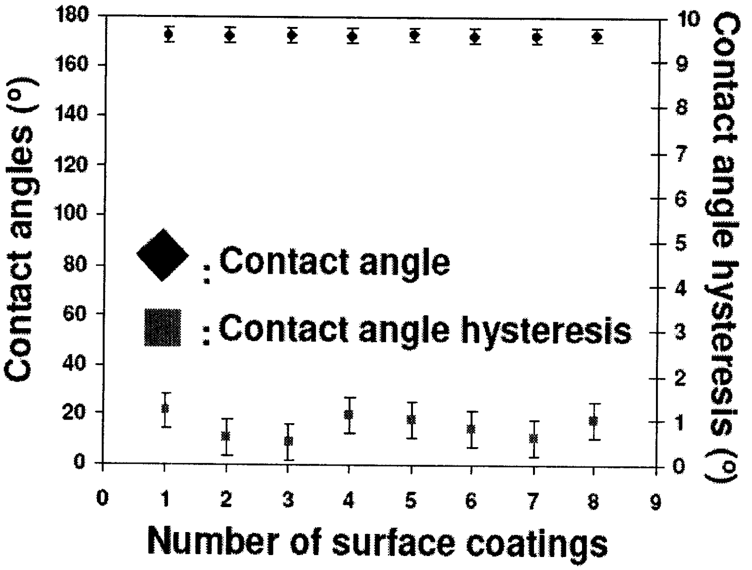

Figure 7: A series of contact angle and hysteresis measurements taken after each transition cycle [2]

This interesting property falls under the area of controlled switchable surfaces. Currently, there are a few ways of achieving this:

i) Photoillumination

Photosensitive Titanium oxide (TiO_2) and Zinc oxide (ZnO) inorganic materials are the most studied semiconductors with reversible surface properties. For example, TiO_2 has a native water contact angle of 72±1° and after UV illumination, it exhibits 0±1° water contact angle. The hydrophilic surface can be converted back to its native hydrophobic surface by long-term storage in the dark. Other materials capable of exhibiting this property is Spiropyrans, an organic material that undergo a reversible transition between closed nonpolar form and highly polar form when irradiated with UV and visible light. However, the contact angle change is small.

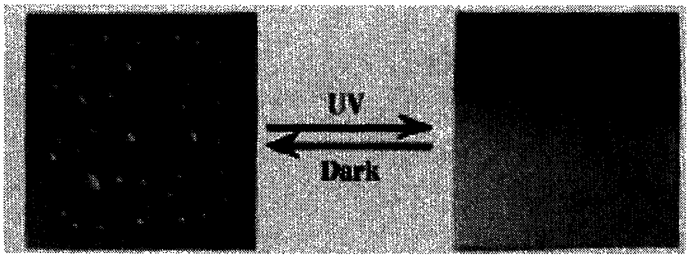

Figure 8: Effect of UV radiation on TiO_2 coated glass, Nature 1997, 388, 431-432.
Copyright 1997 Nature Publishing Group

ii) Thermal treatment

This class of material is characterized by the lower critical solution temperature (LCST). In poly(N-isopropylacrylamide) (PNIPAAm), this temperature is about 32-33°C. The polymer chains hydrates to form expanded structures in water when the temperature is below its LCST, but the compact form that it takes above LCST dehydrates the structure. The wettability change associated with this can be from 0° to 149.3° on a rough surface. This property shows high promise because with a change from room temperature to body temperature, a high change in wettability can be induced.

iii) Surrounding media driven

This is a solvent driven wettability change. For example, a Y-shaped molecule attached to a silicon surface with one end of the Y attached to a hydrophobic polystyrene (PS) polymer, and the other to a hydrophilic polyacrylic acid (PAA) polymer chain exhibits PS wettability behavior when treated with a PS solvent. For example, toluene is a good solvent for PS but not for PAA. After the solvent treatment, the surface becomes predominantly PS and hence hydrophobic. The same goes with treating with a PAA solvent—becomes hydrophilic. The water contact change can be from 25° to 115° on a flat surface.

iv) Electric field response

One of the more mature technologies is the surface tension change due to electrical actuation. Teflon is a hydrophobic material when no voltage is applied, but when a voltage is applied, the silicon dioxide dielectric below is polarized and the water/Teflon area is maximized to minimize electrical energy. Figure 9 (b) illustrates a method of fluid motion by applied electrical potential. When the electrode adjacent to the droplet is turned on, the surface tension is lowered and the droplet is drawn to the right.

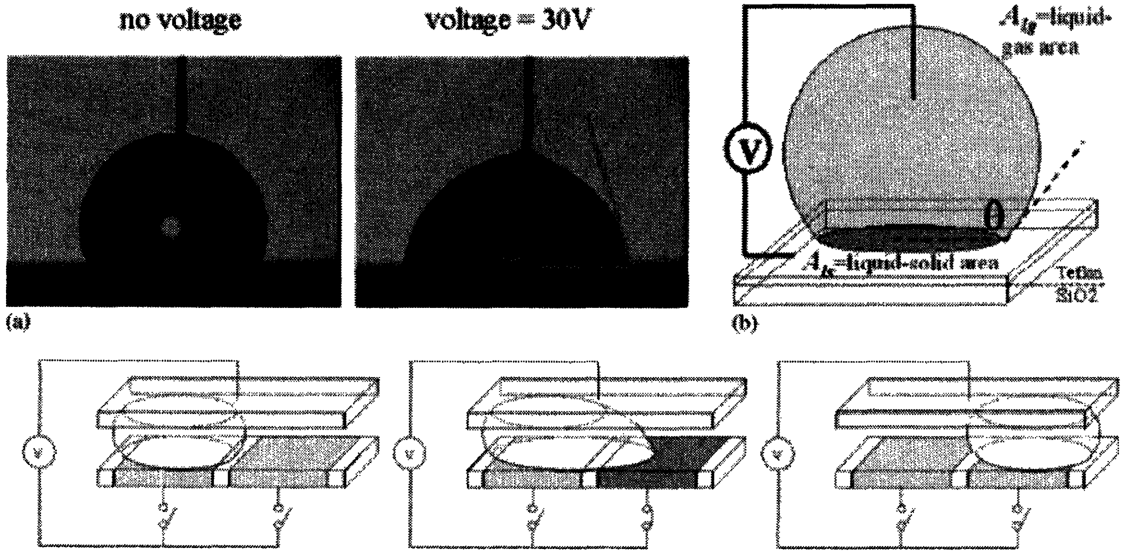

Figure 9: (a) Surface contact angle (water droplet) change when voltage is applied. (b) Experimental set-up for fluid motion induced by application of electrical potential. Application in nanofludics (bottom). Int. J. Robust Nonlinear Control 2005; 15:785-803. Copyright © 2005 Jon Wiley & Sons. Ltd.

These are only a few of the possible ways of changing material wettability property. This area of research is still at its infancy and researchers are focused on basic research of functional surfaces. Applications of this type of technology include nanofluidics, bioanalysis, bioseparation, drug delivery, etc. They fall under the broader domain of BioMEMS. The BioMEMS industry is slowly maturing with more and more products in the market. BioMEMS products have the potential of being disposable, ensuring a constant demand. However, evidence of switchable surfaces being used in a commercial product in the mentioned areas has not been found. This technology is generating a lot of interests but the kinks have not been ironed out and development activities are minimal.

Even though the nanowire paper falls under this category of controlled switchable surfaces and has a wider contact angle change, its surface property change involves the use of CVD deposition of silane at relatively high temperature. This process is impractical in applications like nanofluidics where photoinduced wettability and electric field response have a clear advantage in fluid control in the nano scale. Therefore, the market for the nanowire paper in this area is not apparent.

2) Superhydrophobicity and Oleophilicity

The nanowire paper has high oil absorbency (up to 23 times its weight) while showing superhydrophobicity as shown below.

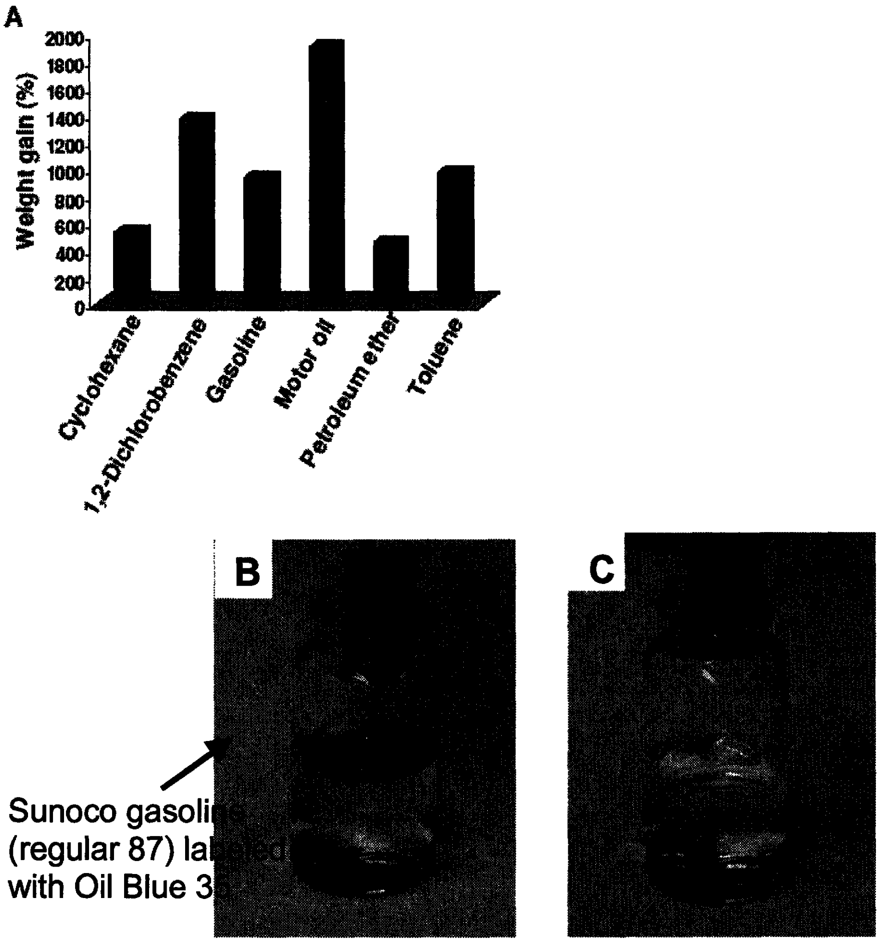

Figure 10: (A) Oil absorption capacities of nanowire paper for a range of organic solvents and oils. (B) and (C) Absorption of surface gasoline by nanowire paper [2]

This suggests that it could be used as an oil sorbent. The paper-like form makes it easy to be stored and applied. However, the oil sorbent market is almost like a commodity market and has minimal differentiation. Three main types of sorbents are: inorganic mineral sorbents, synthetic sorbents and organic sorbents. Inorganic sorbents include zeolites, sorbent clay and silica. They are usually in particulate/granular form. Sorbent clay was widely used in the industry to clean up spills in the 1990s. However, it is less widely used now because of health concerns, high waste generation and intensive labor use. Zeolites are hydrophobic alumino-slicate minerals that have an open honeycomb structure. Their structure gives rise to their oil absorbency property and provides a large adsorption area. Zeolites have high thermal stability up to 1300°C and can be regenerated with steam. They are mainly used as industrial floor absorbent and oil spill control.

Synthetic sorbents include the most widely used industrial sorbent—polypropylene and polyurethane. They come in all shapes and sizes. They can be found in continuous (pads, rolls, booms) or granular/particulate form. Their absorbency varies with packaging and the density and arrangement of the polypropylene fiber (10-20 times their weight). As with most synthetic products, they are not biodegradable and poses disposal problems if recycling services are unavailable.

Finally, organic sorbents are biodegradable materials like straw, wood fiber and cotton. They are usually used in oil spill events because they are cheap and easy to deploy and collect. Their absorbency performance is usually worse than the other two but they are cheap and made from renewable natural materials. The discussion on how to enter this market will be presented over the next few chapters.

3) High Thermal stability

The nanowire paper is stable at up to 380°C, making thermal treatment to regenerate the sorbent possible. Light sorbed oil can be driven off and the sorbent paper reused. Again, the discussion for the value proposition for this will be taken up in the following chapters.

4) Simple fabrication

The key to entering a not so differentiated market is the play on cost. Therefore, it is important to have a simple and cost efficient fabrication process as a pre-requisite.

Market Identification

Several markets are apparent from the discussion of the nanowire paper's differentiating points, and the applications of its reversible wettability property have already been ruled out. Therefore, the following discussion will focus the paper's oleophilicity (while being superhydrophobic) and its market applications. One obvious market opportunity is the oil spill containment/recovery market. The paper would be especially useful during spills on water because it is selectively absorbent. However, sorbent use is only one of the ways of recovering and containing the oil. Most ocean oil spill recovery is performed through mechanical devices like skimmers, booms, etc. In some cases, dispersants are also used to diffuse the oil into the ocean. Sorbent use is usually restricted to recover the last bit of oil from the water surface after mechanical recovery. Furthermore, because of the scale of an oil spill, cost is the main consideration. Thus, people are using cheap natural sorbents like wool that can be easily deployed and collected. The nanowire paper may not fair well in absorbing heavy hydrocarbons because they may clog up the nanowire membrane. Also, because of its paper-like form, it may not be easily deployed and recovered in rough seas.

The next possible market is the industrial sorbent market. This market deals with cleaning up of industrial spills that include oil (mostly), solvents, etc. Industrial sorbents come in all shapes and forms: booms, pads, wipes, and even floor paddings. They can be grouped into three main types: Hazmat sorbents, universal sorbents and selective sorbents. Hazmat sorbents deal with soaking up harzardous liquids like acids and bases. Universal sorbents as the name suggests, absorb all liquids and is useful for water, oil and solvent leaks. Selective sorbents are sorbents that absorb for instance more oil than water. This market is almost commoditized because cost plays a major part in deciding which sorbent to use. Most manufacturers have a product line that spans mainly the universal and selective categories in various forms. However, recent developments create an opening for entry.

The other market that will be discussed is the stormwater Best Management Practice (BMP) device market. Stormwater is water that accumulates after a storm and that includes runoffs from roads. The stormwater drainage system includes roadside drains and drains at industrial facilities that do not go through a sewer or treatment system. However, there is an increasing interest in stormwater treatment. The Environment Protection Agency (EPA) identified stormwater discharges as a significant source of water pollution: 13% of impaired rivers; 21% of impaired lakes, ponds, reservoirs; and 45% of impaired estuaries. Legislative requirements have led to the increase of the use of BMP devices that prevent pollution from going into the stormwater. Oil absorbents come into the picture because the inclusion of sorbents in BMPs can reduce oil and grease contaminants in stormwater[2].

Industrial Sorbent Market

EPA estimates that 1.1 billion gallons of used oil from equipments have to be cleaned up every year[3] (1993). This market is a $500 million/year market (North America) with a 30% annual growth (EPA, 1998). If that growth rate is constant, that would make it a $5.3 billion/year market in 2007. This is certainly a large market to go into, but how do provide value to this market and thus enabling the extraction of revenues/profits?

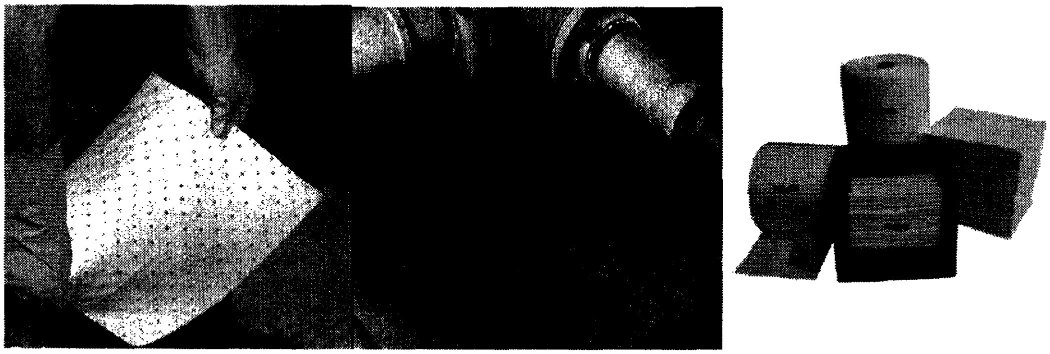

Figure 11: Industrial Oil absorbent pads and rolls for oil leaks and spill clean up. The Gases and Welding Distributor; May/Jun 2003; 47, 3; ABI/INFORM Trade and Industry pg.30.

There is a trend towards waste minimization because of the rising cost of disposal of used sorbents and stricter regulations. Landfill costs are rising--$300-$500 per drum (55 gal or 100lbs) (1994) because of landfill related environmental issues and space constraints.

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[2] Michael K. Strenstrom, Oil and Grease Removal by Floating Sorbent in a CDS Device, 1998

[3] Susan Avery, Buyers socked with regs, sop up more sorbents, Purchasing, December 16, 1993

EPA and state authorities have also come up with policies on disposal of sorbents that made disposal more complicated and costly.

Floor cleaning sorbent clay (particulate form) was once the main sorbent used because it is cheap. However, because of certain health issues, high labor usage and most importantly the large amount of waste generated, the industry moved away from clay. This created an opening for more expensive synthetic sorbents like polypropylene, which moved on to be one of the most used industrial sorbent.

As a result of these developments, there is a greater market for more expensive and recyclable/reusable sorbents. There are several ways of dealing with sorbent waste:

i) Landfilling—There is long-term liability to the generator of the waste, and landfill cost is high

ii) Incineration—Can be costly and there is liability associated with the ash and air emission produced, the energy could be recovered but obviously the sorbents can not be reused

iii) Laundering—Can be costly and generates a waste water stream, but sorbents can be reused

iv) Wringers—Spins used sorbents to remove certain amount of oil. It can be time consuming, messy and not that effective as some percentage of oil will still be in the sorbent. However, a portable unit could be purchased to be used at a user site for convenience

v) Bioremediation—Oil digesting microbes can be incorporated to some sorbents to enable bioremediation upon disposal (for example, Patent 5492881). Again, this method does not permit reuse of sorbents.

vi) Closed-loop recycling—Producers of the sorbents also offer recycling services through improved environmentally friendlier means. This method is more cost effective and eliminates long-term liability

Several companies are already pursuing option (vi)—CRI Recycling Inc. and Circle Environmental Inc. This is the market opening for the nanowire paper because the paper can be heated up to 380°C to drive out the absorbed oil and reused. Also, this is a relatively untapped market with approximately 95% of used sorbents ending up in landfills, 5% are incinerated, and recycling is just starting to pick up[4]. The proposed strategy will follow the closed-loop recycling model but with a different recycling method. The business will be viable if the cost of recycling is lower than the cost of making new sorbents, such that the savings can be passed on to the users. However, it should also show an advantage over competitors' models, in terms of pricing or otherwise.

Stormwater BMP Device Market

Stormwater is highly polluted. EPA estimates that there are 1 million gallons of dissolved hydrocarbons in stormwater—oil and gas from the country's 200 million odd vehicles per year. The Clean Water Act prohibits the discharge of oil into inland and navigable waters if the discharge causes a film or sheen on the surface of water.

The U.S Federal Government requires all municipalities with populations greater than 100,000 to apply for a stormwater discharge permit and develop a stormwater management program. More importantly, EPA has a 2008 deadline for cities with population of more than 10,000 to have a plan to stem the flow of debris and contaminants from curbside into local waterways[5]. As the deadline looms, there is an increased spending in stormwater management systems. For instance, Los Angeles voters agreed to a $500 million bond in November 2005 for just that reason.

In the European Union (EU), the Urban Waste Water Treatment Directive (UWWTD) is a Europe-wide legislation and is now part of the national law in all countries in EU. For this reason, anyone working on urban development projects has to have stormwater management in place to comply with regulations.

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[4] John Markiewicz, CF Technologies, 2000 Environmental Innovator Awards Showcase, Technovation, vol. 2000-3, EPA, New England Office 2000

[5] Cleaning Up an Effluent Society, Business Week Online, 3/22/2006

Stormwater treatment is undoubtedly emerging as the newest and most promising area of environmental management[6]. The discharge permit is called the National Pollutant Discharge Elimination System (NPDES) permit, and a stormwater pollution prevention plan is mandatory under the permit. BMP is part of the implementation of the plan and more broadly part of general stormwater management systems.

BMP devices include:

i) Drain insert (appendix 1)—Easy to install, cheap but has a high maintenance cost and has a tendency to clog

ii) Modified catch basin (appendix 2)—retains 85% of litter but expensive as retrofits

iii) Baffle (appendix 3)—retains 10-50% of litter, big footprint, and usually reserved for new construction

iv) Continuous Deflective Separation Device (CDS) (appendix 4)—Captures more than 95% of litter and debris, baffle box included to remove oil and grease, but retention improved with floating sorbents, it also requires very low maintenance (2 times a year) and comes in precast or cast-in-place form (variable footprint and water treatment capacity)

Dr. Michael Stenstrom from University of California, Los Angeles (UCLA) showed in his 1998 paper that the inclusion of floating sorbents in a CDS device can remove and retain 80-90% of the oil and grease. Presently, although the company includes a baffle to remove floatables in their systems, the use of sorbents increased the permanent capture efficiency of oil and grease as mentioned.

CDS technologies hold the patent for CDS devices (Patent Number: 5,788,848) and has over 2,500 CDS units installed worldwide, with approximately 1,300 units throughout the United States and Canada (2003). The company is doing well with a recent installation of the world's largest CDS unit at the Southern California Freeway system. The system uses fluid flow through a vortex separation chamber to continuously filter out debris and trash,

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[6] K.Ravi, Urban Stormwater Management: Storming Opportunities?, Frost and Sullivan, 7/26/2001

and deposited in a catchment basket. Its continuous flow-based and non-clogging system makes it suitable for both upstream and downstream use.

This presents another market for the nanowire sorbent paper because the paper floats on water and it has high oil absorbency with superhydrophobic properties—suitable as a floating sorbent for the CDS units. Currently, the company does not supply sorbents as part of their units, and the addition of sorbents depends on the individual municipalities. Therefore, there is an opportunity to market the sorbents to existing CDS customers and also to new ones. Even though CDS device is seen as the best match for the sorbent paper, sorbents can also be used in other BMPs like inserts and catch basins. The downside to sorbent use is the increased maintenance requirement to replace the sorbents. As regulations tighten, municipalities may still have to do so. This also presents itself as a constant revenue stream for the sorbent manufacturer. The sorbent waste can again be recycled through a closed loop model.

Sorbents considered for this market are:

i) OARS (Abtech Industries)—Rubber type particulate sorbent originally intended for use in catch basin inserts

ii) Rubberizer (Haz-Mat Response Technologies Inc)—particulate form, or in pillows and booms, similar to OARs and meant as a clean up sorbent for various types of solvents, oils and fuels

iii) Xsorb (Impact Absorbent Technologies)—aluminum silicate sorbent, lightweight and hydrophobic, used for spill clean up and comes in various forms

iv) Sponge Rok (Paramount Perlite Co.)—mesh like with rounded edges, also aluminum silicate based

v) Nanofiber (Nanofiber Tech. Inc.)—polypropylene fiber adsorbent, similar to fibers used in 3M pillow, pad, sausage sorbers oil spill control products

Table 1: Test results for CDS with sorbents

Sorbent Type	Flow (gpm)	% removal of oil and grease	Residual (mg/L)
Nanofiber	125	87	0.08
OARS	75	94	0.68
OARS	125	86	0.5
OARS	190	82	0.84
Rubberizer	125	86	1.96
Sponge Rok	125	41	0.74
Xsorb	125	79	0.74
No Sorbent	125	77	3.35

Source: Stenstrom and Lau, 1998

It should be noted the sorbents performed equally well except for Sponge Rok and Xsorb sorbents because they were lighter (less contact with oil and grease). The sorbents were also retained in the system other than Nanofiber. The residual oil content in effluent water was the highest for Rubberizer and it should also be noted that with no sorbents used, the CDS unit had 3.35 mg/L of residual oil but it is expected to lose all of the retained oil and grease in time.

Again, the sorbents do not seem to have a clear advantage over others and the nanowire paper fit right into this category. However, since no sorbent companies are actively pursuing this market, with the right marketing and contacts, it is still a viable market for early commercialization.

Intellectual Property

The intellectual property (IP) analysis aims to identify possible infringements if the decision to commercialize is made.

Firstly, the area to consider is the fabrication of the free-standing MnO_2 nanowire paper membrane. Patents involving the preparation process for free standing membranes include:

7182894	Process for the preparation of free standing membranes (2007)

The membrane processing method is different from the one presented here. Moreover, gold nanoparticles are incorporated in the free standing membrane to get the hollow structure when they are leached out eventually.

Furthermore, the inventors of the MnO_2 nanowire paper, Jikang, Yuan and Steven Lawrence, Suib hold the patent for the fabrication of the nanowire paper membrane (Patent number: 20060049101). The next step is to file a patent for the use of the nanowire paper as an oil sorbent. This would give the required protection and commercialization opportunity through licensing. In addition, packaging of the oil sorbents can also be patented if it is novel enough, again for maximum protection of the technology. For example, patent 2002008874 was filed for a type of oil absorbent mat assembly that includes a frame formed from strips that can be used to hold the mat in place on a flat surface and reused on a new mat.

Secondly, the proposed closed-loop recycling process contains several patents:

6098306	Cleaning apparatus with electromagnetic drying (2000)
6312528	Removal of contaminants from materials (2001)
20020023662	Removal of contaminants from materials (2002)
6536061	Method and apparatus for cleaning oil absorbent materials (2003)
5538646	Method and system for removing oil from oil-absorbent material (1996)
5244566	Process for deabsorbing oil from oil absorbent (1993)
5569331	Method and apparatus for recycling oil-soaked boom and pads (1996)

Patent 6098306 and 6312528 are owned by CRI Recycling Services Inc and pertain to the use of pressurized solvent to remove contaminants from sorbents and RF radiation to vaporize residual solvents. The solvent and contaminants are subsequently removed for reuse.

Patent 20020023662 is a continuation from patent 6312528 with an improved approach for cleaning and recycling based on liquefied solvents to remove the contaminants from the sorbents. Called the Critical Fluid Processing, the envisioned process is a batch process with the contaminated solvent distilled to recover the oil and solvent. Both can be reused. The inventors claim the absorbent can be recycled with absorptive capacity of 80%-100% of the original.

Patent 6536061 and 5538646 involve the method of removing oil from sorbents through centrifuging the material and dry or wet cleaning after that.

Patent 5244566 pertains to the use of citric oil-in-water emulsion to extract absorbed hydrocarbons from the oil absorbent material. The technology protected by patent 5569331 uses mechanical means to first squeeze out some oil from the sorbents. Then, they are shredded and treated with treatment fluids to remove the rest of the oil. The sorbents are then repackaged.

The filed patents on recycling sorbents do not involve the use of thermal means to remove the absorbed oil. The proposed removal strategy is still viable and licensing requirements can be avoided.

Finally, in the application of sorbents in BMP devices, environmental companies like Abtech Inc. holds numerous patents on the use of inserts and filters to remove trash and hydrocarbons:

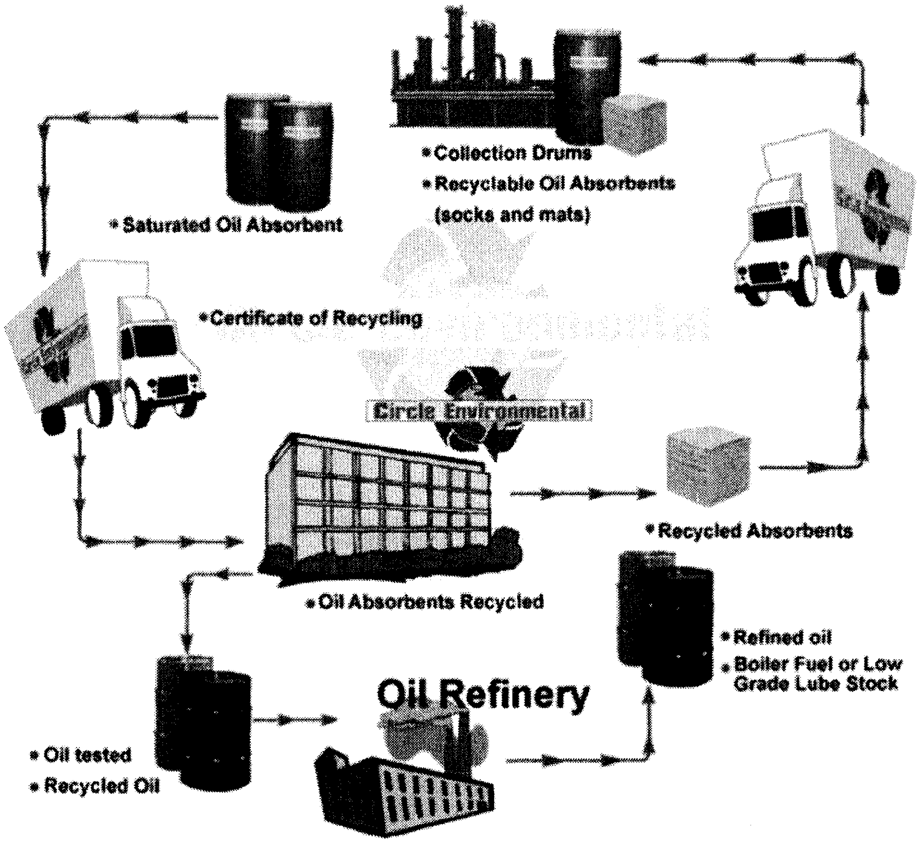
6231758	Curb-inlet storm drain systems for filtering trash and hydrocarbons (2001)
20030127380	Suspended runoff water filter (2003)
6099723	Catchbasin systems for filtering hydrocarbon spills (2000)

Patent 6231758 involves the use of an insert in storm drains to collect trash and hydrocarbons. Patent 20030127380 concerns the use of bracket and filter module that can be suspended from a bracket by flexible supports. Patent 6099723 explains the use of a water- and oil-porous sack containing hydrophobic, oil absorbent material that is suspended below a storm drain to absorb oil from stormwater.

These patent claims are related to the design of the filtering device or drain inserts. Therefore, the use of floating sorbents in a CDS device does not infringe on any patents. In general, the design of the device for the application of the nanowire sorbent in BMP devices should of course be novel to avoid infringement issues.

Value Proposition

As mentioned, the proposed value generation for the nanowire paper is to capitalize on its high thermal stability to enable a thermal desorption process for regeneration of the sorbent. This proposed strategy is similar to Circle Environmental model (Figure 12), but with a different sorbent regeneration/recycling process as mentioned in the IP analysis. The customer pays for the cost of recycling and gets back an equal amount of sorbents (recycled).



http://www.ce-nc.com/flowchart.htm

Figure 12: Close-loop Absorbent Recycling scheme

In this model, the supply chain derives its value through:

i) Save on purchase of new sorbents (only pay for recycling costs)

ii) Eliminate liability and costs associated with disposal of sorbent wastes in landfills. Landfill cost was $300-$500 per drum (100 lbs) in 1994

Purchase of new sorbents is required when the recycled sorbents wear out or there is an increased sorbent use.

Cost Analysis

The analysis of costs associated with the nanowire paper closed-loop model will be carried out firstly, by considering the material cost to fabricate the nanowire paper sorbents, and the absorption costs (of various sorbents and the nanowire paper); secondly, by considering the cost of the thermal desorption recycling process.

Material Cost

The precursors for making the MnO_2 paper is Potassium Sulfate (K_2SO_4), Potassium Persulfate ($K_2S_2O_8$) and Manganese Sulfate Monohydrate ($MnSO_4.H_2O$) in 3:3:2 ratio. The conversion is about 50%, which means 1 mol of $MnSO_4.H_2O$ can produce 0.5 mol of MnO_2.

Table 2: Cost analysis table to produce 1 mol of MnO_2

Precursors	**Molar Mass (g/mol)**	**Ratio**	**Total Mass (g)**	**Cost/grams ($/g)**	**Cost ($)**
K_2SO_4	174.262	3	522.786	0.0992	51.9
$K_2S_2O_8$	270.328	3	810.984	0.0928	75.3
$MnSO_4.H_2O$	169.004	2	338.008	0.122	33.5
Product					
MnO_2	86.938	1	86.938		160.7

Absorption Cost

Oil sorbents in the market have different absorption performance and price. For easy comparison, the prices are normalized to the weight of absorbed oil. This section will present absorption performance in terms of dollars per kilogram of absorbed oil (cost to absorb 1 kg of oil).

The nanowire paper consists of self-assembled nanowires that interpenetrate the membrane structure to form a porous network. Therefore, the paper consists of mainly air and it floats on water, the density of the paper will be taken as the upper bound, i.e. the density of water (1000 kg/m^3) for this analysis.

The density[7] of MnO_2 is 5026 kg/m^3 and thus there is around 20% (1000/5026) of MnO_2 in the nanowire paper. Since the paper is capable of absorbing up to 23 times its own

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[7] O. Madelung, U. Rössler and M. Schulz (2000). *Landolt-Börnstein - Group III Condensed Matte.* Springer-Verlag.

weight (Figure 10), 23,000 kg of oil can be absorbed for each 1 m^3 of the paper. Each 1 m^3 of the nanowire paper contains 20% of MnO_2 (200 kg) and the associated cost to absorb 1 kg of oil is thus $\frac{\$160.7}{86.938kg}x(200kg)x\frac{1}{23000kg} = \$16$ /kg. This is of course calculated by just considering the fabrication cost. The inclusion of desired profit, overhead, manufacturing and marketing costs would surely increase the cost and make it more expensive than the products currently available (shown below). It should be noted that the materials cost to produce 1 kg of the nanowire paper is $\frac{\$160.7}{86.938g}X200g = \$368$

The oil absorption performance of some major absorbents in the market is shown in the table below. For easy comparison, only absorbent pads are compared because they are the most versatile and come in various sizes. The performance is compared by considering the cost of using the product to clean up a normalized unit of absorbed oil, i.e. in dollars per kg.

Table 3: Absorption performance of oil absorbent pads

Distributor/ Manufacturer	Description	Weight per case (kg)	Oil Absorption Capability (kg) (times own weight)	Price per case ($)	Absorption Cost, $ per kg of absorbed oil ($/kg)
AbsorbentOnline	High performance Oil Absorbent Pads, dimpled (WPB100H)	6.54	96.9 (14.8x)	43.00	0.44
	High performance Oil Absorbent Pads, dimpled (WPB100M)	5.13	88.9 (17.3x)	34.00	0.38
	Economy Oil Absorbent pads (quick wicking meltblown polypropylene) (WP100H)	6.54	111.2 (17x)	38.00	0.34
	Economy Oil Absorbent pads (quick wicking meltblown polypropylene) (WP100M)	5.13	88.9 (17.3x)	33.00	0.33
3M	Petroleum Sorbent Pads (HP256)	9.08	219.8 (24.2x)	100.66	0.46
Sorbent Poducts	Oil Absorbent Pad with meltblown core (SXT100)	6.81	76.6 (11.2x)	62.40	0.82

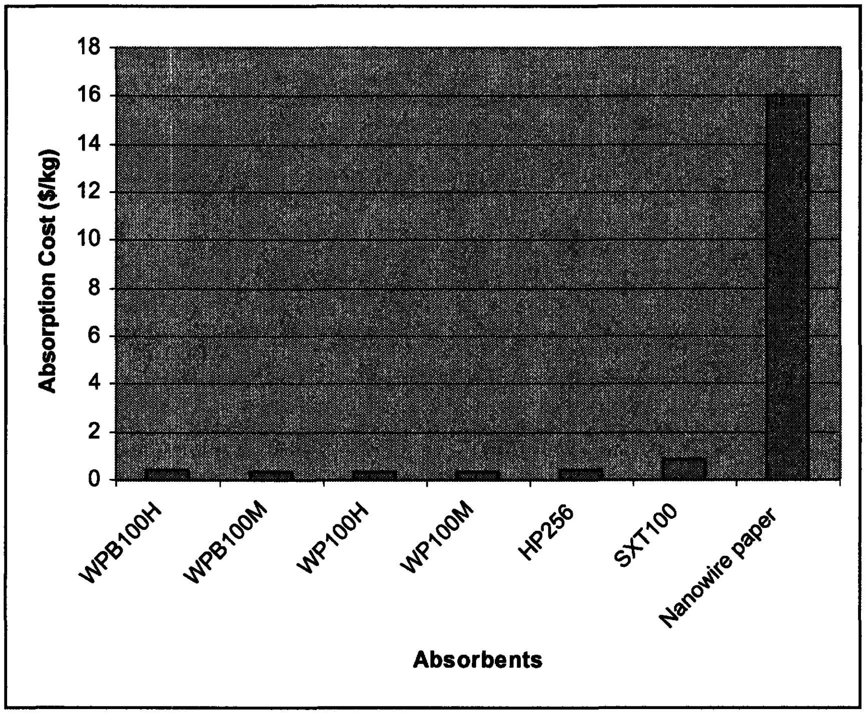


Figure 13: Absorption cost (dollar per kg of absorbed oil) of various oil absorbents and the nanowire paper

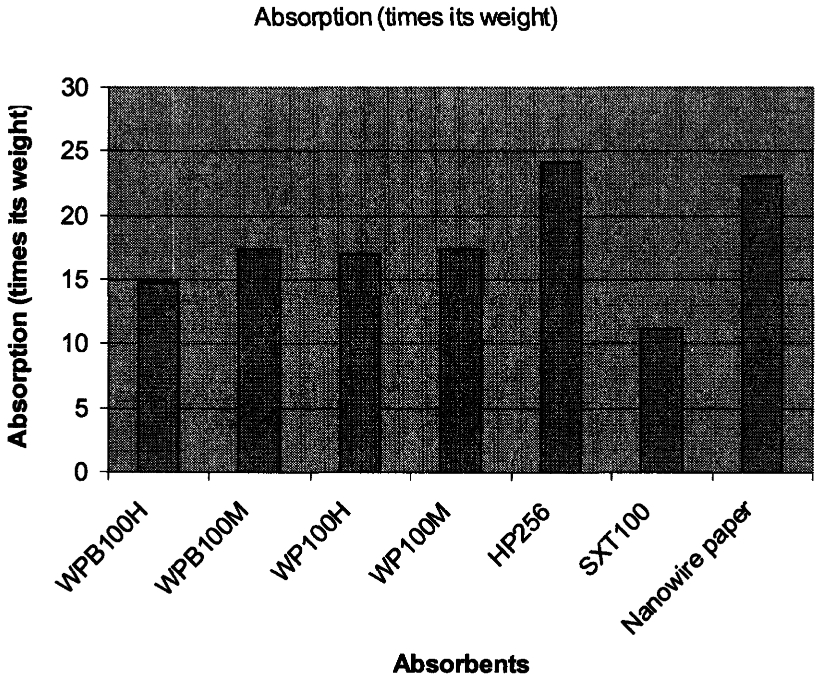


Figure 14: Absorption performance of various absorbents (times its weight)

As mentioned, the absorption cost of the nanowire paper is calculated by only considering the material cost of the nanowire paper. The absorption cost is very high as compared to some of the competition (Figure 13). The nanowire paper would have to be sold at a loss to be competitive. Taking 3M's product (HP256) as a basis for comparison (because of similar absorption capacity), it costs $38/6.54= $5.81 to purchase a kilogram of the sorbent. This is as opposed to the cost of one kilogram of nanowire paper that amounts to $368. The nanowire paper would have to be sold at a loss of $362 per kg. It should be noted that if one assumes that the other sorbents cannot be recycled and therefore landfilled, the landfill cost would add to their absorption cost. That would make them more comparable to the nanowire paper's absorption cost.

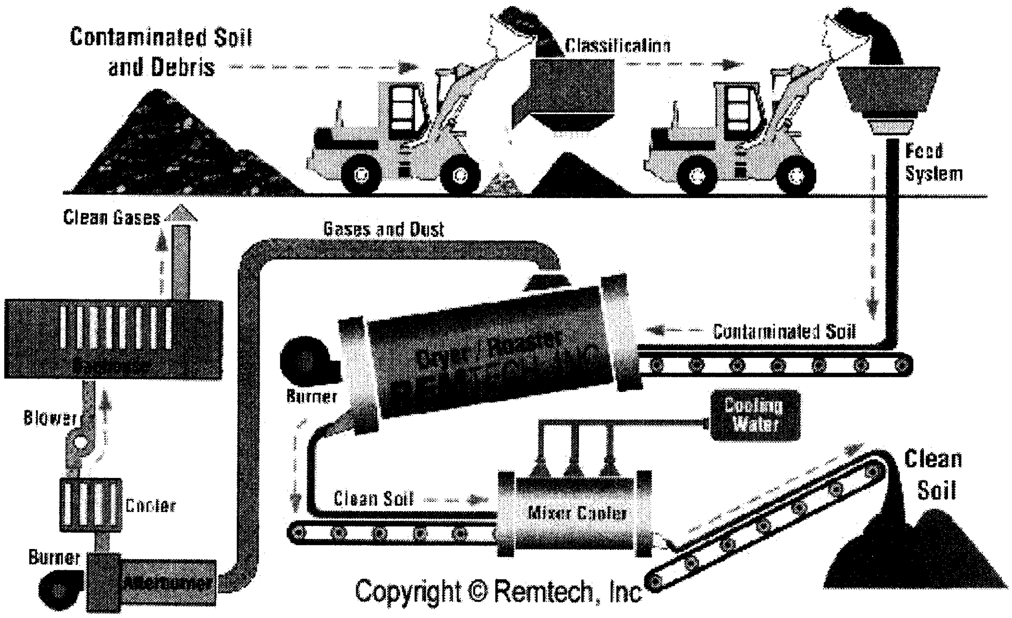
Thermal Desorption Process Cost

Thermal Desorption is a physical separation process where in most applications, contaminated soil is heated through direct or indirect means to drive out the volatile contaminants. The vaporized hydrocarbons are usually treated in a secondary treatment unit before releasing them to the atmosphere. These units include afterburners, catalytic oxidation chambers, condensers, or carbon adsorption units. Afterburners and oxidizers destroy the organic constituents through combustion and the heat from the flue gas can be recovered. Condenser and carbon adsorption units filter out the organic compounds for subsequent treatment or disposal. This secondary treatment step can be replaced with a distillation unit to possibly recover the hydrocarbon constituents for reuse. The low quality recycled oil from the sorbents could be sold to recover some of the thermal desorption costs, making the process more cost efficient. More analysis is required to determine if this is economically viable. The simple cost analysis below uses standard destructive secondary treatment units.

There is a few types of thermal desorption designs, mainly: rotary dryer and thermal screw. Rotary dryers are usually inclined and rotated, while thermal screw units have screw conveyors to transport the medium through the heating chamber. There are some difficulties in using this process to regenerate the nanowire paper sorbent:

i) The used sorbents tend to clump together and this decreases the efficiency of heat transfer to the sorbents and thus requires longer processing time, affecting throughput. The sorbents may have to be treated to separate them before putting it through the process as the thermal desorption of soil requires soil particles of less than 2 inches in diameter.

ii) The condition of the paper-like sorbent may degrade (aesthetically or otherwise) after the process



http://www.remtech1.com/thermal_desorption.htm
Figure 15: Thermal Desorption Process for Treating Contaminated Soil

Figure 15 shows the process flow of a typical thermal desorption process applied to remediate contaminated soil from hydrocarbons. Engineering changes will definitely have to be made for the application in regeneration of used nanowire sorbent paper. However, assuming it mainly affects the capital cost and not so much the processing cost, this process will be used as an approximation to the thermal regeneration processing cost of the nanowire paper. Low Temperature Thermal Desorption (LTTD) (90-320°C) is more appropriate for this application because it operates below the thermal stability point of the nanowire paper while still able to drive out most hydrocarbons (from kerosene at 200°C to industrial fuel oil at 370°C). The hydrocarbons can be destroyed or recovered as mentioned.

The cost analysis is based on the Remediation Technology Cost Compendium, 2000, prepared by the U.S. Environmental Protection Agency (EPA)[8]. The thermal desorption process cost model serves to illustrate trends derived from historical data from a number of thermal desorption projects. The process cost was clearly differentiated from capital and operation and maintenance cost. Inflation and location adjustments were also made so that cost figures can be compared and analyzed between projects. According to the report, there is a correlation between unit cost and quantity treated (Figure 16) but no correlation between unit cost and other factors, such as soil properties and treatment temperature. Most plants operate at 18- 35 tons per hour.

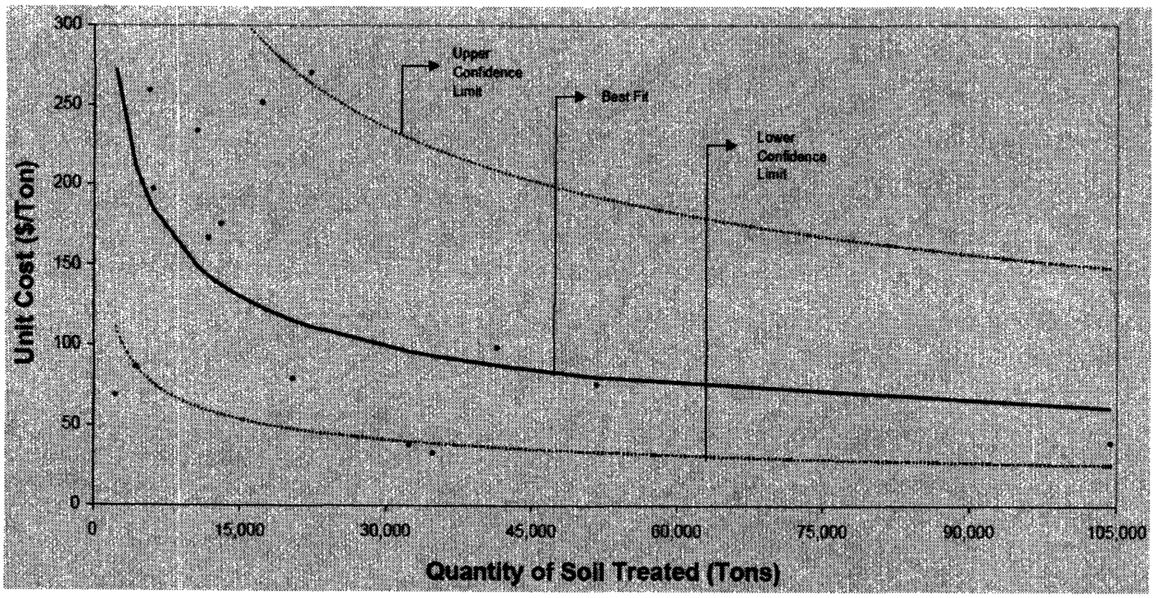


Figure 16: Thermal Desorption—Unit Cost vs. Quantity of Soil Treated (with 68-percent Confidence Interval

The unit cost decreases with the increase in amount treated. If this venture carried out, the target volume should be around 30,000 tons where most of the cost savings from operating at higher volumes have already been made.

Also, from a paper by Timothy P. Sullivan, Thermal Desorption: The basics, Chemical Engineering Progress; Oct 1999, the average cost/ton to process soil with a rotary unit with hydrocarbon recovery is $176. However, this includes the cost to excavate

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[8] http://www.epa.gov/tio

contaminated soil. To factor that out, the cost breakdown of a thermal desorption process by the Federal Remediation Technology Roundtable[9] showed roughly that the cost associated with excavation is 17% of the total cost. So, the thermal desorption cost for recycling nanowire paper can be estimated at $146/ton (without considering transport and repackaging costs). This further confirms the data in Figure 16.
In contrast, the Wisconsin Army National Guard (Dec 2002) indicated that CRI charged $8,625 to recycle 6,900lbs (3.13 tons) of sorbents ($2,755/ton).

It is obvious that if the thermal desorption process can be successfully applied to recycle nanowire paper (with lower efficiency or otherwise), and factoring in transportation and packaging, it may still be competitive because the processing cost is much lower than the competitor's (CRI).

For 10,000 tons of used sorbents, the thermal desorption cost to process this amount is $150 x 10,000= $1.5 million (Figure16). 10,000 tons of used sorbents contain 10,000,000/23 = 434,782 kg of sorbent material that would be sold at a loss of 434,782 kg x $362/kg= $157.391 million to match 3M's price (as mentioned).

CRI's recycling cost for 10,000 tons of sorbents is $2,755 x 10,000 tons= $27.55 million. Even though the thermal desorption recycling cost ($1.5 million) is much lower than CRI's, it is not enough to recover the loss incurred ($157.391 million) to remain competitive.

The disposal cost of used sorbents in a landfill is $500 per 100lbs or $11,000 per ton. For 10,000 tons, that amounts to $110 million, again, the savings from the thermal desorption process is not enough to recover the loss.

However, the density of the nanowire paper can be modified depending on the casting method. As for the absorbency of the paper at various densities, there should be an optimum density for maximum adsorption as a less dense structure would have a more

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[9] http://www.frtr.gov/matrix2/section4/4_29.html

open structure to hold the oil, but at some point the adsorption would decrease with decreasing density. This is because the adsorption surface decreases with density as well. Therefore, it is worthwhile to do an analysis on the density required for this paper to be able to compete with other recycling companies like CRI.

CRI's recycling cost for 10,000 tons of sorbents is \$27.55 million, and the thermal desorption cost for the same amount is \$1.5 million. So, the savings of \$26.05 million from using a thermal desorption process could be used to recover the loss. By equating that amount to the loss incurred in matching with the 3M product, the corresponding percentage of MnO_2 in the paper should be 3.6% with a paper density of 178 kg/m^3. Studies should also be conducted to determine the effect of density on the absorption/adsorption performance.

Conclusion

The technology has some interesting properties that at first glance looked good. However, after careful analysis, its impressive reversible wettability property requires processing steps that eliminated it from the earliest commercialization market (BioMEMs, nanofluidics).

In terms of its selective oil absorbency, its performance is good, with high absorption capacity that is better than most oil absorbents in the market. However, it has a high cost over performance ratio, making it more expensive than other products in the market.

Its high thermal stability creates an opportunity to regenerate or recycle the sorbent through thermal treatment. The thermal desorption process for treating contaminated soil was used to model the cost of this thermal treatment process. The thermal desorption process requires the soil to have particle sizes of less than 2 inches and would not be directly applicable to volatizing hydrocarbons from used sorbents. Some engineering modifications and tests would have to be performed to achieve reasonable throughputs and processing efficiency. However, the processing cost gathered from the standard thermal desorption process would serve as a guide.

The thermal desorption processing cost was found to be in the hundreds of dollars range to process each ton of material. This is as opposed to thousands of dollars (per ton) required to recycle absorbents with CRI Recycling Inc. and tens of thousands (per ton) required to dispose off the absorbents through landfilling. Thus, the thermal treatment process looks promising.

Two markets were analyzed: industrial sorbent and stormwater BMP device markets. Both markets are highly promising with relatively big market sizes. The proposed value for the nanowire paper is the thermal regenerative process that could be used in a closed-loop recycling process. The value from such a model is the savings that the customers get from not needing to pay for new absorbents (just pay for the recycling process) and from waste disposal liabilities and fees.

Capital costs were not discussed in this thesis as the discussion was focused on establishing whether a sustainable business is possible through the analyzed markets. If such a venture were to be considered, a more detailed cost/benefit and break-even analysis would have to be done to determine its profitability.

The simple analysis showed that commercialization of the nanowire paper is not feasible due to its high material cost. At $368 per kilogram of sorbent, the nanowire sorbent cannot compete with cheaper sorbents in the market that sell for less than $10 per kilogram (for example, 3M's HP256 at $5.81/kg). Although the thermal desorption recycling process is cheaper than the alternatives (CRI Recycling and landfilling), the savings from the process is not enough to offset this material cost.

The material cost is the main problem in the commercialization of this technology. The material cost can be decreased sufficiently to be competitive in cost through modification of the fabrication process to get a lower density paper with similar or better absorption performance. In this case, there are two commercialization paths—set up a new manufacturing company or license the technology. The thermal regeneration offers much savings and is the main selling point for this technology as the landfill cost is increasing, especially in Europe. Also, as China's neglected environmental issues hit critical mass, a large market would present itself for environmentally friendly technologies such as this one. However, venturing into a new manufacturing segment like nanowire oil absorbent membranes is difficult as there are many manufacturing yield and quality issues that has to be sorted out and no precedence can be followed.

Therefore, licensing this technology to existing players like 3M, Dupont and CRI recycling that have expertise in this field would be a better option. By leveraging on their manufacturing capabilities and existing customer base, this technology could serve as an extension to their product offerings.

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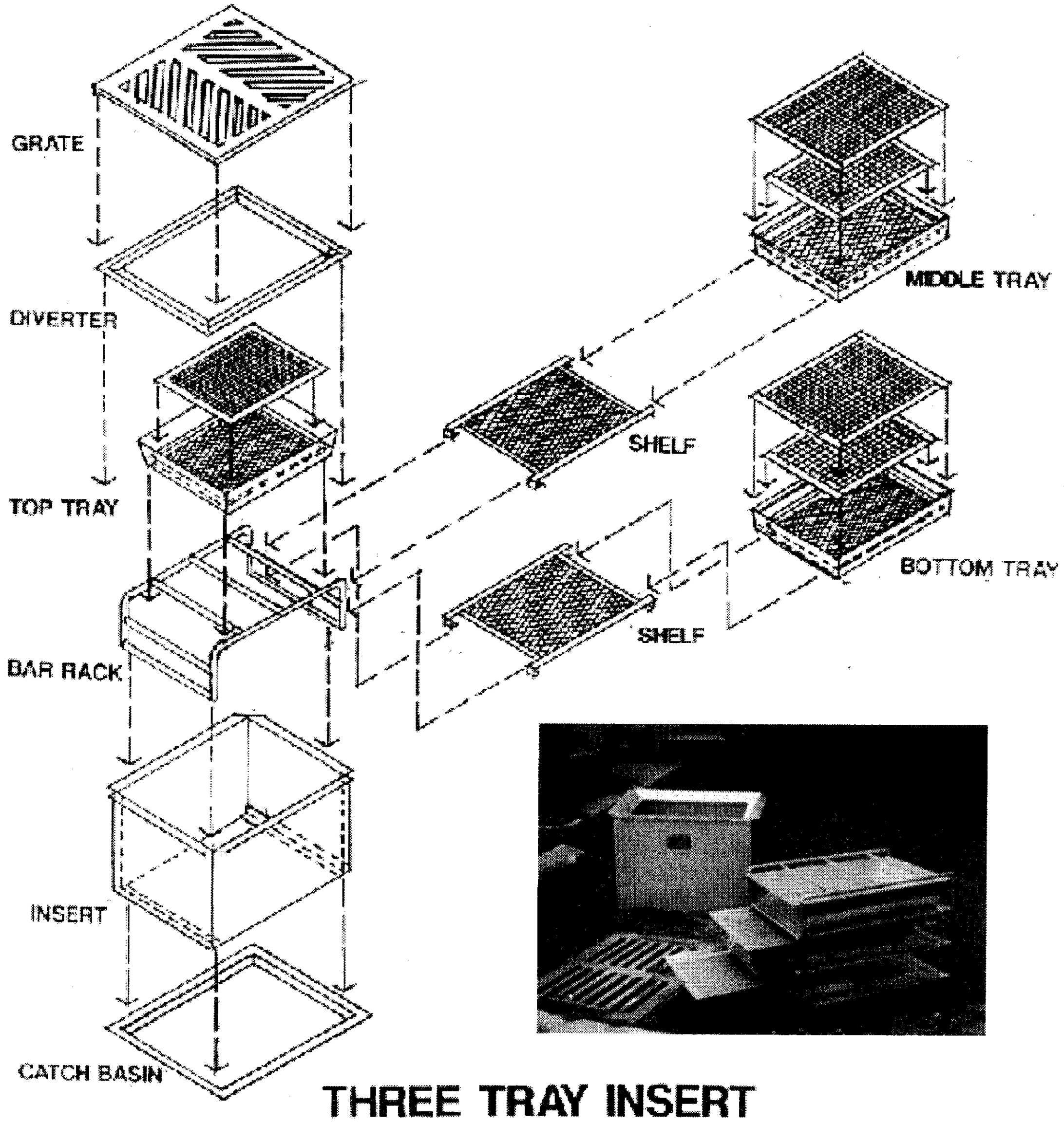


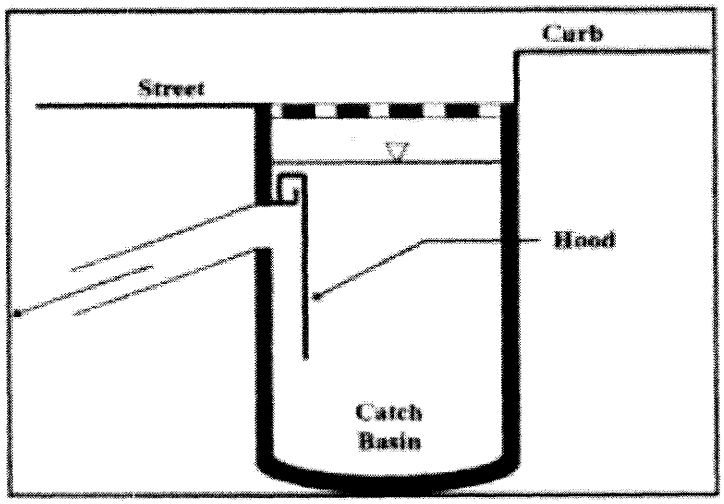
THREE TRAY INSERT

ENVIRO-DRAIN© 1994

Source: www.enviro-drain.com/

Appendix 1: Drain Inserts

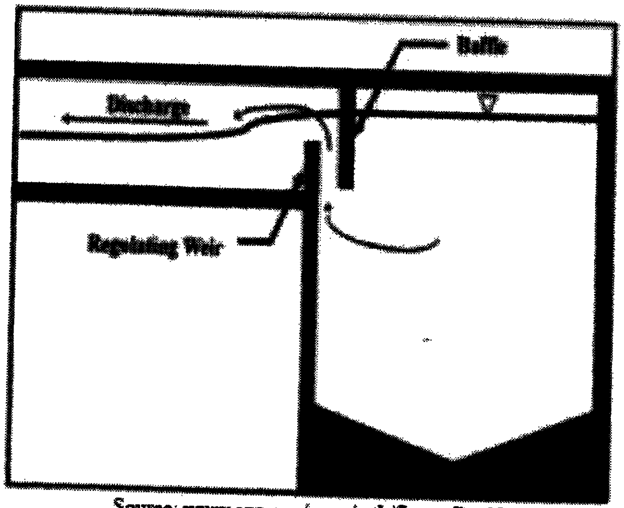
Source: www.epa.gov/npdes/menuofbmps/post_7html



Source: www.epa.gov/owm/mtb/floatctfl.pdf

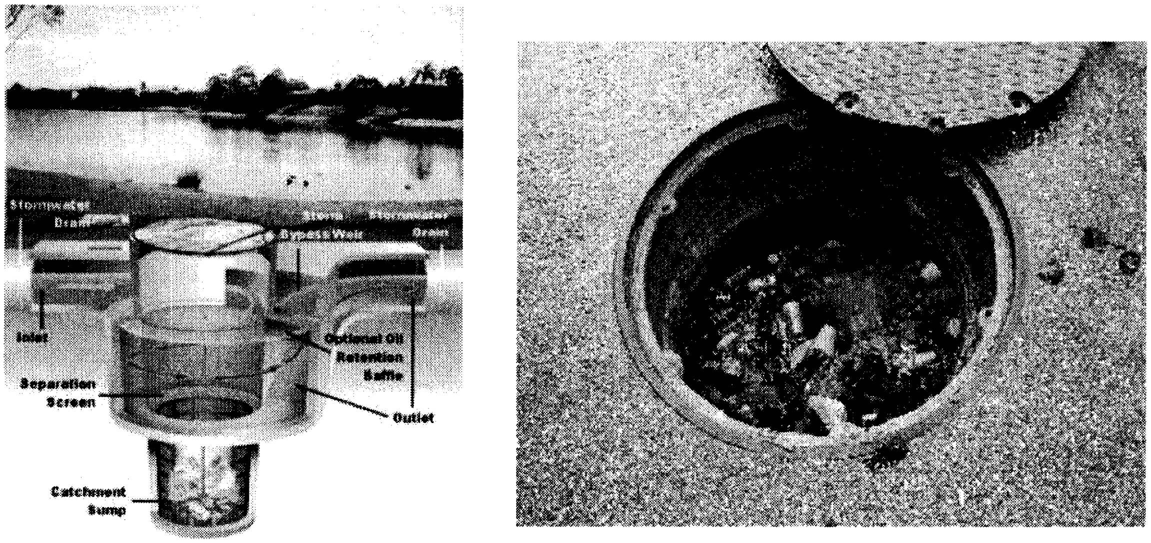
Appendix 2: Modified Catch Basin

Source: www.forester.net/sw_0103_creative.html



Source: www.epa.gov/owm/mtb/floatctfl.pdf

Appendix 3: Baffle Boxes



Source: www.cdstech.com.au/products.html

Appendix 4: CDS device