Nanofactory-Based Environmental Remediation: Cleanup of Polluted Oil Sands Tailings Pond Water in Alberta, Canada

Syncrude oil sands tailings pond, Mildred Lake Settling Basin, Fort McMurray, Alberta, Canada
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Cite as: Robert A. Freitas Jr., "Nanofactory-Based Environmental Remediation: Cleanup of Polluted Oil Sands Tailings Pond Water in Alberta, Canada," IMM Report No. 51, 10 April 2023; http://www.imm.org/Reports/rep051.pdf.

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1. Introduction

Oil sands,[1] tar sands, crude bitumen, or bituminous sands, are a type of unconventional petroleum deposit consisting of loose sands or partially consolidated sandstone containing a naturally occurring mixture of sand, clay, and water, soaked with bitumen[2] (image, right), a dense and extremely viscous form of petroleum. Oil sands tailings ponds are engineered dam and dyke systems used to capture oil sand tailings containing a mixture of salts, suspended solids and dissolvable chemical compounds and toxic hydrocarbons produced as a byproduct of bitumen extraction from the oil sands. Managing these tailings is one of the most difficult environmental challenges facing the oil sands industry. The purpose of this paper is to describe and analyze a future nanotechnological opportunity for remediation of tailings pond water, or TPW, specifically in the context of the tar sands petroleum industry of Alberta, Canada (map, left). This is a revised and updated version of an earlier (previously unpublished) paper originally authored in 2013.

After a quick description of the Alberta tailings ponds architecture and water contamination problem, we summarize the most troublesome pollutants and conclude that naphthenic acids are by far the highest-volume and highest-toxicity contaminant in the tailings pond water (Section 2). For expediency, most of the following analysis is focused on removing this one key pollutant.

Section 3 briefly mentions a few of the conventional methods either proposed or currently in use to remove naphthenic acid contaminants from pond water.

Section 4 describes the proposed nanotechnological method of molecular filtration in more detail, specifically targeted at the most troublesome naphthenic acid pollutants. Section 4.1 estimates the total volumes of contaminated tailings pond water that requires remediation in Alberta, along with the anticipated annual inflows of additional pollutants from existing tar sands operations. Molecular sorting rotors are described in Section 4.2, along with some ideas for naphthenic acid-specific binding site design in Section 4.3. Section 4.4 presents a conceptual general design for a

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[1] https://en.wikipedia.org/wiki/Oil_sands.

[2] Bitumen is a sticky, black, highly viscous liquid or semi-solid form of petroleum, commonly referred to as asphalt; https://en.wikipedia.org/wiki/Bitumen.

molecular filter system, while Section 4.5 summarizes the likely performance of such a system along with the manufacturing capacity that will be required to build it. Section 4.6 briefly describes a new manufacturing technology – the nanofactory – that will be needed to fabricate molecular filters, and thus must be developed to enable the pathway to remediation proposed in this paper. Section 4.7 considers an advanced remediation strategy in which large numbers of free-swimming nanorobots, manufactured in nanofactories, are released into the tailings pond lakes and swim through the polluted water, absorbing and metabolizing naphthenic acids into carbon dioxide and water inside an onboard processing plant, using free ambient oxygen.

Section 5 briefly describes (1) how other contaminants besides naphthenic acids can be removed from pond water using modified versions of the same molecular filter system, and (2) how contaminants can be removed from the solid tailings material that lies below the pond water layer, and also from upstream sources to reduce the flow of contaminants into the tailings ponds.

Section 6 summarizes our insights on how molecular filters in particular, and nanofactories in general, can be employed for a wide range of environmental remediation challenges.

Throughout this paper, the unit “tonne” refers to a metric ton or 1000 kg, and the energy unit “zJ” refers to the zeptojoule or 10^{-21} joules. The cost of industrial electricity is assumed in all scenarios to be \$0.07/kWh (1.94 x 10^{-8} \$/J).[3]

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[3] Table 9.8. Average Prices of Electricity to Ultimate Customers, 1960-2022 (Cents per Kilowatt-hour, Including Taxes). U.S. Energy Information Administration, Feb 2023; https://www.eia.gov/totalenergy/data/monthly/pdf/sec9_11.pdf.

2. Composition of Tailings Pond Water (TPW)

The oil sands in Alberta, Canada, covering over 100,000 km^2 of land area, produce over 1.3 million barrels of bitumen per day.[4] Extraction of bitumen by surface mining of oil sands requires large amounts of water and hydrocarbon solvents. The resulting byproduct creates huge volumes of mixtures of water, sands, clays, residual hydrocarbons, heavy metals, naphtha diluents, and naphthenic acids, which are called tailings. Due to operational policies preventing zero discharge of any liquids into the environment, these fine tailings are collected and confined into settling basins to create tailings ponds (**Figure 1**). Despite the toxicity of tailings, microbial communities exist in these tailings ponds which aid to accelerate tailings sedimentation while being able to degrade certain compounds in the tailings.[5]

Figure 1. Tailings ponds at Suncor operations in Fort McMurray.

Water flowing into ponds brings fresh contaminants. For instance, 0.202 µg/L of PACs (polycyclic aromatic compounds, especially polycyclic aromatic hydrocarbons[6] or PAHs) are found in the Athabasca River water downstream of oil sand development during summer, and up to 4.8 µg/L of dissolved PACs are found in snow melt (possibly toxic to fish embryos).[7]

Close to the pond inflow, the largest particles of sand settle quickly. However, tailings consolidation of fine clays (Mature Fine Tailings or MFTs) occurs by gravity at a slow rate over

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[4] Golby S, Ceri H, Gieg LM, Chatterjee I, Marques LL, Turner RJ. Evaluation of microbial biofilm communities from an Alberta oil sands tailings pond. FEMS Microbiol Ecol. 2012 Jan;79(1):240-50; https://pubmed.ncbi.nlm.nih.gov/22029695/.

[5] "Oil Sands Tailings Pond," http://microbewiki.kenyon.edu/index.php/Oil_Sands_Tailings_Pond.

[6] https://en.wikipedia.org/wiki/Polycyclic_aromatic_hydrocarbon.

[7] Kelly EN, Short JW, Schindler DW, Hodson PV, Ma M, Kwan AK, Fortin BL. Oil sands development contributes polycyclic aromatic compounds to the Athabasca River and its tributaries. Proc Natl Acad Sci U S A. 2009 Dec 29;106(52):22346-51; https://www.pnas.org/doi/full/10.1073/pnas.0912050106.

5-10 years.[8] Stratification therefore results with older and denser fine tailings settled to the bottom and fresh tailings deposited on top. Temperature also increases with depth due to lack of surface cooling and retention of heat at 30-60 ^{o}C by deposited tailings.[9] Densification remains an operational challenge, which prevents water from being recycled while delaying the land reclamation process.

Microbial processes cause gradual degradation of the organic pollutants. Anaerobic methanogenic activities by syntrophic bacteria[10] and methanogenic archaea[11] enhance the rate of tailings sedimentation. Microbe-formed gas channels assist the escape of methane gas bubbles which also aid to drain pore water from deeper tailings. About 43,000 m^3 /day of methane (CH_4),[12] or 2000 tons/day by another estimate,[13] may be released from Albertan tailings ponds. Sulfate and nitrate reduction by sulfate and nitrate-reducing bacteria, however, impede the actions of methanogenesis, thus slowing the rate of tailings densification. Densification is reached when the volumetric fraction of solids increase to 85% (w/w).[14]

Along with the 20-30 wt% of solids (sands and clays) and slightly alkaline water ($pH > 7.5$), mature tailings consist of 1-3 wt% of residual bitumen and naphtha, comprising of a mixture of paraffins (n-alkanes), iso-paraffins (branched alkanes), olefins (alkenes), naphthenes (cycloalkanes), olefins, naphthenic acids (cyclopentyl and cyclohexyl carboxylic acids), and monoaromatics (benzene, toluene, ethylbenzene, and xylenes, or BTEX).[15] Other minor elements include trace metals (Cr, Mn, Co, Ni, Cu, Zn, As, Sr, Mo, Ba), and ions (HCO_3^-, PO_4^{3-},

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[8] Siddique T, Penner T, Klassen J, Nesbø C, Foght JM. Microbial communities involved in methane production from hydrocarbons in oil sands tailings. Environ Sci Technol. 2012 Sep 4;46(17):9802-10; https://pubmed.ncbi.nlm.nih.gov/22894132/.

[9] Penner TJ, Foght JM. Mature fine tailings from oil sands processing harbour diverse methanogenic communities. Can J Microbiol. 2010 Jun;56(6):459-70; https://pubmed.ncbi.nlm.nih.gov/20657616/.

[10] https://en.wikipedia.org/wiki/Syntrophy.
[11] https://en.wikipedia.org/wiki/Methanogen.

[12] "Oil Sands Tailings Pond," http://microbewiki.kenyon.edu/index.php/Oil_Sands_Tailings_Pond

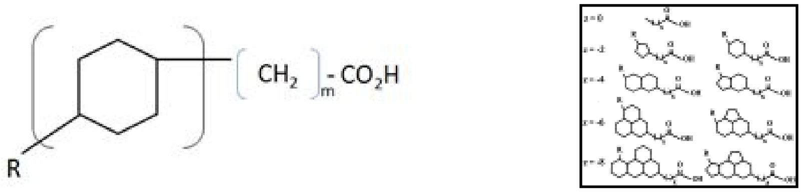
[13] 12 gm/day-m^2 of CH_4 x 170 km^2 of ponds. See: "Tailings, A Lasting Oil Sands Legacy," 2010, World Wildlife Federation (WWF), p.7; http://awsassets.wwf.no/downloads/tailings__a_lasting_oil_sands_legacy___wwf.pdf

[14] Brown D, Ramos-Padron E, Gieg L, Voorduow G. Effect of calcium ions and anaerobic microbial activity on sedimentation of oil sands tailings. Intl Biodeter & Biodegrad 2013 Jul;81:9-16; https://www.sciencedirect.com/science/article/abs/pii/S0964830512001783.

[15] Siddique T, Fedorak PM, MacKinnon MD, Foght JM. Metabolism of BTEX and naphtha compounds to methane in oil sands tailings. Environ Sci Technol. 2007 Apr 1;41(7):2350-6; https://pubs.acs.org/doi/pdf/10.1021/es062852q. Siddique T, Fedorak PM, Foght JM. Biodegradation of short-chain n-alkanes in oil sands tailings under methanogenic conditions. Environ Sci Technol. 2006 Sep 1;40(17):5459-64; https://pubs.acs.org/doi/pdf/10.1021/es060993m.

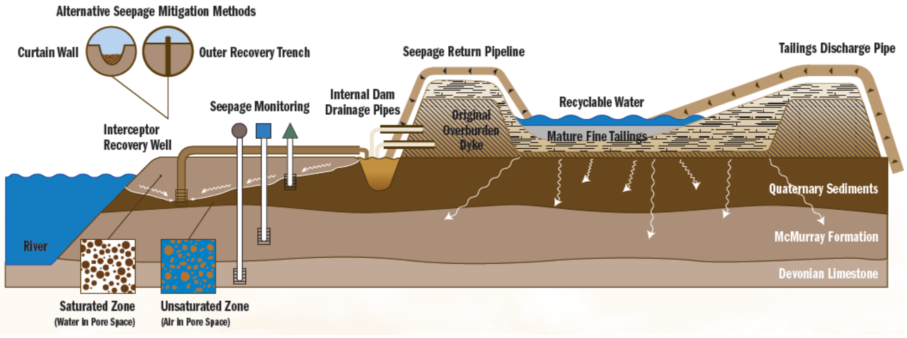
NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-).[16] Toxicity of tailings ponds to aquatic organisms is often associated with naphthenic acids (**Figure 2**), which have surfactant properties that penetrate the cell membrane.[17]

Figure 2. Examples of naphthenic acids – monocyclic (left) and polycyclic (right).



In active ponds, wastes from bitumen extraction are continually collected in the basin (**Figure 3**). This results in a continual input of electron donors and acceptors of metal ions into the pond. In active ponds, gypsum is added to aid densification while microbial activities are dominated by anaerobes at lower depths. In inactive ponds, wastes from bitumen extractions are no longer collected. In this situation, there are no inputs of electron donor and acceptors while microbial activities are confined to the upper depths with lower anaerobic activities. Therefore, the status of the pond influences the composition of the microbial community that is present.[18]

Figure 3. A typical tailings pond system.[19]



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[16] Mahdavi H, Ulrich AC, Liu Y. Metal removal from oil sands tailings pond water by indigenous micro-alga. Chemosphere. 2012 Sep;89(3):350-4; https://pubmed.ncbi.nlm.nih.gov/22583786/.

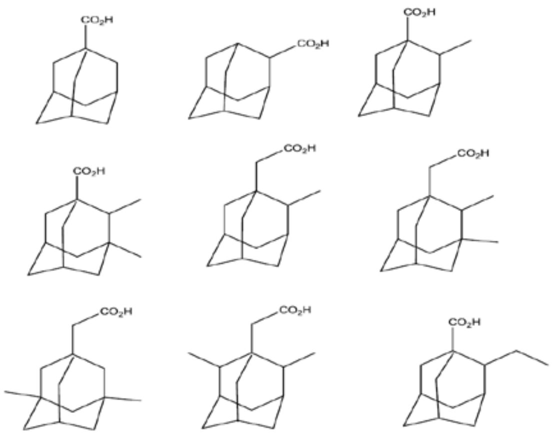
[17] Quagraine EK, Peterson HG, Headley JV. In situ bioremediation of naphthenic acids contaminated tailing pond waters in the athabasca oil sands region--demonstrated field studies and plausible options: a review. J Environ Sci Health A Tox Hazard Subst Environ Eng. 2005;40(3):685-722; https://pubmed.ncbi.nlm.nih.gov/15756978/.

[18] Lisa Gieg, "Microbial Activities and Communities in Oil Sands Tailings Ponds," http://www.ismos-3.org/Presentations/Gieg-ISMOS-3.pdf.

[19] "Oil Sands – Tailings Ponds," 2011, http://www.nrcan.gc.ca/energy/sites/www.nrcan.gc.ca.energy/files/files/OilSands-TailingsPonds_e.pdf.

Naphthenic acids[20] are the most serious class of carcinogen in tailings pond water (TPW).[21] One study[22] found naphthenic acids present in Athabasca oil sands TPW at a concentration of about 81 mg/L, with a highly heterogeneous mixture with nearly equal proportions of monocyclic, polycyclic, and acyclic acids with molecular weights primarily between 220-360 gm/mole. Biphenyls, naphthalenes, and phenanthrene/anthracene were also found at much lower concentrations (<13 µg/L). Another study[23] confirmed naphthenic acids in TPW at 40-70 mg/L concentrations, but as high as 130 mg/L in fresh tailing ponds. More recently, tricyclic diamondoid acids (**Figure 4**), an interesting class of polycyclic naphthenic acid, have been found in TPW, suggesting "an unprecedented degree of biodegradation of some of the oil in the oil sands."[24]

Figure 4. A selection of diamondoid acids found in tailings pond water.



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[20] Naphthenic acids are the main oxygen-containing components of petroleum (0.5%-3.0%). Naphthenic acids (b.p. 220-300 °C) are viscous, colorless liquids that turn yellowish upon standing, and are virtually insoluble in water but dissolve readily in petroleum products and other organic solvents, having all the properties characteristic of carboxylic acids; http://encyclopedia2.thefreedictionary.com/Naphthenic+Acids. Naphthenic acids are typically represented by the formula C_nH_{2n-z} O_2; https://en.wikipedia.org/wiki/Naphthenic_acid.

[21] In the Athabasca oil sands, NAs have been identified as the largest component of dissolved organic matter in the tailings waters from oil sands extraction processes. They are the major contributor to the acute toxicity of the fine tailings wastewaters at the oil sands extraction plants in northeastern Alberta, Canada; http://www.ncbi.nlm.nih.gov/pubmed/11456157.

[22] Rogers VV, Liber K, MacKinnon MD. Isolation and characterization of naphthenic acids from Athabasca oil sands tailings pond water. Chemosphere. 2002 Aug;48(5):519-27; https://pubmed.ncbi.nlm.nih.gov/12146630/.

[23] Allen EW. Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives. J Environ Eng Sci 2008;7:123-138; http://documents.techno-science.ca/documents/tailingsallenoilsandswatermanagement.pdf.

[24] Rowland SJ, Scarlett AG, Jones D, West CE, Frank RA. Diamonds in the rough: identification of individual naphthenic acids in oil sands process water. Environ Sci Technol. 2011 Apr 1;45(7):3154-9; https://pubs.acs.org/doi/pdf/10.1021/es103721b.

Table 1 summarizes the most important components of TPW for the purposes of environmental discharge or reclamation. Items in parens are not regarded as serious pollutants. The table includes waterborne components only and excludes additional pollutants present in tailings pond sludge, tailings sand (i.e., Mature Fine Tailings or MFT), and pond sedimentary layers which would require additional remediation.

Table 1. Major Pollutants in Alberta Oil Sands Tailings Pond Water[25]

Pollutant	**Oil Sands TPW Concentration** (mg/L)	**Pollutant**	**Oil Sands TPW Concentration** (mg/L)
Organic			
Naphthenic acids	50-70 (max 130)	Phenols	0.02-1.5
Oil and grease	9-92	Cyanide	0.01-0.5
Benzene	<0.01-6.3	PAHs	0.01
Toluene	<0.01-3	BTEX	<0.01
Inorganic			
Total Dissolved Solids	1900-2221	(Calcium)	17-25
Bicarbonate	775-950	(Total Suspended Solids)	15-70
Sulfate	218-290	(Magnesium)	8-22
Chloride	80-540	Ammonia	3.4-14
(Sodium)	16-659	(Silica)	1.75
Trace Metals			
Iron	0.8-3	Copper	0.002-0.9
Zinc	0.01-3.2	Aluminum	0.07-0.5
Nickel	0.006-2.8	Lead	0.04-0.19
Chromium	0.003-2	Arsenic	0.006-0.015

The most toxic pollutant, and one of the highest concentration contaminants, is the naphthenic acid group. We will focus almost exclusively on this group of chemicals for the remainder of this paper, keeping in mind that the other TPW contaminants can be dealt with in a substantially similar manner.

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[25] Allen EW. Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives. J Environ Eng Sci 2008;7:123-138, Table 5; http://documents.techno-science.ca/documents/tailingsallenoilsandswatermanagement.pdf.

3. Conventional Removal of Naphthenic Acids from TPW

Many conventional methods have been reported for removal of the naphthenic acids (NAs) that are contaminating oil sands tailings pond water (TPW), including chemical,[26] photolysis/photocatalysis treatment,[27] and biodegradation.[28] These processes, in their present forms, invariably use expensive chemicals, require long retention times, and have large annual

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[26] MacKinnon MD, Boerger H. Description of Two Treatment Methods for Detoxifying Oil Sands Tailings Pond Water. Water Qual Res J 1986;21(4):496-512; https://iwaponline.com/wqrj/article/21/4/496/40597/Description-of-Two-Treatment-Methods-for. Scott AC, Zubot W, MacKinnon MD, Smith DW, Fedorak PM. Ozonation of oil sands process water removes naphthenic acids and toxicity. Chemosphere. 2008 Mar;71(1):156-60; https://pubmed.ncbi.nlm.nih.gov/18068212/. Brown LD, Ulrich AC. Oil sands naphthenic acids: a review of properties, measurement, and treatment. Chemosphere. 2015 May;127:276-90; https://pubmed.ncbi.nlm.nih.gov/25753852/.

[27] McMartin DW, Headley JV, Friesen DA, Peru KM, Gillies JA. Photolysis of naphthenic acids in natural surface water. J Environ Sci Health A Tox Hazard Subst Environ Eng. 2004;39(6):1361-83; https://pubmed.ncbi.nlm.nih.gov/15244322/. Headley JV, Du JL, Peru KM, McMartin DW. Electrospray ionization mass spectrometry of the photodegradation of naphthenic acids mixtures irradiated with titanium dioxide. J Environ Sci Health A Tox Hazard Subst Environ Eng. 2009 May;44(6):591-7; https://pubmed.ncbi.nlm.nih.gov/19337922/. VanMensel D, Chaganti SR, Boudens R, Reid T, Ciborowski J, Weisener C. Investigating the Microbial Degradation Potential in Oil Sands Fluid Fine Tailings Using Gamma Irradiation: A Metagenomic Perspective. Microb Ecol. 2017 Aug;74(2):362-372; https://pubmed.ncbi.nlm.nih.gov/28246922/.

[28] Herman DC, Fedorak PM, MacKinnon MD, Costerton JW. Biodegradation of naphthenic acids by microbial populations indigenous to oil sands tailings. Can J Microbiol. 1994 Jun;40(6):467-77; https://pubmed.ncbi.nlm.nih.gov/8050066/. Quagraine EK, Peterson HG, Headley JV. In situ bioremediation of naphthenic acids contaminated tailing pond waters in the athabasca oil sands region--demonstrated field studies and plausible options: a review. J Environ Sci Health A Tox Hazard Subst Environ Eng. 2005;40(3):685-722; https://pubmed.ncbi.nlm.nih.gov/15756978/. Scott AC, MacKinnon MD, Fedorak PM. Naphthenic acids in athabasca oil sands tailings waters are less biodegradable than commercial naphthenic acids. Environ Sci Technol. 2005 Nov 1;39(21):8388-94; http://www.cec.org/wp-content/uploads/wpallimport/files/10-2-rsub-appendix_xi-_naphthenic_acids_paper.pdf. Biryukova OV, Fedorak PM, Quideau SA. Biodegradation of naphthenic acids by rhizosphere microorganisms. Chemosphere. 2007 May;67(10):2058-64; https://pubmed.ncbi.nlm.nih.gov/17250872/. Han X, Scott AC, Fedorak PM, Bataineh M, Martin JW. Influence of molecular structure on the biodegradability of naphthenic acids. Environ Sci Technol. 2008 Feb 15;42(4):1290-5; https://pubmed.ncbi.nlm.nih.gov/18351107/. Mohamad Shahimin MF, Foght JM, Siddique T. Preferential methanogenic biodegradation of short-chain n-alkanes by microbial communities from two different oil sands tailings ponds. Sci Total Environ. 2016 May 15;553:250-257; https://pubmed.ncbi.nlm.nih.gov/26925736/. Lv X, Ma B, Cologgi D, Lee K, Ulrich A. Naphthenic acid anaerobic biodegrading consortia enriched from pristine sediments underlying oil sands tailings ponds. J Hazard Mater. 2020 Jul 15;394:122546; https://pubmed.ncbi.nlm.nih.gov/32203719/.

operating costs.[29] Indeed, the Alberta Energy Regulator confirmed in 2022 that no tailings have ever been certified reclaimed to date,[30] and that across the entire oil sands region only 1 km^2 of the total area disturbed by mining operations has ever been certified reclaimed.[31]

The more cost-effective biodegradation techniques[32] have had limited success to date in biodegrading NAs to levels below 19 mg/L. Some tailing pond waters have been stored for more than 10 years, and it appears that the remaining high molecular weight NAs resist degradation by the natural biodegradation process in the ponds. Some plausible options to further degrade the NAs in the tailings pond water include: bioaugmentation with bacteria selected to degrade the more refractory classes of NAs; the use of attachment materials such as clays to concentrate both the NA and the NA-degrading bacteria in their surfaces and/or pores; synergistic association between algae and bacteria consortia to promote efficient aerobic degradation; and biostimulation with nutrients to promote the growth and activity of the microorganisms.[33]

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[29] Mishra S, Meda V, Dalai AK, McMartin DW, Headley JV, Peru KM. Photocatalysis of Naphthenic Acids in Water. J Water Resource and Protection 2010;2:644-650; http://www.scirp.org/journal/PaperDownload.aspx?paperID=2239

[30] Anderson D. Ponds of toxic waste in Alberta's oilsands are bigger than Vancouver — and growing. The Narwhal, 4 Jun 2022; https://thenarwhal.ca/oilsands-tailings-ponds-growth/.

[31] OSIP – Data Library, Govt. of Alberta, 13 Mar 2010; https://osip.alberta.ca/library/Dataset/Details/27.

[32] Kannel PR, Gan TY. Naphthenic acids degradation and toxicity mitigation in tailings wastewater systems and aquatic environments: a review. J Environ Sci Health A Tox Hazard Subst Environ Eng. 2012;47(1):1-21; https://pubmed.ncbi.nlm.nih.gov/22217078/.

[33] Quagraine EK, Peterson HG, Headley JV. In situ bioremediation of naphthenic acids contaminated tailing pond waters in the athabasca oil sands region--demonstrated field studies and plausible options: a review. J Environ Sci Health A Tox Hazard Subst Environ Eng. 2005;40(3):685-722; https://pubmed.ncbi.nlm.nih.gov/15756978/.

4. Molecular Filtration of Naphthenic Acids from TPW

We propose to remove naphthenic acids (NAs) from tailings pond water (TPW) using a new technique based on atomically precise nanomechanical systems called "molecular filters" that maximize the efficiency of molecular capture and transport across barrier membranes.

The most efficient of all modes of molecular transport involves receptor sites capable of recognizing and selectively binding specific molecular species. Many receptors reliably bind only a single molecular type. Other receptors, such as sugar molecule transporters in biochemistry, can recognize and transport several related sugar molecule types. In nanomechanical systems, artificial binding sites with a wide variety of size, shape, and electronic charge can be created and employed in the construction of a range of highly efficient molecular sortation and transport devices.[34]

Molecular filters can be fabricated in commercial quantities using molecular manufacturing methods such as nanofactories (Section 4.6) that have been described elsewhere.[35]

4.1 Volume of Tailings Pond Water to be Remediated

A reasonable environmental treatment target for the removal of naphthenic acid from Alberta oil sands tailings pond water might be a concentration of about 1 mg/L,[36] which is roughly the background concentration in surface waters.[37] Allen (2008) explains: "As the principal source of toxicity in the tailings ponds, NAs represent the main pollutant of concern with respect to reclamation or environmental discharge. Although the acutely toxic fraction of NAs have been shown to degrade naturally over time in experimental pits and wetlands, the lengthy water residence time required for degradation may not be practical where the direct discharge of water

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[34] Drexler KE. Nanosystems: Molecular Machinery, Manufacturing, and Computation, John Wiley & Sons, New York, 1992, Section 13.2.1(a) "Modulated receptors for selective transport: Basic concepts"; https://www.amazon.com/dp/0471575186/. Freitas RA Jr. Nanomedicine, Volume I: Basic Capabilities, Landes Bioscience, Georgetown, TX, 1999; Section 3.4.2, "Sorting Rotors"; http://www.nanomedicine.com/NMI/3.4.2.htm.

[35] Drexler KE. Nanosystems: Molecular Machinery, Manufacturing, and Computation. John Wiley & Sons, New York, 1992, Section 14.4.3; https://www.amazon.com/dp/0471575186/. Freitas RA Jr., Merkle RC. Kinematic Self-Replicating Machines, Landes Bioscience, Georgetown, TX, 2004; Section 4; http://www.molecularassembler.com/KSRM/4.htm.

[36] Allen EW. Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives. J Environ Eng Sci 2008;7:123-138, Table 5; http://documents.techno-science.ca/documents/tailingsallenoilsandswatermanagement.pdf.

[37] Headley JV, McMartin DW. A review of the occurrence and fate of naphthenic acids in aquatic environments. J Environ Sci Health A Tox Hazard Subst Environ Eng. 2004;39(8):1989-2010; https://pubmed.ncbi.nlm.nih.gov/15332664/.

is required. Also, high molecular weight NA compounds appear to be resistant to biodegradation and could persist in reclaimed environments. Further research is needed to determine if recalcitrant NAs in reclaimed environments pose a chronic toxicity risk. Since concentration-based limits have not been established in Canada, background concentrations in local surface- and groundwater (i.e., ~1-5 mg/L) are suggested as a target for NA removal. Given typical NA concentrations of 50-70 mg/L in TPW, the corresponding water treatment objective would be 90%-99% removal."

Another more conservative source[38] claims that "decades of storage in tailings ponds under various conditions have not proven effective at decreasing NA concentrations to below 20 mg/L," and asserts that NAs must ultimately be reduced to "below toxic levels (<0.15 mg/L)." Since Allen also notes that NA concentrations as high as 130 mg/L have been observed in fresh tailing ponds, we shall very conservatively assume that our task is to reduce the total concentration of NAs in TPW from 130 mg/L to 0.1 mg/L.

A tailings pond remediation effort has two obvious natural targets.

First, the existing ponds should be remediated, including removal of both the existing naphthenic acid (NA) contaminants and the inflow of fresh NA contaminants as they arrive.

Second, the influx of fresh NA contaminants from oil sand mining operations into the ponds should be eliminated by filtration at the source, thus preventing NAs from entering the ponds in the first place. It is possible that a successful implementation of this second target, especially if extended beyond NAs to include other selected contaminants, might vastly reduce the total acreage requirement for tailings ponds – and possibly eliminate the need for them entirely.

By 2013 there were 170 km^2 of tailings ponds in Alberta,[39] with 71 km^2 under active reclamation using currently available methods.[40] As of today there are an estimated 1-4 billion m^3 of contaminated water in tailings pond water (TPW).[41] Here we tentatively assume a **3 x 10^9 m^3**

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[38] Birkholz DA. Naphthenic Acids in the Environment: State of the Union. Water Tech 2012; https://www.esaa.org/wp-content/uploads/2015/01/WaterTech2012-P33.pdf.

[39] "Tailings", Government of Alberta, 2013; https://web.archive.org/web/20130325200914/http://oilsands.alberta.ca/tailings.html.

[40] "Reclamation", Government of Alberta, 2013; https://web.archive.org/web/20130325201002/http://oilsands.alberta.ca/reclamation.html.

[41] A range of estimates: (1) Birkholz DA (Naphthenic Acids in the Environment: State of the Union. Water Tech 2012; https://www.esaa.org/wp-content/uploads/2015/01/WaterTech2012-P33.pdf) asserts "greater than **1 x 10^9 m^3**" of tailings pond water (TPW) now in storage. (2) An Oct 2021 Alberta Energy Regulator (AER) report said that in 2020 the tailings ponds increased by another 90 million cubic meters and contained **1.36 billion cubic metres** of fluids (https://www.thestar.com/news/canada/2021/10/18/enviro-groups-want-feds-to-step-in-after-report-reveals-albertas-tailings-ponds-are-growing.html). (3) Total pond volume is **1.7-3.4 x 10^9 m^3**, taking avg. pond depth of 10-20 meters (http://microbewiki.kenyon.edu/index.php/Oil_Sands_Tailings_Pond). (4) With the volume of impounded process water at Syncrude's Lease 17/22 approaching 1 billion m^3 in 2004 (M.D. MacKinnon, "Oil sands water quality issues: properties, treatment, and discharge options," Canadian Oil Sands Network for

TPW figure. (According to one estimate,[42] there was a comparable volume of Mature Fine Tailings (MFT) of about **0.8406 x 10^9 m^3** in 2010.[43])

As for TPW inflows, estimates again vary widely in the 100-400 x 10^6 m^3/yr range,[44] with tar sands oil producers currently licensed to withdraw up to 652 x 10^6 m^3 of Athabasca River water.[45] Here we tentatively assume a **200 x 10^6 m^3/yr** TPW inflow figure.

Making these assumptions, our molecular filtration system, when optimally deployed in the tailings ponds throughout all of Alberta, must remove (130 mg/L – 0.1 mg/L) (10^{-6} kg/mg) (1000

Research and Development (CONRAD) Oil Sands Water Usage Workshop, 24-25 February 2005; http://www.conrad.ab.ca/seminars/water_usage/2004/Agenda.htm) when only 70 km^2 of ponds existed (M. Dominski, "Surface mined oil sand: tailings practices, performance, and projections," Alberta Energy and Utilities Board, in Proceedings of the 3rd International Heavy Oil Conference, 5-7 March 2007, Calgary, Alta. Alberta Energy and Utilities Board), then at 170 km^2 of ponds of similar size in 2013 the volume would be about **2.4 x 10^9 m^3** of TPW, and more today. (5) From Schneider K, Kean S. Tar Sands Oil Production, An Industrial Bonanza, Poses Major Water Use Challenges. WaterNews, 10 Aug 2010; http://www.circleofblue.org/waternews/2010/world/tar-sands-oil-production-is-an-industrial-bonanza-poses-major-water-use-challenges/), Alberta has "more than a trillion gallons" of TPW, or **3.8 x 10^9 m^3**.

[42] "Tailings, A Lasting Oil Sands Legacy," World Wildlife Federation (WWF), 2010; http://awsassets.wwf.no/downloads/tailings__a_lasting_oil_sands_legacy___wwf.pdf.

[43] Mature Fine Tailings or MFT, is the term used to describe the mix of fine clay particles and water after the slurry has settled for several years. From that point on, further settling occurs only at a vastly reduced rate. With a consistency of thin yogurt, MFT is unable to support reclamation activities. Untreated, MFT is expected to persist in a fluid state for several hundred years. MFT is too toxic to be released to the environment so it is stored on the landscape. Inventories of MFT continue to accumulate, creating what is essentially a growing and long-term liability. Based upon mine operator submissions, the total volume of MFT stored on the landscape could reach **2.4 billion m^3** by 2040. From: "Tailings, A Lasting Oil Sands Legacy," World Wildlife Federation (WWF), 2010; http://awsassets.wwf.no/downloads/tailings__a_lasting_oil_sands_legacy___wwf.pdf.

[44] Again, a range of estimates: (1) A personal communication (G.S., 2013) of 200 x 10^6 liters/day gives an estimate of **73 x 10^6 m^3/yr** of tailings pond water (TPW) fresh inflows. (2) If wastewaters are accumulating at a rate of about 0.1-0.2 m^3 of TPW per ton of oil sands processed ("Toronto BioRad 2010", http://2010.igem.org/Team:Toronto/Project), and if 2 tons of tar sand are required to produce 1 bbl of tar oil (Matthew Yeomans, *Oil: A Concise Guide to the Most Important Product on Earth*, The New Press, 2006), then a 2011 production of 1.6 x 10^6 bbl/day of tar oil yields **116.8-233.6 x 10^6 m^3/yr** of TPW inflow. (3) From Schneider and Kean, 2010, *supra*: In 2008 tar sands mines used 184.3 x 10^6 m^3 of water of which 10% was returned to the river and 90% was "poured into toxic tailing ponds," yielding an inflow rate of **165.87 x 10^6 m^3/yr** of TPW. (4) A requirement of 3.1 bbl water per bbl of oil (Allen, 2008, *supra*) and a 2011 production of 1.6 x 10^6 bbl/day of tar oil gives **287.8 x 10^6 m^3/yr** of TPW inflow. (5) A model (Allen, 2008, *supra*) assuming 200,000 bbl/day tar oil production predicts 6364 tonnes/hr or 55.7 x 10^6 m^3/yr of TPW "free water" entering tailings ponds; a 2011 production of 1.6 x 10^6 bbl/day of tar oil thus predicts **446 x 10^6 m^3/yr** of TPW inflow.

[45] Keith Schneider, Sam Kean, "Tar Sands Oil Production, An Industrial Bonanza, Poses Major Water Use Challenges", 10 Aug 2010, http://www.circleofblue.org/waternews/2010/world/tar-sands-oil-production-is-an-industrial-bonanza-poses-major-water-use-challenges/.

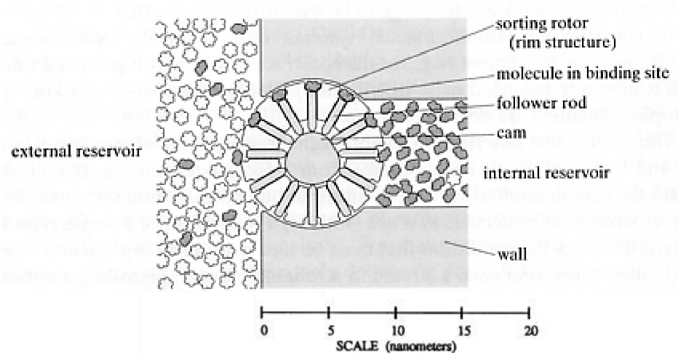
L/m^3) (3 x 10^9 m^3 TPW) ≈ **400 x 10^6 kg** of naphthenic acids over some appropriate remediation time period. In addition, our system must also deal with a continuing inflow of (130 mg/L – 0.1 mg/L) (10^{-6} kg/mg) (1000 L/m^3) (200 x 10^6 m^3/yr TPW) ≈ **30 x 10^6 kg/yr** of naphthenic acids entering the existing tailings ponds throughout all of Alberta.[46]

A minimal NA removal rate of 30 x 10^6 kg/yr, matching the total Albertan inflow rate, would halt any increase in concentration of NAs in the ponds. A more aggressive target NA removal rate of 200 x 10^6 kg/yr would complete the remediation of all Albertan tailings ponds in 2.3 years, leaving plenty of surplus filtration capacity in place to accommodate expansion of the Alberta oil sands extraction industry in future years. This compares favorably with the natural half-lives of NAs in TPW of 12.8-13.6 years.[47]

4.2 Sorting Rotors

The molecular filter consists of a barrier or wall that is penetrated by one or more nanomechanical devices that act as molecule-specific pumps, analogous to the transporter pumps found on the surfaces of living biological cells. One simple such pump is a nanomechanical device called a “molecular sorting rotor” that is capable of selectively binding molecules from solution and then transporting these bound molecules against concentration gradients (**Figure 5**), moving only the molecules of a specific type (such as NAs) from one side of the wall to the other. Each pump mechanically transports individual molecules, one by one, through the barrier. The molecular filter is simply a sheet with large numbers of surface-embedded pumps.

Figure 5. An exemplar molecular sorting rotor design, with target molecules (dark) passing from left to right as the rotor turns in the clockwise direction.



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[46] It is also alleged that as much as 11 million liters/day (4 x 10^6 m^3/yr) seeps out of the tailings ponds: “Losing ground on toxic tailings,” 30 Aug 2013, http://tarsandssolutions.org/member-blogs/losing-ground-on-toxic-tailings.

[47] Birkholz DA. Naphthenic Acids in the Environment: State of the Union. Water Tech 2012; https://www.esaa.org/wp-content/uploads/2015/01/WaterTech2012-P33.pdf.

The archetypal sorting rotor illustrated above is a disk about 10 nm in diameter and about 3 nm thick having 12 binding site “pockets” along the rim that are exposed alternately to the source fluid at left and the receiving chamber at right by the clockwise axial rotation of the disk.[48] (Other designs may have more, or fewer, pockets.) Each pocket selectively binds a specific molecule when exposed to the source fluid at left. The rotor turns clockwise, moving the pocket containing the bound molecule through the wall from left to right. Once the binding site has rotated far enough to expose it to the receiving chamber at right, the bound molecules are forcibly ejected by rods thrust outward by the cam surface. Other means, whether mechanical or electronic, could also be used to reversibly alter the binding site affinity for the transported molecule during the transport process.

Molecular sorting rotors can be designed from about 100,000 atoms (including rotor housing and pro rata share of the mechanical drive system), measuring roughly 7 nm (wide) x 14 nm (tall) x 14 nm (deep) in size with a mass of about 2 x 10^{-21} kg if composed mostly of diamondoid structure. The classic sorting rotor turns at about 86,000 rev/sec which exposes 1 million binding sites per second to the source fluid, giving a conservative rim speed of 2.7 mm/sec, sorting and transporting small molecules like NAs at a rate of 10^6 molecules/sec assuming laminar flow as in the case of an aqueous source fluid and assuming high concentration. Given the mid-range concentrations of NAs in TPW, the binding sites would probably not be fully occupied at that rim speed so that speed would have to be reduced. Binding site occupancy is critically determined by the as-yet undetermined dissociation constant for the interaction between target molecule, binding site, and solvent, but a reasonable estimate is that sortation speed may fall to 10^5 molecules/sec at the peak 130 mg/L naphthenic acid concentration (3.1 x 10^{-4} molecules/nm^3) and to 10^2 molecules/sec at the minimum 0.1 mg/L naphthenic acid concentration (2.4 x 10^{-7} molecules/nm^3). We conservatively assume that the lower 10^2 molecule/sec sortation rate will apply to all NA-filtration scenarios discussed later in this paper.

Molecular pumps generally operate in a four-phase sequence: (1) recognition (and binding) by the transporter of the target molecule from a variety of molecules presented to the pump in the source fluid; (2) translocation of the target molecule through the wall, inside the transporter mechanism; (3) release of the molecule by the transporter mechanism; and (4) return of the transporter to its original condition, so that it is ready to accept another target molecule. It should be noted that molecular transporters that rely on protein conformational changes are ubiquitous in biological systems.

The minimum energy required to pump uncharged molecules is the change in free energy ΔG (joules) in transporting the species from one environment having concentration c_1 to a second environment having concentration c_2, given by:

$$\Delta G = k_B T \ln(c_2/c_1) \qquad (1)$$

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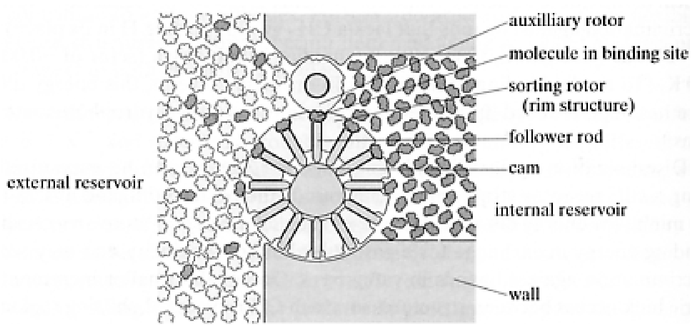
[48] Drexler KE. Nanosystems: Molecular Machinery, Manufacturing, and Computation, John Wiley & Sons, New York, 1992, Section 13.2.1(a) “Modulated receptors for selective transport: Basic concepts”; https://www.amazon.com/dp/0471575186/. Freitas RA Jr. Nanomedicine, Volume I: Basic Capabilities, Landes Bioscience, Georgetown, TX, 1999; Section 3.4.2, “Sorting Rotors”; http://www.nanomedicine.com/NMI/3.4.2.htm.

where $k_B = 0.01381$ zJ/K (Boltzmann constant) and T = temperature in kelvins. So for example, transport of one uncharged molecule from a low concentration to a high concentration environment across a $c_2/c_1 = 1000$ gradient (typical in biology) costs $\Delta G \sim 30$ zJ/molecule at 300 K. A more aggressive $c_2/c_1 = 10^6$ concentration gradient costs $\Delta G \sim 60$ zJ/molecule.

Plausibly assuming the use of low-friction molecular bearings inside the rotor mechanism, the primary source of energy loss is speed-dependent viscous drag of the rotor surface as it moves through the fluid environment on either side of the barrier wall. For a TPW fluid environment having the approximate viscosity of water ($\sim 10^{-3}$ kg/m-sec at 20 ^{o}C) on both sides of the wall, the sorting rotor described as above has an estimated continuous drag power loss of 10^{-16} W while transporting 10^6 molecules/sec, or ~0.1 zJ/molecule transported. At lower speeds, drag power scales as the square of velocity, so rotors turning 10,000 times slower would dissipate negligible energy in overcoming drag forces.

Binding site discrimination against certain types of competing target molecules[49] can be further increased, if necessary, by employing a tight-binding mechanism (**Figure 6**) that allows the binding site to entirely enclose the target molecule.[50] In this paired-rotor approach, all competing molecular species are in fast equilibrium with the fully exposed receptors on the left, but only the preferred species (and strictly smaller ligands) can pass through the fully enclosed position between the two rotors without encountering a large barrier caused by overlap repulsion (barriers >0.2 eV should be easily implemented). Timing of the rotor potential energy function can effectively eliminate barriers when passing the preferred target molecule (the common case for a purification process).

Figure 6. A sorting rotor like that shown in Figure 5, but with an auxiliary rotor that forces bound molecules to pass through a totally enclosed state, effectively excluding molecular species that can't fit within a volume of defined size and shape.



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[49] e.g., (1) target molecules that resemble the preferred target, but occupy a strictly larger volume in all conformations, and (2) target molecules of all other shapes; discrimination is not improved for targets of similar shape having strictly small volume in some conformation. *Nanosystems*, Section 13.2.1(c).

[50] Drexler KE. Nanosystems: Molecular Machinery, Manufacturing, and Computation, John Wiley & Sons, New York, 1992, Section 13.2.1(d) "A class of tight-receptor mechanism"; https://www.amazon.com/dp/0471575186/.

This paired-rotor, tight-receptor sorting rotor motif requires a compliant drive mechanism to operate properly. With an excessively stiff drive mechanism, even bulky competing ligands would routinely be forced through the gap (which must permit their passage in order to avoid failure by mechanical obstruction, regardless of drive stiffness). With a sufficiently compliant drive mechanism, however, the rotor moves (on short time scales) as if in free rotational diffusion. The rotational relaxation time for a rotor this size would be <0.1 μsec, assuming a mean viscosity of the surrounding medium like that of water.[51] Accordingly, in a system transferring receptors at mean intervals of 1 μsec, a bulky competing target molecule momentarily blocked by a barrier has ample time to be carried backward by several receptor diameters and escape into the surrounding solution. A nonlinear compliance can provide a small driving force (e.g., ~1 pN, measured at the rotor rim) with negligible stiffness over a certain angular range of motion (e.g., several radians), while still providing a strong, stiff constraint that prevents larger excursions of the rotor relative to an underlying drive mechanism of ordinary stiffness. Mechanisms of this sort can strongly discriminate against ligands unable to fit within the space occupied by the preferred target molecule.

4.3 Binding Site Design for Naphthenic Acids

The strength of the binding of the target molecule to the artificial receptor site can be designed to be sufficient to achieve high occupancy of all pockets (e.g., 99%) at the given relatively low speeds of rotor rotation. The mechanical energy consumed to force the target molecule out of its binding site into the receiving chamber is delivered from the cam to the rods, but this energy is largely returned with minimal losses to the cam on the source side by the compression of the rods during the binding of the target molecule to the receptor, a process that generates mechanical energy. The artificial receptors are best designed for high affinity binding in the presence of a dominant background of quite different molecules.

A computational modeling and simulation effort will be required to create good selective binding site designs for naphthenic acids. “Naphthenic acids” is the name given to an unspecific mixture of a large group of cyclopentyl and cyclohexyl carboxylic acids with molecular weight of 120-700 gm/mole (**Figure 2** and **Figure 4**). The main fraction are carboxylic acids with a carbon backbone of 9-20 carbon atoms. Naphthenic acids are alkyl-substituted cyclic and aliphatic carboxylic acids that are removed from bitumen during the tar sands oil extraction process. Natural naphthenic acids present in Athabasca oil sands are a highly heterogeneous mixture with nearly equal proportions of monocyclic, polycyclic, and acyclic acids with molecular weights primarily between 220-360 gm/mole.[52] The naphthenic acids in oil sands tailings are highly

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[51] Creighton TE. *Proteins*,W. H. Freeman and Company, NY, 1984; https://www.amazon.com/Proteins-Structures-Properties-Thomas-Creighton/dp/0716718200.

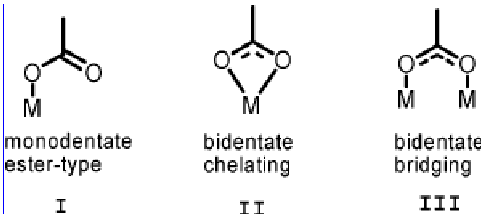
[52] Rogers VV, Liber K, MacKinnon MD. Isolation and characterization of naphthenic acids from Athabasca oil sands tailings pond water. Chemosphere. 2002 Aug;48(5):519-27; https://pubmed.ncbi.nlm.nih.gov/12146630/.

soluble and have an extremely low volatility (i.e., average Henry's constant = 8.56 x 10^{-6} atm-m^3/mole).[53]

While the chemical structures of NAs vary widely, the one thing that all of these disparate molecules have in common is one or more -COOH carboxyl groups. Thus a good binding site for COOH would extract all NAs from the tailings pond water, constituting by far the largest mass of COOH-containing species present in the water, along with a small mass of numerous unrelated carboxylic acid molecules that are undoubtedly present at very low concentrations (e.g., formic acid, acetic acid, oxalic acid, etc.).

How can a carboxyl binding site be designed? Much research remains to be done on this, but we can offer a few ideas to kick off the analysis. For example, one possibility is that carboxylic acids and their derivatives (COOMe, COONa, COCl) are known to form stable covalent bonds with single-crystal metal oxide nanoparticles such as TiO_2, SnO_2, ZrO_2 and ZnO,[54] mainly through carboxylate bidentate bonds (**Figure 7**). Carboxylic acid also binds to indium tin oxide (ITO) primarily via the formation of salt between carboxyl and In.[55] The ITO-COOH bond has a measured scission force of about 0.2 nN with an average binding energy of ~20 kJ/mol, whereas the estimated desorption energy of carboxylic acid on metal oxide is more typically ~70 kJ/mol.[56]

Figure 7. The three main binding modes between a COOH group and a metal oxide surface.



Another, albeit weaker, COOH-binding motif is the oligopeptide carboxylate-binding loop (Gly-Leu-Gly-Phe, aka. "GLGF repeats") that appears in modular protein interaction domains called "PDZ domains" and plays a role in protein targeting and protein complex assembly. Binding is

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[53] Rogers VV, Wickstrom M, Liber K, MacKinnon MD. Acute and subchronic mammalian toxicity of naphthenic acids from oil sands tailings. Toxicol Sci. 2002 Apr;66(2):347-55; http://toxsci.oxfordjournals.org/content/66/2/347.full.pdf.

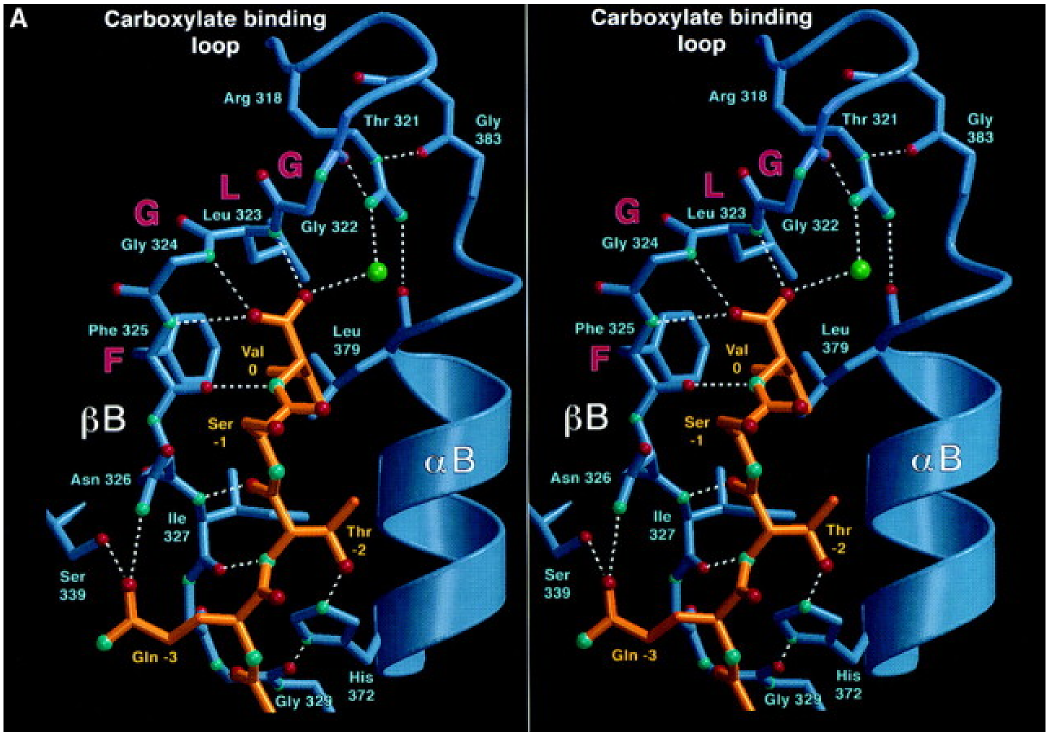
[54] Taratula O, Galoppini E, Wang D, Chu D, Zhang Z, Chen H, Saraf G, Lu Y. Binding studies of molecular linkers to ZnO and MgZnO nanotip films. J Phys Chem B. 2006 Apr 6;110(13):6506-15; https://pubs.acs.org/doi/full/10.1021/jp0570317.

[55] Chen F, Huang Z, Tao N. Forming single molecular junctions between indium tin oxide electrodes. Appl Phys Lett 2007;91:162106; https://web.archive.org/web/20170809083428/http://www.public.asu.edu/~ntao1/Downloads/forming.pdf.

[56] Ulman A. An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly. Academic Press, NY, 1991, First Edition, Part Three, pp. 237-245; https://www.amazon.com/Introduction-Ultrathin-Organic-Films-Langmuir-Blodgett/dp/0127082301.

mediated by hydrogen bonding and is thus much weaker than with metal bonds: "The carboxylate-binding loop (residues 318-324 in **Figure 8**) is designed for this purpose. The residues Gly-Leu-Gly-Phe (residues 322-325) within this loop form a cradle of amide nitrogens that hydrogen bond with the terminal carboxylate group. The glycine residues provide the architectural flexibility necessary to form the cradle. The loop also provides an arginine residue (Arg-318) that interacts with the carboxylate via a highly ordered water molecule. This arrangement would allow a proton to shift from the Arg-318 guanidinium toward the carboxylate anion. In total, the two carboxylate oxygens participate in hydrogen bond formation with three amide nitrogens (from Leu-323, Gly-324, and Phe-325) and the water associated with Arg-318."[57] A simple binding site could also be created using a pendant COOH group, relying on the observation that two R-COOH molecules can form dimers via two hydrogen bonds, but this interaction may be too weak and non-specific to serve as a binding site motif.

Figure 8. Stereo view of the "carboxylate binding loop" peptide-binding site demonstrating protein-peptide interactions via hydrogen bonds (dashed white lines) in PDZ domain, with oxygen atoms shown in red, nitrogen atoms in blue, and the green sphere showing a well-ordered water molecule linking the carboxylate group to Arg-318 (Doyle et al, 1996).



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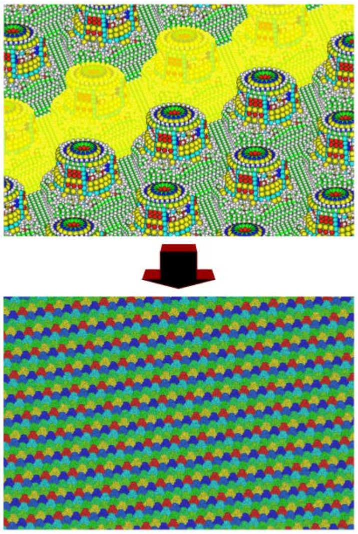
[57] Doyle DA, Lee A, Lewis J, Kim E, Sheng M, MacKinnon R. Crystal structures of a complexed and peptide-free membrane protein-binding domain: molecular basis of peptide recognition by PDZ. Cell. 1996 Jun 28;85(7):1067-76; http://www.sciencedirect.com/science/article/pii/S0092867400813070.

Another potential lead for naphthenic acid binding site designers is the observation that various nanofiltration materials are known to act as supramolecular sorbents for NAs. For example, commercially available granular activated carbon (GAC) with active surface area 795 m^2/gm has a sorption capacity of 100-160 mg NA per gram of material, while finely divided cyclodextrin-based polymeric materials with active surface area 36-657 m^2/gm has a sorption capacity of 20-30 mg NA per gram of material, over the experimental conditions investigated.[58] Carboxylic groups in naphthenic acids from crude oil are also the most strongly adsorbed onto reservoir mineral, clay, and rock surfaces.[59]

It would also be possible, and maybe desirable, to assay many specific classes of NA molecules within the more heterogeneous group of naturally-occurring "naphthenic acids" – and design a separate binding site for each one of them, possibly a dozen or more if necessary to get adequate specificity and binding strength for all members of the NA group. Sorting rotors can be manufactured with adjacent rotors on a membrane having different binding site types, or with multiple binding sites on a single sorting rotor.

4.4 Molecular Filter System Design



In the basic molecular filter design, the sorting rotors are operated as pumps requiring external power input to transport the target molecule in the source fluid, e.g., naphthenic acids (NAs) in tailings pond water (TPW), from a relatively low-concentration environment to a high-concentration collection system when the NAs are present in liquid form at ambient temperature and pressure. Some additional design effort will be required to determine the best method for delivering external power to the rotors. Conceptually, we can envision a nanoscale filtration system that is submerged in the pond water and pumps out (mostly) naphthenic acid molecules selectively, then passes the purified NA fluids up a drainage tube and into a reservoir for convenient external disposal.

In this scheme, the molecular filter is comprised entirely of atomically-precise sorting rotors tightly packed side by side to form a thin sheet of adjacent mechanical devices (images, above). This solid sheet of rotors (ensconced in their mechanically stiff housings) must be of sufficient

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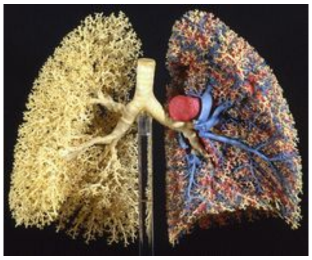
[58] Mohamed MH, Wilson LD, Headley JV, Peru KM. Novel materials for environmental remediation of tailing pond waters containing naphthenic acids. Proc Safety Environ Protection 2008 Jul;86(4): 237-243, http://www.sciencedirect.com/science/article/pii/S0957582008000529.

[59] Zou L, Han B, Yan H, Kasperski KL, Xu Y, Hepler LG. Enthalpy of Adsorption and Isotherms for Adsorption of Naphthenic Acid onto Clays. J Colloid Interface Sci. 1997 Jun 15;190(2):472-5; https://pubmed.ncbi.nlm.nih.gov/9241192/. Madsen L, Lind I. Adsorption of Carboxylic Acids on Reservoir Minerals from Organic and Aqueous Phase. SPE Reservoir Eval & Eng 1998 Feb:47-51; https://onepetro.org/REE/article/1/01/47/170216. Wu Y, Shuler PJ, Blanco M, Tang Y, Goddard WA III. A Study of Wetting Behavior and Surfactant EOR in Carbonates with Model Compounds. SPE 99612, 2006, p. 24; https://onepetro.org/SPEIOR/proceedings-abstract/06IOR/All-06IOR/141157.

thickness to withstand pressure differentials on the order of ~1 atm without tearing. We can envision the sheet of rotors rolled into a seamless tube through which extracted NA molecules may flow for collection downstream. The minimum wall thickness of a cylinder wall of radius R_{cyl} = 1 mm made of diamondoid material with a conservative failure strength of $\sigma_w = 10^{10}$ N/m^2 (~0.2 times the failure strength of diamond) that can withstand a pressure differential of ΔP = 1 atm without bursting is $t_{wall} \geq R_{cyl}\ \Delta P / \sigma_w$ = 10 nm, roughly equivalent to the 14 nm thickness of the exemplar sorting rotor housing described in Section 4.2. These tubes will be short enough in length to avoid significant energy losses due to Poiseuille fluid flow drag.



The exemplar sorting rotor design (**Figure 5**) includes a channel ~5 nm deep (i.e., the "internal reservoir") that can be employed to carry off the chosen fluid molecules once they have been selectively removed from the source fluid in which the molecular filter resides. The most efficient filter system architecture has yet to be determined, but might consist of a multiscale branching collection system roughly analogous to the structure of the human lung (image, left)[60] – an architecture that nature has already optimized for efficient gas exchange and transport – but using continuous unidirectional flow rather than the pulsatile flow commonly employed in biological lungs. The lowest-level branches might possibly be some tens of nanometers in diameter. Filtered fluids would pass to progressively larger branches, finally reaching the uppermost branches measuring on the order of millimeters in diameter, whereupon the NA fluid collects in a drainage tube that empties into a large macroscale collection reservoir for further processing.

In the case of tailings pond water, NAs are initially present at maximum concentrations on the order of 130 mg/L. For purposes of illustration, we conservatively assume that the goal is to reduce the NA content of the TPW from 130 mg/L down to 0.1 mg/L, which is considered to be "below toxic levels" for this contaminant (Section 4.1). This implies that we will be extracting 99.92% of all the NAs present in the TPW.

The energy cost of capturing naphthenic acids and compressing them to liquid form using molecular filters can be crudely approximated using Eqn. (1) (Section 4.2). Assuming a typical density of 920 kg/m^3 for naphthenic acids,[61] a mean molecular weight of 250 gm/mole for NAs, and collection in liquid form on the right side of the sorting rotor shown in **Figure 5**, then c_2 = 2.2 molecules/nm^3 in the liquid state. At the initial 130 mg/L concentration of NAs in TPW, $c_1 = 3.1 \times 10^{-4}$ molecules/nm^3, falling to $c_1 = 2.4 \times 10^{-7}$ molecules/nm^3 by the end of the extraction process when the concentration of NAs in TPW has been reduced to 0.1 mg/L.

Initially at 130 mg/L of NA concentration, c_2/c_1 = 7100 and the rotors will be drawing ΔG = 37 zJ/molecule of NA transported. By the end of the filtration process when there is only 0.1 mg/L of NA concentration, c_2/c_1 = 9,200,000 and the rotors will be drawing ΔG = 66 zJ/molecule of

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[60] "Fractals in the Body," Ewald Weibel, Institute of Anantomy, University of Berne; https://fractalfoundation.org/OFC/OFC-1-2.html.

[61] "70340 - Naphthenic acid, technical: Properties, density," Sigma-Aldrich MSDS, 2013, https://www.sigmaaldrich.com/US/en/product/aldrich/70340.

NA transported. Given that the first 80% of all NA molecules are transported at an energy cost between 37-43 zJ/molecule, and the next 15% are transported between 43-49 zJ/molecule, the average transport cost for all molecules is about 43 zJ/molecule of NA transported. In other words, using a molecular filter collection system we can scrub naphthenic acids out of tailings pond water down to nontoxic levels for an energy cost of about 43 zJ/molecule, or about **\$0.002/kg of NA** assuming an input energy cost of \$0.07/kWh. This provides an output stream from the filters of 90-99%+ pure liquid naphthenic acid concentrate, ready for transport or other disposition.

However, all of this energy cost could be recovered by disposing of the waste NA concentrate via combustion in an electric power plant.[62] Ignoring the metal corrosion problems commonly associated with NAs and focusing on energy alone, combustion of NAs in oxygen yields ~3 x 10^7 J/kg.[63] Assuming a power plant efficiency of 30% (typical for oil-fired plants),[64] then at the commercial price of \$0.07/kWh the electricity generated by burning the naphthenic acids has a market value of **\$0.170/kg of NA** – which is 85 times larger than the \$0.002/kg cost of extracting the NAs from the pond water. In other words, only ~1% of the naphthenic acid concentrate need be burned to provide power for all of the NA extraction processes. Note that the combustion in air of 100% of the 400 x 10^6 kg of naphthenic acids found in all of Alberta's tailings ponds would produce at most 1.5 x 10^9 kg of CO_2, adding a mere 0.00005% to the existing 3.12 x 10^{15} kg of carbon dioxide already present in Earth's atmosphere – a negligible contribution to global warming and itself easily remediated by related nanotechnology solutions.[65]

Alternatively, naphthenic acid concentrate could simply be sold off as a commodity – cheap technical grade naphthenic acid is currently available from one Chinese wholesaler[66] in quantities up to 30,000 kg/month for \$2/kg, which theoretically would value 400 x 10^6 kg of naphthenic acids at \$800M.[67]

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[62] Naphthenic acids burn quite well. For example, NA was the major component (along with palmitic acid) of the gelling agent in the original formulation of napalm; http://en.wikipedia.org/wiki/Napalm. Similarly, a 1975 patent ("Fuel composition with increased octane number," US 3,902,869) describes a method for increasing the octane value of hydrocarbon fuels such as gasoline using a naphthenic acid-based microemulsion; https://patents.google.com/patent/US3902869A/en.

[63] E.g., 2-naphthoic acid ($C_{10}H_7COOH$) has a heat of combustion of 1227.6 kcal/mole (*CRC Handbook of Chemistry and Physics*, 49th Edition, 1968, D-187) and a molecular weight of 172.18 gm/mole, thus yielding 2.98 x 10^7 J/kg when burned in oxygen.

[64] http://en.wikipedia.org/wiki/Electric_power_plant#Cooling_towers.

[65] Freitas RA Jr. The Nanofactory Solution to Global Climate Change: Atmospheric Carbon Capture," IMM Report No. 45, Dec 2015; http://www.imm.org/Reports/rep045.pdf.

[66] https://www.alibaba.com/product-detail/Manufacturer-supply-Technical-grade-Naphthenic-acid_1600609554534.html. Accessed 31 Jan 2023.

[67] To avoid flooding the market and depressing prices, this material might need to be sold over a period of 1-2 decades, given that the annual global market for naphthenic acid is projected as \$67.9M in 2025; https://www.prnewswire.com/news-releases/the-global-naphthenic-acid-market-size-is-projected-to-reach-usd-67-9-million-by-2025--300755466.html.

Further analysis of the details of implementation would be needed to compare the total cost of this process to the costs of conventional remediation technologies. For example, Syncrude (a major Alberta oil sands operator) estimates their cost of remediating Mature Fine Tailings or MFT (the layer of contaminated solid fines just below the water layer in the tailings ponds) at \$1.50-\$4.90/m^3, using centrifuging or other conventional techniques.[68] Assuming the ratio of NAs to all contaminants in MFT is 4% (cf. 3.5%-4.4% in TPW; **Table 1**), and given the density of MFT is 1300 kg/m^3,[69] then the effective industry cost of remediating the NA component of the contamination using conventional means is (\$1.50-\$4.90/m^3) / [(4%) (1300 kg/m^3)] ~ \$0.03-\$0.09/kg of NA -- roughly 15-45 times more expensive than the \$0.002/kg energy cost for molecular filter-based NA remediation of TPW estimated above.

It seems possible that at least the naphthenic acid component of the TPW remediation process could generate positive cash flow, and might even be profitable, using the molecular filter approach.

4.5 Molecular Filter System Performance

One possible deployment configuration for the TPW molecular filtration system is a small surface “filter boat” (**Figure 9A**) that is driven around the pond in random sweeping paths. A multiscale branching collection system having tube walls studded with numerous sorting rotors, with some components perhaps geometrically similar to the fine tentacles of a jellyfish (**Figure 9C**), is tethered to the filter boat and submerged in the pond water, and is either dragged or steered underwater in a manner similar to the actions of an automatic pool sweeper. The underwater sweeper (**Figure 9B**) absorbs molecules of naphthenic acid contaminant selectively and passes the purified NA fluid up a drainage tube to the boat. The fluid collects there in an onboard reservoir, perhaps similar in size and shape to an oil drum.

A tiny fraction of the NA concentrate could be siphoned off and burned in a small electrical combustion generator to provide onboard power for the electrically-powered boat and filter activities, with full net CO_2 capture from the onboard generator effluent as described elsewhere[70] to ensure a zero carbon footprint. (The small onboard generator may require ceramic plumbing to avoid long-term corrosion[71] issues.) When the storage reservoir is full of NA concentrate, the

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[68] “Tailings, A Lasting Oil Sands Legacy,” WWF (World Wildlife Federation) Report, Canada, 2010, p.28; https://web.archive.org/web/20160817143606/http://awsassets.wwf.no/downloads/tailings__a_lasting_oil_sands_legacy___wwf.pdf.

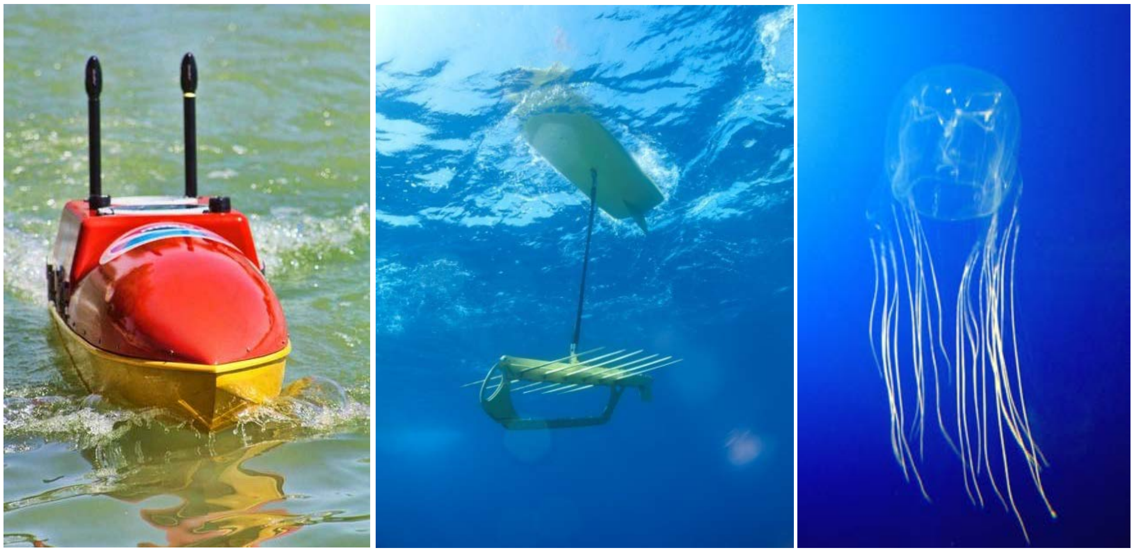
[69] Abusaid A, Pollock G, Fear C, McRoberts E, Wells S. “Update to the Construction of the Suncor Oil Sands Tailings Pond 5 Cover,” Tailings and Mine Waste '11, 6-9 Nov 2011, Fairmont Pacific Rim, Vancouver, Canada; https://open.library.ubc.ca/media/download/pdf/59368/1.0107701/1.

[70] Freitas RA Jr. The Nanofactory Solution to Global Climate Change: Atmospheric Carbon Capture,” IMM Report No. 45, Dec 2015; http://www.imm.org/Reports/rep045.pdf.

[71] Bradley S. Naphthenic Acid Corrosion, the Bane of a Refiner. CorrosionPedia, 19 Aug 2022; https://www.corrosionpedia.com/naphthenic-acid-corrosion-the-bane-of-a-refiner/2/7411.

filter boat docks, transfers the contents of the reservoir to an onshore storage tank for convenient off-site disposition (e.g., electrical power plant fuel, hydrogen generation, sale in the global industrial chemicals market, etc.), then undocks and resumes another cycle of its pond sweeping activities.

Figure 9. Tailings pond "filter boat" configuration: (A) Left: A filter boat[72] *cruises the pond surface, with reservoir tank visible in the bow. (B) Center: Underwater sweeper*[73] *with molecular filters (below in photo) is dragged along by the boat, absorbing contaminants and pumping them up to the reservoir tank in the boat. (C) Right: Portions of the submerged components of the molecular filtration system may resemble the fine strandlike tentacles of the jellyfish.*[74]



Earlier we estimated that the total volume of existing tailings pond water in Alberta is 3 x 10^9 m^3 with a 200 x 10^6 m^3/yr inflow rate, implying an existing toxic contaminant of naphthenic acids of 400 x 10^6 kg with 30 x 10^6 kg/yr of fresh NA contaminants entering the existing tailings ponds throughout all of Alberta (Section 4.1). A target NA removal rate of **200 x 10^6 kg/yr** would complete the remediation of all Albertan tailings ponds in 2.3 years, leaving 170 x 10^6 kg/yr of surplus NA extraction capacity in place to accommodate future expansion of the Alberta oil sands petroleum industry in future years.

We can estimate the total mass of molecular filters required to extract essentially all of the NA contaminants from all tailings ponds water everywhere in Alberta. Assuming each sorting rotor in a molecular filter (including its share of housings and drive systems) can pump 10^2 molecules/sec of NA and has a mass of 100,000 carbon atoms or 2 x 10^{-21} kg (Section 4.2), then the total manufacturable rotor mass requirement for molecular filters able to achieve the target NA removal rate for remediating all tailings pond water everywhere in Alberta is: [(200 x 10^6

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[72] https://www.google.com/search?q=sfl-robotic-boats-hurricane-forecasts-pictures-003.

[73] https://www.fastcompany.com/2680091/friendly-wave-powered-robots-now-working-for-oil-and-gas-companies.

[74] http://en.wikipedia.org/wiki/Box_jellyfish

kg/yr) (2 x 10^{-21} kg/rotor)] / [(100 molecules/rotor-sec) (4.2 x 10^{-23} kg/molecule) (3.14 x 10^{7} sec/yr)] ≈ 300 kg of sorting rotor devices. Some additional mass will be required for rotor power supply mechanisms, tube wall reinforcement, anti-fouling mechanisms, and other support structures, so an allowance of ~3000 kg of atomically-precise filtration system nanocomponents seems adequate for all of Alberta, at a total capital cost of $3-30M given a likely future estimated nanomanufacturing cost of $1K-$10K/kg.[75] The capital cost of the non-nanotech components of the filter boats and the operating costs to run the boats will be additional. The significant initial R&D costs to develop nanofactories (Section 4.6) capable of fabricating molecular filters are also excluded from the above capital cost estimate because this versatile nanomanufacturing technology is likely to be extensively developed for other more financially lucrative applications.[76]

Assuming ~1000 distinct tailings ponds throughout Alberta and allocating one filter boat per pond, then each pond averages ~3 million cubic meters of polluted water volume and each filter boat has a target naphthenic acid removal rate of ~200,000 kg/yr. On such a boat, about 7 cm^3 of NA concentrate will be dribbling from the drainage tube into the onboard reservoir every second, with about 700 watts required to run all of the underwater sorting rotor pumps. The filter boat will unload about one thousand 200-kg drums' worth of naphthenic acid concentrate at the dock each year. That's 3 visits to the dock each day, on average, with up to 1 month per year set aside for downtime and maintenance.

4.6 Manufacture of Molecular Filters using Nanofactories

The nanofactory is a high quality, extremely low cost, and very flexible manufacturing system in which products are built atom by atom – an atomically precise manufacturing system employing controlled molecular assembly. Nanofactories will enable the creation of fundamentally novel products having the intricate complexity and reliability currently found only in biological systems, but operating with greater speed, power, predictability, and, most importantly, entirely under human engineering control.

The principal inputs to a nanofactory may be simple hydrocarbon feedstock molecules such as natural gas or propane, along with water and small supplemental amounts of other simple molecules containing trace atoms of a few additional chemical elements needed to make useful products, such as oxygen, nitrogen, sulfur, or silicon. The nanofactory must also be provided with electrical power and a means for cooling the working unit.

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[75] Freitas RA Jr., Merkle RC. Kinematic Self-Replicating Machines, Landes Bioscience, Georgetown, TX, 2004; http://www.molecularassembler.com/KSRM.htm.

[76] e.g., Freitas RA Jr. Nanomedicine, Volume I: Basic Capabilities, Landes Bioscience, Georgetown, TX, 1999; http://www.nanomedicine.com/NMI.htm. Freitas RA Jr. Nanomedicine, Volume IIA: Biocompatibility, Landes Bioscience, Georgetown, TX, 2003; http://www.nanomedicine.com/NMIIA.htm. Freitas RA Jr. The Alzheimer Protocols: A Nanorobotic Cure for Alzheimer's Disease and Related Neurodegenerative Conditions. IMM Report No. 48, Jun 2016; http://www.imm.org/Reports/rep048.pdf. Merkle RC, Freitas RA Jr., Hogg T, Moore TE, Moses MS, Ryley J. Molecular Mechanical Computing Systems. IMM Report No. 46, Mar 2016; http://www.imm.org/Reports/rep046.pdf.

4.6.1 Mechanosynthesis, Tools, and Nanoparts

At the most primitive level of the manufacturing process, atomically precise objects will be built atom by atom using a process called mechanosynthesis. Mechanosynthesis, involving molecular positional fabrication, is the formation of covalent chemical bonds using precisely applied mechanical forces to build, e.g., organic molecules or diamondoid[77] structures. Mechanosynthesis employs chemical reactions driven by the mechanically precise positioning of extremely reactive chemical species in an ultra-high vacuum environment. Mechanosynthesis may be automated via computer control, enabling programmable molecular positional fabrication.

Atomically precise fabrication involves holding feedstock atoms or molecules, and a growing nanoscale workpiece, in the proper relative positions and orientations so that when they touch they will chemically bond in the desired manner. In this process, a mechanosynthetic tool is brought up to the surface of a workpiece. One or more transfer atoms are added to, or removed from, the workpiece by the tool. Then the tool is withdrawn and recharged. This process is repeated until the workpiece (e.g., a growing nanopart) is completely fabricated to molecular precision with each atom in exactly the right place. The sequence of three frames in the images below shows a "DCB6Ge" tooltip[78] depositing two carbon atoms on a diamond surface. The tooltip is attached to a much larger tool handle structure (not shown) which is attached, in turn, to the macroscale tip of a laboratory-scale scanning probe microscope. Note that the transfer atoms are under positional control at all times to prevent unwanted side reactions from occurring. Side reactions are also prevented using proper reaction design so that the reaction energetics help us avoid undesired pathological intermediate structures.

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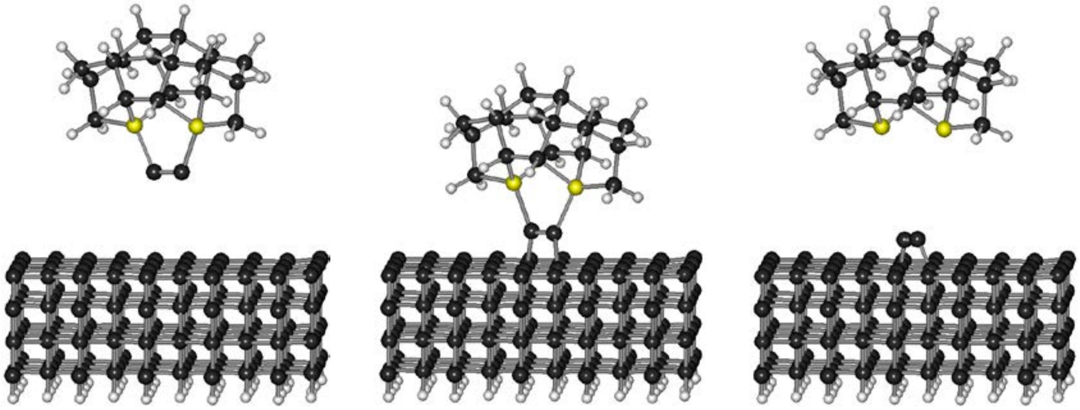
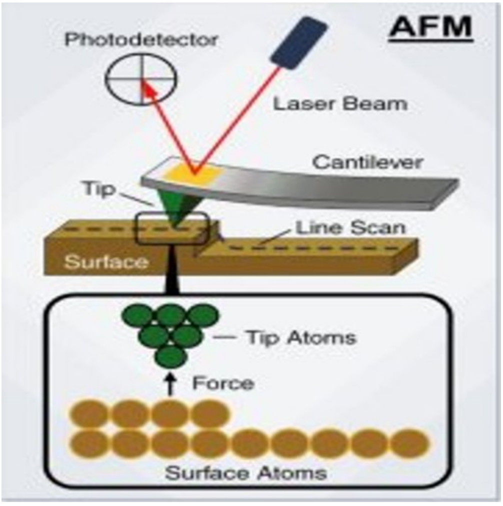
[77] Most diamondoids resemble ceramics. First and foremost, diamondoid materials include pure diamond, the crystalline allotrope of carbon. Among other exceptional properties, diamond has extreme hardness, high thermal conductivity, low frictional coefficient, chemical inertness, a wide electronic bandgap, and is the strongest and stiffest material presently known at ordinary pressures. Diamondoid materials also may include any stiff covalent solid that is similar to diamond in strength, chemical inertness, or other important material properties, and possesses a dense three-dimensional network of bonds. Examples of such materials are carbon nanotubes and fullerenes, several strong covalent ceramics such as silicon carbide, silicon nitride, and boron nitride, and a few very stiff ionic ceramics such as sapphire (monocrystalline aluminum oxide) that can be covalently bonded to pure covalent structures such as diamond. Of course, large pure crystals of diamond are brittle and easily fractured. The intricate molecular structure of a diamondoid nanofactory macroscale product will more closely resemble a complex composite material, not a brittle solid crystal. Such atomically precise products, and the nanofactories that build them, should be extremely durable in normal use.

[78] Merkle RC, Freitas RA Jr. Theoretical analysis of a carbon-carbon dimer placement tool for diamond mechanosynthesis. J Nanosci Nanotechnol. 2003 Aug;3(4):319-24; http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.162.2289&rep=rep1&type=pdf.





Mechanosynthesis has been extensively discussed in the theoretical literature since 1992,[79] was first demonstrated experimentally in 2003[80] and repeatedly in later years,[81] and the first U.S. patent on diamond mechanosynthesis was issued to Freitas in 2010.[82]

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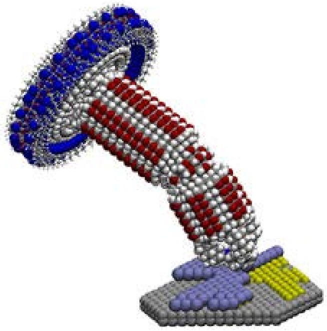
[79] Drexler KE. Nanosystems: Molecular Machinery, Manufacturing, and Computation, John Wiley & Sons, New York, 1992; https://www.amazon.com/dp/0471575186/. Freitas RA Jr., Merkle RC. A minimal toolset for positional diamond mechanosynthesis. J Comput Theor Nanosci. 2008;5:760-861; http://www.molecularassembler.com/Papers/MinToolset.pdf.

[80] Oyabu N, Custance O, Yi I, Sugawara Y, Morita S. Mechanical vertical manipulation of selected single atoms by soft nanoindentation using near contact atomic force microscopy. Phys Rev Lett. 2003 May 2;90(17):176102; https://link.aps.org/pdf/10.1103/PhysRevLett.90.176102.

[81] Oyabu N, Custance O, Abe M, Moritabe S. Mechanical vertical manipulation of single atoms on the Ge(111)-c(2x8) surface by noncontact atomic force microscopy. Abstracts of Seventh International Conference on Non-Contact Atomic Force Microscopy, Seattle, Washington, USA, 12-15 Sep 2004, p. 34;



A scanning probe-based system would enable the fabrication of more precise, more easily rechargeable, and generally much improved mechanosynthetic tools. These more capable tools may include more stable handles of standardized dimensions, such as the rechargeable DCB6Ge dimer placement tool with the more reliable crossbar design (above, left),[83] or tools with more complex handles incorporating moving components (above, right).[84]

Later systems will incorporate more complex components such as the all-hydrocarbon diamond logic rod (below, left), the hydrocarbon bearing (below, center), the diamond universal joint (below, right), and related devices. The end result of this iterative development process will be a mature set of efficient, positionally controlled mechanosynthetic tools that can reliably build atomically precise diamondoid structures – including more mechanosynthetic tools.

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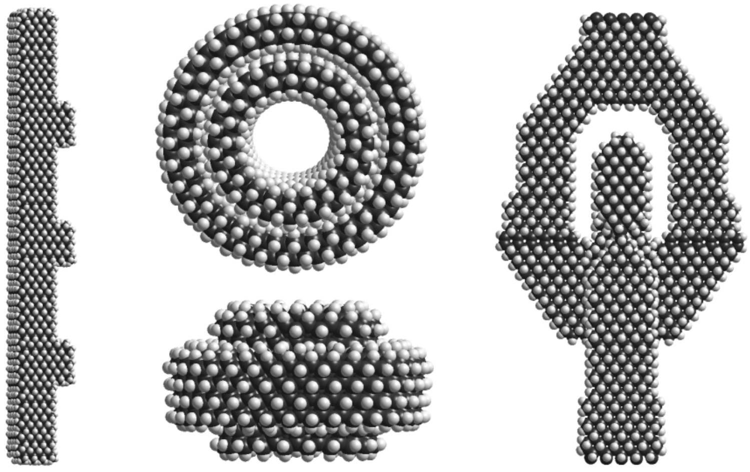
http://www.engr.washington.edu/epp/afm/abstracts/15Oyabu2.pdf. Sugimoto Y, Pou P, Custance O, Jelinek P, Abe M, Perez R, Morita S. Complex patterning by vertical interchange atom manipulation using atomic force microscopy. Science. 2008;322(5900):413-417; http://www.sciencemag.org/cgi/content/full/322/5900/413. Xie Y, Ma L, Zhang P, Cai X, Zhang W, Gan F, Ning XJ, Zhuang J. Reversible atomic modification of nanostructures on surfaces using direction-depended tip-surface interaction with a trimer-apex tip. Appl Phys Lett. 2009 Aug 18;95:073105; https://aip.scitation.org/doi/abs/10.1063/1.3180814. Chen C, Zhang J, Dong G, Shao H, Ning BY, Zhao L, Ning XJ, Zhuang J. Site-selective substitutional doping with atomic precision on stepped Al(111) surface by single-atom manipulation. Nanoscale Res Lett. 2014 May 13;9(1):235; https://core.ac.uk/download/pdf/81056816.pdf. Kawai S, Foster AS, Canova FF, Onodera H, Kitamura S, Meyer E. Atom manipulation on an insulating surface at room temperature. Nat Commun. 2014 Jul 15;5:4403; http://viesti.physics.aalto.fi/~asf/publications/Nature%20Comm%20manip.pdf. Bamidele J, Lee SH, Kinoshita Y, Turanský R, Naitoh Y, Li YJ, Sugawara Y, Štich I, Kantorovich L. Vertical atomic manipulation with dynamic atomic-force microscopy without tip change via a multi-step mechanism. Nat Commun. 2014 Jul 31;5:4476; https://www.nature.com/articles/ncomms5476. Huff TR, Labidi H, Rashidi M, Koleini M, Achal R, Salomons MH, Wolkow RA. Atomic White-Out: Enabling Atomic Circuitry through Mechanically Induced Bonding of Single Hydrogen Atoms to a Silicon Surface. ACS Nano. 2017 Sep 26;11(9):8636-8642; https://arxiv.org/pdf/1706.05287.

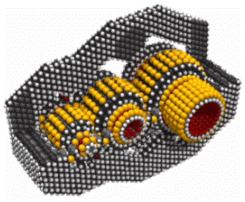
[82] Freitas RA Jr. Simple Tool for Positional Diamond Mechanosynthesis, and its Method of Manufacture. U.S. Patent 7,687,146, 30 Mar 2010; https://patents.google.com/patent/US7687146B1/en.

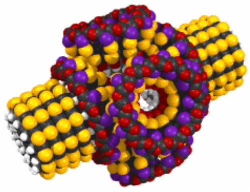
[83] Peng J, Freitas RA Jr., Merkle RC, Von Ehr JR, Randall JN, Skidmore GD. Theoretical analysis of diamond mechanosynthesis. Part III. Positional C_2 deposition on diamond C(110) surface using Si/Ge/Sn-based dimer placement tools. J Comput Theor Nanosci. 2006 Feb;3(1):28-41; http://www.MolecularAssembler.com/Papers/JCTNPengFeb06.pdf.

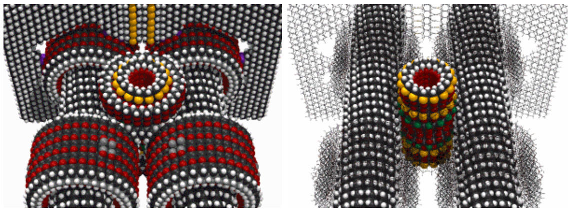
[84] Image and design courtesy of Damian G. Allis.

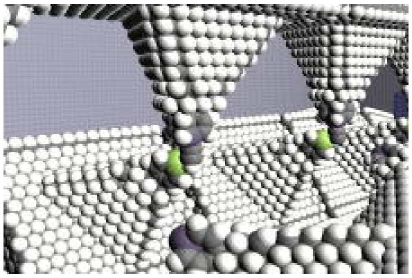


Once mechanosynthetic tooltips are developed for a few additional element types, a still wider variety of nanomachines can be fabricated incorporating atoms other than hydrogen, carbon and germanium (e.g., silicon, oxygen, nitrogen, and sulfur). Examples of these more varied diamondoid nanomachines include the speed reduction gear (below, left), in which the train of gears reduces the speed from the high-speed one on the left to the half-speed one on the right, and the differential gear (below, center) that smoothly converts mechanical rotation in one direction into mechanical rotation in the opposite direction. The largest publically reported molecular machine model that has been simulated using molecular dynamics is the worm drive assembly (below, pair at right), consisting of 11 separate components and over 25,000 atoms. The two tubular worm gears progress in opposite directions, converting rotary into linear motion.





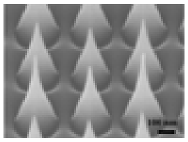




Using computer-automated tooltips performing positionally-controlled mechanosynthesis in lengthy programmed sequences of reaction steps, we will be able to fabricate simple diamondoid nanomechanical parts such as bearings, gears, struts, springs, logic rods and casings, to atomic precision. Early tools will rapidly progress from single tools manipulated by laboratory scanning-probe-like mechanisms, to more complex multitip tools and jigs which the simple tools could initially fabricate, one at a time. In a factory production line (right), individual mechanosynthetic tooltips may be affixed to rigid moving support structures and guided through repeated contact events with workpieces, recharging stations, and other similarly-affixed opposable tooltips. These "molecular mills" can then perform repetitive fabrication steps using simple, efficient mechanisms in the manner of a production line. Such production lines can, in principle, be operated at very high speeds – with positionally constrained mechanosynthetic encounters possibly occurring at up to megahertz frequencies.

4.6.2 Nanofactories

The ultimate goal of molecular nanotechnology is to develop a manufacturing technology able to inexpensively manufacture most arrangements of atoms that can be specified in molecular detail – including complex arrangements involving millions or billions of atoms per product object. This will provide the ultimate manufacturing technology in terms of precision, flexibility, and low cost. To be practical, a nanofactory must also be able to assemble very large numbers of identical atomically precise nano- or microstructures very quickly. Two central technical objectives thus form the core of our current strategy for atomically precise manufacturing: (1) programmable positional assembly including fabrication of diamondoid structures using molecular feedstock, as discussed above, and (2) massive parallelization of all fabrication and assembly processes, briefly discussed below.



Conceptually, nanofactory systems capable of massively parallel fabrication[85] might employ, at the lowest level, large arrays of mechanosynthesis-enabled scanning probe tips all building similar diamondoid product structures in unison, superficially similar to the highly-uniform, well-aligned ultrasharp silicon nanotips (image, left) fabricated at a surface density of ~10^9 tips/cm^2 in 2012.[86]

Analogous approaches are found in present-day larger-scale systems. For example, simple mechanical ciliary arrays consisting of 10,000 independent microactuators on a 1 cm^2 chip have been made at the Cornell National Nanofabrication Laboratory for microscale parts transport applications, and similarly at IBM for mechanical data storage applications.[87] Active probe arrays of 10,000 independently-actuated microscope tips were developed by Mirkin's group at

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[85] Freitas RA Jr., Merkle RC. Kinematic Self-Replicating Machines, Landes Bioscience, Georgetown, TX, 2004; Section 5.7, pp. 182-184; http://www.MolecularAssembler.com/KSRM/5.7.htm.

[86] Wu CC, Ou KL, Tseng CL. Fabrication and characterization of well-aligned and ultra-sharp silicon nanotip array. Nanoscale Res Lett. 2012 Feb 13;7(1):120; http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3292956/.

[87] "1000 Tips for Ultrahigh-Density Data Storage," IBM News, Zurich Research Lab, 11 Oct 1999, http://www.zurich.ibm.com/news/99/millipede.html. IBM Research: Millipede, http://domino.research.ibm.com/Comm/bios.nsf/pages/millipede.html. Vettiger P, Cross G, Despont M, Drechsler U, Durig U, Gotsmann B, Haeberle W, Lantz M, Rothuizen H, Stutz R, Binnig G. The Millipede – nanotechnology entering data storage. Technical Report, IBM Zurich Research Lab; http://domino.research.ibm.com/Comm/bios.nsf/pages/millipede.html/$FILE/pv7201-preprint.pdf; also published in: Vettiger P, Cross G, Despont M, Drechsler U, Durig U, Gotsmann B, Haeberle W, Lantz M, Rothuizen H, Stutz R, Binnig G. The Millipede – nanotechnology entering data storage. IEEE Trans. Nanotechnol. 2002 Mar;1(1):39-55; http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.159.7003&rep=rep1&type=pdf.

Northwestern University for dip-pen nanolithography using DNA-based “ink”.[88] Almost any desired 2D shape can be drawn using 10 tips in concert. A million-tip DPN array was fabricated by the Micro Nano Technology Research Group at the University of Illinois,[89] and another microcantilever array manufactured by Protiveris Corp. had millions of interdigitated cantilevers on a single chip.[90] Martel’s group at École Polytechnique Montreal has investigated using fleets of independently mobile wireless instrumented microrobot manipulators called NanoWalkers to collectively form a nanofactory system that might be used for positional manufacturing operations.[91] Zyvex Corp. (http://www.zyvexlabs.com) received a $25 million, five-year, National Institute of Standards and Technology (NIST) contract to develop prototype microscale assemblers using microelectromechanical systems.[92]

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[88] Hong S, Mirkin CA. A nanoplotter with both parallel and serial writing capabilities. Science 2000 Jun 9;288:1808-11; http://www.nanotechnology.northwestern.edu/press/Science%20.Vol288.9june2000.pdf. Zhang M, Bullen D, Ryu KS, Liu C, Hong S, Chung S, Mirkin C. Passive and active probes for dip pen nanolithography. First IEEE Conference on Nanotechnology, 28-30 Oct 2001, Maui, HI; http://mass.micro.uiuc.edu/publications/papers/64.pdf. Bullen D, Zhang M, Liu C. Thermal-mechanical optimization of thermally actuated cantilever arrays. Smart Electronics, MEMS, and Nanotechnology Conference (4700), SPIE’s 9th Annual International Symposium on Smart Structures and Materials, 17-21 Mar 2002, San Diego, CA; http://mass.micro.uiuc.edu/publications/papers/70.pdf. Zhang M, Bullen D, Chung SW, Hong S, Ryu KS, Fan Z, Mirkin CA, Liu C. A MEMS nanoplotter with high-density parallel dip-pen nanolithography probe arrays. Nanotechnology 2002 Apr;13:212-217; http://mass.micro.uiuc.edu/publications/papers/72.pdf. Wang X, Bullen D, Zou J, Ryu K, Liu C, Chung SW, Mirkin CA. Linear probe arrays for dip-pen nanolithography. Intl. Conf. on Micro & Nano Systems (ICMNS 2002), 11-14 Aug 2002, Kunming, China; http://mass.micro.uiuc.edu/publications/papers/74.pdf. Bullen D, Chung S, Wang X, Zou J, Liu C, Mirkin C. Development of parallel dip pen nanolithography probe arrays for high throughput nanolithography. (Invited) Symposium LL: Rapid Prototyping Technologies, Materials Research Society Fall Meeting, Boston, MA, Proceedings of the MRS, Vol. 758, 2-6 Dec 2002; http://mass.micro.uiuc.edu/publications/papers/84.pdf. Bullen D, Wang X, Zou J, Hong S, Chung S, Ryu K, Fan Z, Mirkin C, Liu C. Micromachined arrayed dip pen nanolithography probes for sub-100 nm direct chemistry patterning. Proc. 16th IEEE International Micro Electro Mechanical Systems Conference, MEMS 2003, Kyoto, Japan, 19-23 Jan 2003; http://mass.micro.uiuc.edu/publications/papers/86.pdf. Zou J, Bullen D, Wang X, Liu C, Mirkin CA. Conductivity-based contact sensing for probe arrays in dip-pen nanolithography. Appl Phys Lett. 2003 Jul 21;83(3):581-583; https://pdfs.semanticscholar.org/a3cd/c5436f893274a9a6ad81485ae8d54c0ac427.pdf.

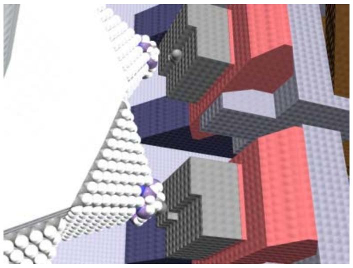
[89] “MNTR Research Focus Slide Show: Passive Parallel DPN Array,” 2006, http://mass.micro.uiuc.edu/research/current/nanolithography/2006-focus-intro/slide11.html.

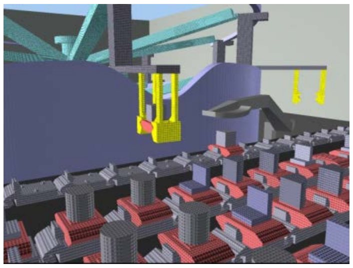
[90] “Microcantilever Arrays,” Protiveris Corp., 2003; http://www.protiveris.com/cantilever_tech/microcantileverarrays.html.

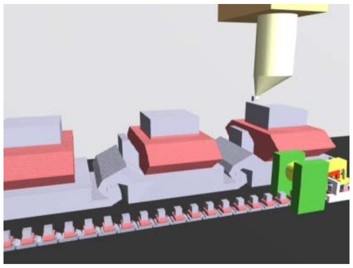
[91] Martel S, Hunter I. Nanofactories based on a fleet of scientific instruments configured as miniature autonomous robots. Proc. 3rd Intl Workshop on Microfactories; 16-18 Sep 2002; Minneapolis MN, pp. 97-100.

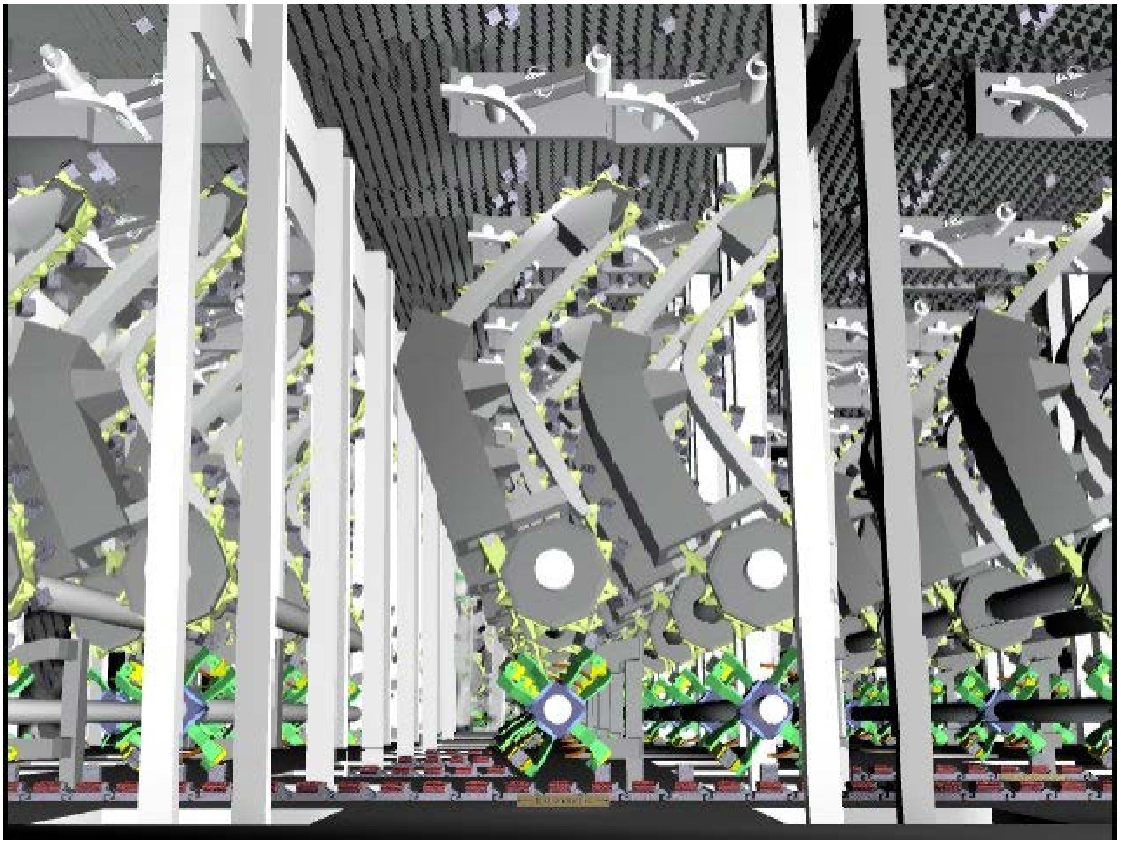
[92] Freitas RA Jr., Merkle RC. Kinematic Self-Replicating Machines. Landes Bioscience, Georgetown, TX, 2004, Section 4.20 “Zyvex Microscale Assemblers”; http://www.MolecularAssembler.com/KSRM/4.20.htm.

At the end of a carefully focused development program, analogous work could lead to the design and fabrication of numerous production lines comprising a nanofactory, both for diamondoid mechanosynthesis and for component assembly operations. Ultimately, atomically precise macroscale products – including components of additional nanofactories – could be manufactured in desktop nanofactories efficiently designed for this purpose. The nanofactory system will include a progression of fabrication and assembly lines at several different physical scales, as conceptually illustrated in the images below which show the assembly of nanoparts into larger components and product structures using mechanical manipulators at various size scales (e.g., roughly 0.01 µm, 0.1 µm, 1 µm, and 10 µm in the four images below) on interconnected production lines inside a diamondoid nanofactory.[93]









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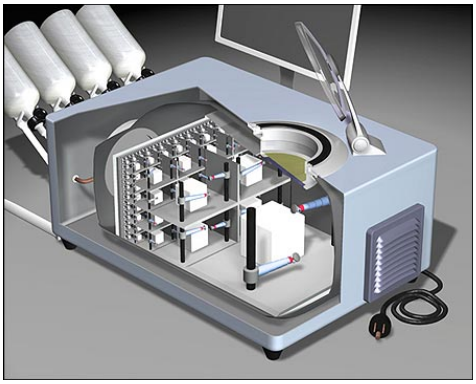
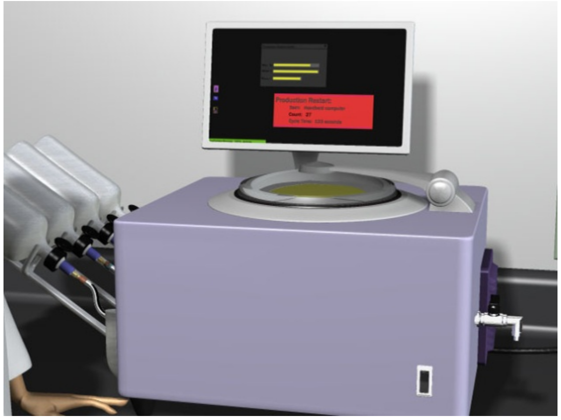
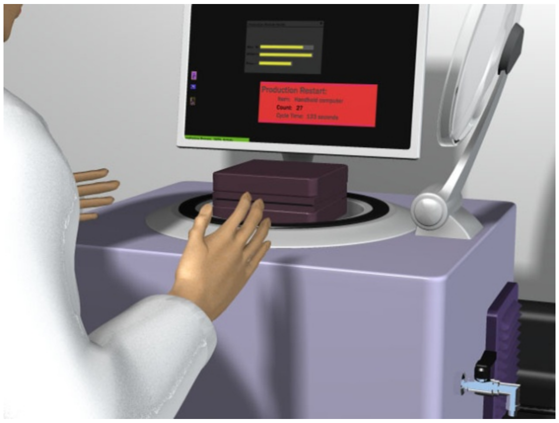
[93] https://web.archive.org/web/20110716171312/http://www.lizardfire.com/html_nano/themovies.html.



In one conceivable design (right), at the smallest scale, molecular mills could manipulate individual molecules to fabricate successively larger submicron-scale building blocks. These would be passed to larger block assemblers that assemble still larger microblocks, which would themselves be passed to even larger product assemblers that put together the final product. The microblocks would be placed in a specific pattern and sequence following construction blueprints created using modern "Design for Assembly" and "Design for Manufacturability" (DFM) philosophies. As plane after plane is completed, the product extrudes outward through the surface of the nanofactory output platform. Of course, these images represent idealized conceptualizations of just one possible nanofactory architecture. Other architectural approaches may readily be conceived.[94]

As shown in the conceptual image of the desktop nanofactory below,[95] the finished product in this example is a billion-CPU laptop supercomputer,[96] built to molecular precision all the way down to its constituent atoms. The laptop supercomputer product is emerging from the output port at the top of the nanofactory at the end of a production cycle.





Rather than a laptop supercomputer, the nanofactory can be used to build molecular filters of modular design. The nanofactory for filters would likely be a specialized type of limited-use nanofactory optimized for the fabrication and assembly of a small number of nanorobotic

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[94] Freitas RA Jr., Merkle RC. Kinematic Self-Replicating Machines, Landes Bioscience, Georgetown, TX, 2004; Section 4; http://www.molecularassembler.com/KSRM/4.htm.

[95] https://web.archive.org/web/20110716171312/http://www.lizardfire.com/html_nano/themovies.html.

[96] Merkle RC, Freitas RA Jr., Hogg T, Moore TE, Moses MS, Ryley J. Molecular mechanical computing systems. IMM Report No. 46, 29 March 2016; http://www.imm.org/Reports/rep046.pdf.

modules that could be snapped together to make entire molecular filters at a ~1 kg/hour initial production rate.[97]

The end result of a dedicated nanofactory development program would be the creation of extremely clean, efficient, and inexpensive manufacturing systems capable of producing macroscale quantities of atomically precise products. Nanofactories will make possible the manufacture of covalently-bonded products (e.g. nanomachines) having the intricate complexity and reliability of biological systems combined with the greater speed, power, and predictability of engineered mechanical systems.

4.7 Advanced Remediation Strategies Using Nanorobots

The nanofiltration strategy described above seems fairly straightforward to implement using early-generation nanofactories and nanorobotic systems. Later-generation systems may provide quicker and more efficient results.

Consider an advanced remediation strategy in which large numbers of free-swimming nanorobots, manufactured in nanofactories, are released into the tailings pond lakes in a more-or-less even distribution. The nanorobots swim through the polluted water, absorbing naphthenic acids (NAs) and metabolizing these oxyhydrocarbon molecules into carbon dioxide and water inside an onboard processing plant, using free ambient oxygen. The nanorobots can gain regular access to atmospheric oxygen by using buoyancy control[98] or active swimming[99] to rise to the surface to collect oxygen from the air, then dive back into the depths of the lake to collect the naphthenic acids to be consumed. Once all the NAs have been extracted and chemically broken down in about 1 month of activity, the robots can establish positive buoyancy and float to the surface, allowing them to collect as a film on the surface of the lake to be removed in a single pass by a skimmer, and recycled. Alternatively, in a crude analogy to a honeybee returning to its hive, end-of-mission nanorobots could be designed to swim short distances to collection boxes emitting acoustic homing signals, which the robots enter and become inert, again allowing easy capture and recycling.

Performance numbers are easy to estimate and appear plausible. Specifically, a 2×10^{-21} kg molecular filter can remove 4.15×10^{-23} kg/sec of NAs (Section 4.5), a specific removal rate of

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[97] Drexler KE. Nanosystems: Molecular Machinery, Manufacturing, and Computation. John Wiley & Sons, New York, 1992, Section 14.4.3; https://www.amazon.com/dp/0471575186/.

[98] Freitas RA Jr. Exploratory design in medical nanotechnology: a mechanical artificial red cell. Artif Cells Blood Substit Immobil Biotechnol. 1998 Jul;26(4):411-30; https://www.tandfonline.com/doi/pdf/10.3109/10731199809117682. A longer version of this paper appears at: https://web.archive.org/web/20100420085137/http://www.foresight.org/Nanomedicine/Respirocytes.html. See also: Freitas RA Jr. Cryostasis Revival, Alcor Life Extension Foundation, Scottsdale AZ, 2022; Appendix M. Nanorobot Extraction from the Body; https://www.alcor.org/cryostasis-revival/.

[99] Freitas RA Jr. Nanomedicine, Volume I: Basic Capabilities. Landes Bioscience, Georgetown, TX, 1999, Section 9.4.2, “Sanguinatation”; http://www.nanomedicine.com/NMI/9.4.2.htm.

0.0208 kg_{NA}/kg_{filter}-sec, so extracting 400 x 10^6 kg of NAs (Section 4.1) from all Albertan tailings ponds requires 1.93 x 10^{10} kg_{filter}-sec to accomplish, or ~7400 kg of filters to accomplish the mission in ~1 month (2.62 x 10^6 sec). If the filters comprise ~10% of total nanorobot mass, then the mission requires **~74,000 kg of nanorobots**.

Waste heat is generated by the nanorobots from two sources. First, extracting 400 x 10^6 kg (9.64 x 10^{32} molecules) of naphthenic acids of average molecular weight 250 gm/mole (Section 4.4) from pond water at an average energy cost of 43 zJ/molecule (Section 4.4) requires an energy expenditure of 4.15 x 10^{13} J. Second, complete combustion of 400 x 10^6 kg of NAs in ambient oxygen releases ~3 x 10^7 J/kg (Section 4.4) or 1.2 x 10^{16} J of heat, which is ~300 times more than the filtration energy cost, giving a total energy release of 1.204 x 10^{16} J. This will produce an **average water temperature rise of ~ 1 °C** if this energy is released into 3 x 10^9 m^3 (Section 4.1) of tailings pond water at 20 °C having a volumetric heat capacity of 4.19 x 10^6 J/m^3-K. Metabolizing 400 x 10^6 kg of NA from all oil sands tailing ponds in Alberta would generate ~1500 x 10^6 kg of CO_2 (Section 4.4), which, when released into the air, would **increase the global CO_2 concentration by only 0.0002 ppm**, compared to a typical annual increase of ~2 ppm/yr in present circumstances.[100]

Metabolization of NA molecules can provide all necessary onboard power for the nanorobots. Disassembly of diamondoid materials is described in an early book chapter[101] (note that tricyclic diamondoid acids are an interesting class of polycyclic naphthenic acids; Section 2 and **Figure 4**), and onboard molecular breakdown of various carbon-rich chemical substances is described in the microbivore nanorobot paper.[102]

The entire nanorobot population emits 4.60 x 10^9 W throughout the 1-month mission, giving an onboard nanorobot power density of 62,100 W/kg. This is only twice the estimated maximum power density of 31,400 W/kg (i.e., 382.66 pW / 12.2 pg) for the microbivore,[103] a medical nanorobot intended for use inside a sensitive human body. Early analyses suggested that power densities on the order of 0.1-1 MW/kg are reasonable upper bounds in medical nanorobot power scaling.[104] A remediation nanorobot of 1 µm diameter (5.24 x 10^{-19} m^3) and mean density 2000 kg/m^3 would generate a modest 65 pW of waste heat.

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[100] https://en.wikipedia.org/wiki/Carbon_dioxide_in_Earth%27s_atmosphere.

[101] Freitas RA Jr. Nanomedicine, Volume I: Basic Capabilities. Landes Bioscience, Georgetown, TX, 1999, Section 9.3.5.3, "Diamondoid Decomposition"; http://www.nanomedicine.com/NMI/9.3.5.3.htm.

[102] Microbivore paper, digestion chamber Section Freitas RA Jr. Microbivores: Artificial mechanical phagocytes using digest and discharge protocol. J Evol Technol 2005;14:1-52; Section 3.1.4 Digestion Chamber and Exhaust Port; http://www.jetpress.org/volume14/freitas.html.

[103] Freitas RA Jr. Microbivores: Artificial mechanical phagocytes using digest and discharge protocol. J Evol Technol 2005;14:1-52; Table 5. Microbivore Baseline Design: External Surface Area, Internal Volume, and Maximum Power Allocations; http://www.jetpress.org/volume14/freitas.html.

[104] Freitas RA Jr. Nanomedicine, Volume I: Basic Capabilities. Landes Bioscience, Georgetown, TX, 1999, Section 6.5.3, "Nanorobot Power Scaling"; http://www.nanomedicine.com/NMI/6.5.3.htm.

5. Molecular Filtration of Other Contaminants and Sources

The discussion so far has mainly described a method for the removal of a single contaminant, naphthenic acid, from tailings pond water. In this Section, we briefly describe three related targets: removal of non-NA contaminants from tailings pond water (Section 5.1), removal of contaminants from Mature Fine Tails residing beneath the water level in the tailings ponds (Section 5.2), and removal of contaminants from process water at the tar oil mine site, thus eliminating the inflow of fresh contaminants into the tailings ponds (Section 5.3). The discussions here are conceptual summaries only, but suffice to make the point that more extensive cleanup should be feasible using the techniques previously outlined in Section 4.

5.1 Clearing Non-Naphthenic Acid Pollutants from TPW

The methods previously described for the removal of a single contaminant, naphthenic acids, from tailings pond water can also be applied to other contaminants in the TPW. **Table 2** lists the major pollutants present in TPW, including their maximum normal concentration and the most restrictive hypothetical treatment objectives for environmental discharge of oil sands process water as determined by Canadian Environmental Quality Guidelines, the Alberta Environmental Protection and Enhancement Act, the Government of British Columbia, and the United States Environmental Protection Agency, as collected and summarized in 2008 by Allen.[105] Of course, not all of the pollutants listed are present at maximum concentrations in all tailings ponds, so simultaneously pursuing all the remediation objectives in **Table 2** should be regarded as a very conservative “worst-case” scenario.

A set of molecular binding sites specific to each of the 20 pollutants listed in **Table 2** will have to be designed, analogous to the effort described in Section 4.3 for naphthenic acids. Many of the pollutants probably need only a single binding site type, but, as was the case for the naphthenic acids, a few pollutants such as phenols and polycyclic aromatic hydrocarbons (PAHs) include multiple molecular species which may require the design of several binding site types to catch all of the species present in TPW. A larger catch-all category is total dissolved solids (TDS), which could require dozens of different binding sites depending upon which soluble solids are determined by chemical assay to be present and requiring remediation. Nanomachine filtration systems can match or exceed the abilities of biological hyperaccumulators[106] – plant species that preferentially concentrate a variety of heavy metal contaminants[107] up to 100-1000 times ambient levels. Finally, the “oil and grease” component (probably mainly bitumen) will require additional analysis of molecular targets and binding site possibilities that is beyond the scope of this paper.

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[105] Allen EW. Process water treatment in Canada’s oil sands industry: I. Target pollutants and treatment objectives. J Environ Eng Sci 2008;7:123-138, Table 5; http://documents.techno-science.ca/documents/tailingsallenoilsandswatermanagement.pdf.

[106] https://en.wikipedia.org/wiki/Hyperaccumulator.

[107] https://en.wikipedia.org/wiki/List_of_hyperaccumulators.

Table 2 also gives crude estimates for the range of rotor speeds and energy cost per pollutant molecule for sortation, making the simplifying assumptions that pollutants have a “typical” density of ~1000 kg/m^3 and a “typical” molecular weight of ~100 gm/mole. The sorting rotor energy cost per kilogram of pollutant can then be calculated assuming the average input energy cost of $0.07/kWh for industrial electricity. The number of sorting rotors required for each pollutant to remediate all Alberta ponds to target levels in 2 years can be calculated by very conservatively assuming the lowest indicated rotor speed and taking the net rotor energy cost per molecule as the geometric average of the low and high figures for the energy cost of sortation. Both of these results are tabulated in the two rightmost columns of **Table 2**.

Table 2. Molecular Filtration of All Major Pollutants in Alberta Tailings Pond Water

Pollutant	Max. TPW Concentration (mg/L)	Environmental Guideline (mg/L)	Est. Range of Rotor Sort Speeds (molecule/sec)	Est. Range, Energy Cost of Sortation (zJ/molecule)	Est. Pumping Cost ($/kg)	Est. Mass of Rotors for all Alberta Ponds (kg)
TDS[1]	2221	1340	10^6	25-27	$0.0030	1
Bicarbonate	950	500	10^5	29-31	$0.0035	3
Chloride	540	150	10^5	31-36	$0.0039	2
Sulfate	290	50	10^5-10^4	34-41	$0.0044	14
Oil and grease	92	5	10^4-10^3	39-51	$0.0052	50
Naphthenic acid	70	0.1	10^4-10^2	40-67	$0.0060	402
Ammonia	14	0.8	10^4-10^2	46-58	$0.0060	76
Benzene	6.3	0.37	10^3-10^2	50-61	$0.0065	34
Zinc	3.2	0.12	10^3-10^2	52-66	$0.0068	18
Iron	3	0.3	10^3-10^2	53-62	$0.0067	16
Toluene	3	0.002	10^3-10^0	53-83	$0.0077	1725
Nickel	2.8	0.052	10^3-10^1	53-69	$0.0071	158
Chromium	2	0.074	10^3-10^1	54-68	$0.0071	111
Phenols	1.5	0.001	10^3-10^0	56-86	$0.0081	863
Copper	0.9	0.002	10^2-10^0	58-83	$0.0081	517
Cyanide	0.5	0.005	10^2-10^0	60-79	$0.0080	285
Aluminum	0.5	0.1	10^2	60-67	$0.0074	2
Lead	0.19	0.0025	10^2-10^0	64-82	$0.0085	108
Arsenic	0.015	0.005	10^1-10^0	75-79	$0.0090	6
PAHs[2]	0.01	0.00001	10^1-10^{-2}	76-105	$0.0104	575
Totals	**4200.915**	**2046.93351**				**4966**

[1] TDS = total dissolved solids
[2] PAHs = polycyclic aromatic hydrocarbons

Several conclusions may be drawn from the data in this table.

First, the proposed molecular filtration scenario would remove ~2154 mg/L of pollutants from all 3 x 10^9 m^3 of TPW in Alberta tailings ponds, a total extraction of 6.5 x 10^9 kg of pollutants at an average energy cost of $0.007/kg or $45 million assuming the average input energy cost of $0.07/kWh for industrial electricity. However, this scenario also envisions the extraction of 210 million kg of naphthenic acid, which can generate $0.170/kg of NAs in surplus electricity from a combustion generator (Section 4.4) or a total of $36 million worth of electricity, potentially offsetting much of the energy input costs. It is true that the filter boats will consume some of this surplus energy if they are not solar powered, but it is also true that the benzene, toluene, phenols, PAHs, and "oil and grease" can in principle provide additional combustible fuel for surplus electrical energy generation.

Second, switching to the less stringent EPA guideline for toluene in drinking water (1.3 mg/L) and the less stringent EPEA (Alberta environmental law) guideline for phenols (1 mg/L) cuts the rotor mass requirement in half to 2380 kg, down from 4966 kg. Other modest relaxations of cleanup requirements may provide additional significant reductions in the mass of molecular filters that must be manufactured, and this total mass will likely be further reduced because most ponds will have lower concentrations of at least some pollutants than the maximum concentration of pollutants at any pond in Alberta (as assumed here).

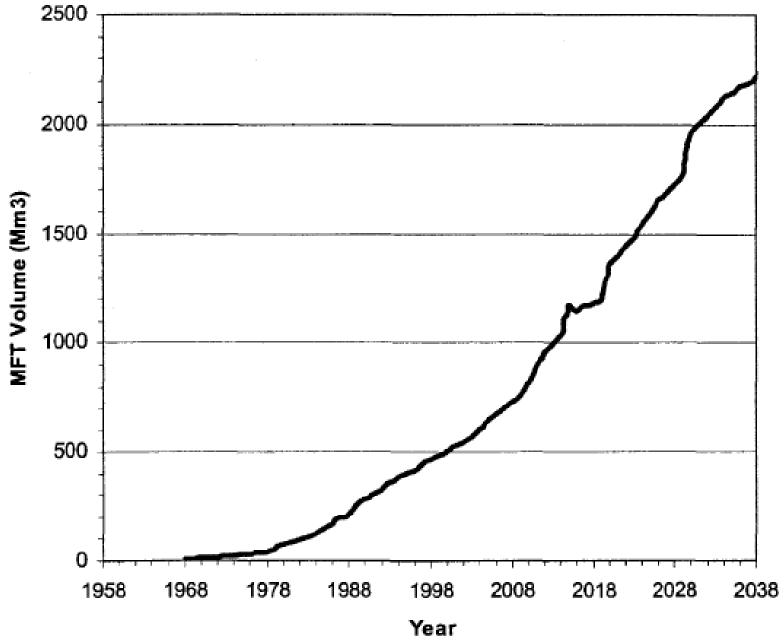
Third, and in summary: A total nanomanufactured mass somewhere in the vicinity of **1-10 tonnes of molecular filter sorting rotors should suffice to remove all major contaminants from all tailings pond water throughout all of Alberta**, assuming an operational remediation time period of about 2 years.

The economics and methods of final disposal of contaminant concentrates will vary depending on the particular pollutant chemicals that are targeted. This topic is worthy of further study but is beyond the scope of this paper.

5.2 Clearing Pollutants from Mature Fine Tailings

Similar techniques of molecular filtration can be employed to remove naphthenic acids and other contaminant chemicals from the Mature Fine Tailings (MFT), but this will require further study of the specifics because MFT material becomes significantly compacted with depth in the pond. It is estimated that by 2014 there will be 1 x 10^9 m^3 of MFT in Albertan tailings ponds, rising to 2 x 10^9 m^3 of MFT by 2034 (**Figure 10**).[108] Existing conventional technologies for treating MFT are generally of five types: physical/mechanical processes, natural processes, chemical/biological amendments, mixtures/co-disposal, and permanent storage. It is important to note that molecular filtration (e.g., using sorting rotors) is not included on this list, and is an approach that has not previously been considered by the industry.

Figure 10. Current and predicted MFT volume in Fort McMurray[109]



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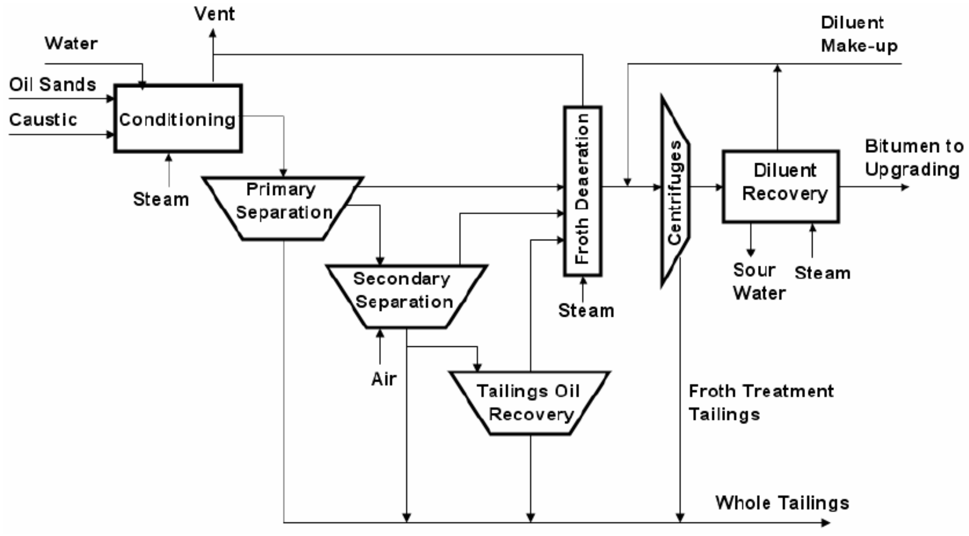
[108] BGC Engineering Inc., Oil Sands Tailings Technology Review, Oil Sands Research and Information Network, University of Alberta, School of Energy and the Environment, Edmonton, Alberta, OSRIN Report No. TR-1, July 2010, http://era.library.ualberta.ca/public/datastream/get/uuid:f0274a41-8cea-4b10-be80-79f497d8711e/DS1

[109] Houlihan R, Mian H. Oil Sand Tailings: Regulatory Perspective. In Sego D, ed., Proceedings of the First International Oil Sand Tailing Conference, Edmonton, Alberta, Canada, 7-10 Dec 2008.

A brief review of the source of MFT is useful. A schematic flow diagram of the oil sands process, from open pit to final product is shown in **Figure 11**. The initial extraction process uses a combination of hot water, steam and caustic to separate bitumen from oil sands and the process is called the Clark Hot Water Extraction Process (CHWE). The tailings, mainly from primary separation and froth treatment vessels with insignificant quantities of tailings coming from upgrading units, are transported to tailing management area through pipelines. The tailings are pumped into large tailing ponds where the coarse solids settle out to form dykes and beaches while much of the fines and residual bitumen are carried out into the ponds as a thin slurry stream with approximately 8% solids. Upon discharge, segregation between sand and fine occurs, resulting in coarse solids settling adjacent to the discharge point while fines are carried further into the pond.

Figure 11. Generalized scheme of Clark Hot Water Extraction Process[110]



Over time, three zones develop in the tailing ponds (**Figure 12**). Settling of the fines takes place leaving a supernatant water layer on the top. The top 1-3 meters of the pond will be clear water which is continuously pumped back to the extraction processes. Under the clear water is the immature fine tailing zone – a transition zone of water and settling particles that is about 1-2 meters thick. Below this zone is the mature fine tailings (MFT) zone, a layer of silts and clays, fine sands, bitumen, and water which increases in density with depth due to sand settling through the MFT. The sands are wind blown from the dyke of the tailings pond. The depth of the mature fine tailings zone can vary from 15-20 meters not including the higher sand content material at the bottom, although the pond can have a maximum depth of about 50 meters in some areas.

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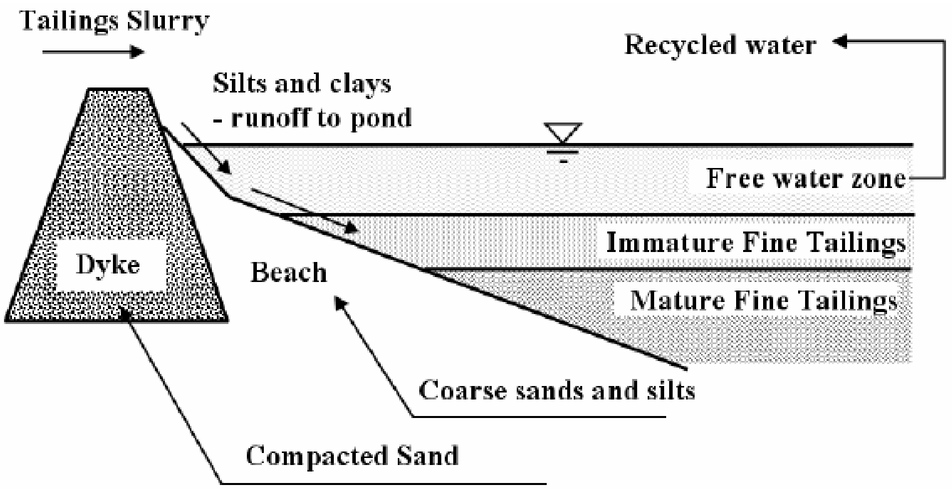
[110] Jeeravipoolvarn S. Compression Behaviour of Thixotropic Oil Sands Tailings. PhD. Thesis, University of Alberta, Edmonton, Alberta, Spring 2005; https://era.library.ualberta.ca/items/503d4ea1-bfc5-472f-89e3-bb4847c914c5/download/eeeb44f1-99c5-47c3-8d6f-8cdd21cbae84.

Figure 12. Cross-section of an oil sands tailings basin[111]



As noted earlier in Section 2, along with the 20-30 wt% of solids (sand, silt and clays) and slightly alkaline water (pH > 7.5), mature tailings consist of 1-3 wt% of residual bitumen and naphtha (added during oil processing), comprising of a mixture paraffins (n-alkanes), iso-paraffins (branched alkanes), olefins (alkenes), naphthenes (cycloalkanes), olefins, naphthenic acids (cyclopentyl and cyclohexyl carboxylic acids), and monoaromatics (benzene, toluene, ethylbenzene, and xylenes, or BTEX).[112] Other minor elements include trace metals (Cr, Mn, Co, Ni, Cu, Zn, As, Sr, Mo, Ba), and ions (HCO_3^-, PO_4^{3-}, NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-).[113] These species are similar in variety to those present in the tailings pond water, and so a similar range of sorting rotor binding sites would probably be required to extract them.

Assuming 1 x 10^9 m^3 of MFT in Albertan tailings ponds needing to be cleaned up and an average density close to 1000 kg/m^3 for the pollutants, then a 1-3 wt% concentration of organics and trace metal contaminants implies a requirement for extracting about 10-30 x 10^9 kg of pollutant molecules. That's only about 2-5 times more than the total extraction requirement of 6.5 x 10^9 kg for all pollutants in tailings pond water as described earlier in Section 5.1, which suggests that

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[111] Jeeravipoolvarn S. Compression Behaviour of Thixotropic Oil Sands Tailings. PhD. Thesis, University of Alberta, Edmonton, Alberta, Spring 2005; https://era.library.ualberta.ca/items/503d4ea1-bfc5-472f-89e3-bb4847c914c5/download/eeeb44f1-99c5-47c3-8d6f-8cdd21cbae84.

[112] Siddique T, Fedorak PM, MacKinnon MD, Foght JM. Metabolism of BTEX and naphtha compounds to methane in oil sands tailings. Environ Sci Technol. 2007 Apr 1;41(7):2350-6; https://pubmed.ncbi.nlm.nih.gov/17438786/. Siddique T, Fedorak PM, Foght JM. Biodegradation of short-chain n-alkanes in oil sands tailings under methanogenic conditions. Environ Sci Technol. 2006 Sep 1;40(17):5459-64; https://pubmed.ncbi.nlm.nih.gov/16999125/.

[113] Mahdavi H, Ulrich AC, Liu Y. Metal removal from oil sands tailings pond water by indigenous micro-alga. Chemosphere. 2012 Sep;89(3):350-4; https://pubmed.ncbi.nlm.nih.gov/22583786/.

under 10 tonnes of molecular filter sorting rotors might be sufficient to remediate all MFTs in all tailings ponds throughout all of Alberta, assuming an operational remediation time period of about 2 years.

5.3 Clearing Pollutants from Upstream Sources

Molecular filtration could also be employed to remove pollutants from upstream sources before they can be discharged into the tailings ponds. Molecular filters can probably be used to clear naphthenic acids and other contaminant chemicals directly from the process water at tar sands mine sites, thus eliminating the inflow of fresh contaminants into the tailings ponds.

This topic seems worthy of further study but is beyond the scope of this paper.

6. Opportunities for Environmental Remediation

Nanofactories (Section 4.6) are a potential new manufacturing technology that will enable the fabrication of commercial quantities of products comprised of nanoscale components constructed with atomic precision, with every atom located in the desired place. Such products can be used for environmental remediation[114] efforts – extracting toxic[115] and hazardous[116] wastes, pollutants,[117] and other environmental hazards[118] that are harmful to human or other biological life, from oceans, rivers, lakes, groundwater, and landfills.

Once developed, nanofactories can manufacture molecular filters consisting of large numbers of sorting rotors containing binding sites for all specific chemical pollutant molecules needing to be removed. These bound undesirable substances can be transferred through molecular-scale pumps and transported away from the polluted site, then safely decomposed into environmentally benign molecules.

In one specific example analyzed in this paper, 1-10 tonnes of molecular filter sorting rotors should suffice to remove ~6.5 x 10^9 kg of pollutants from all oil sands tailings pond water throughout all of Alberta,[119] reducing the concentration of all major contaminants to harmless background levels in an operational remediation time period of about 2 years. In a second more advanced scenario, ~74 tonnes of free-swimming nanorobots could extract and metabolize hydrocarbon pollutants from all oil sands tailings ponds in ~1 month, warming the water by ~1 °C and adding only 0.0002 ppm CO_2 to Earth's air, while afterwards being easily and completely removed from the now-purified pond water, thereafter to be recycled.

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[114] https://en.wikipedia.org/wiki/Environmental_remediation.
[115] https://en.wikipedia.org/wiki/Toxic_waste.
[116] https://en.wikipedia.org/wiki/Hazardous_waste.
[117] https://en.wikipedia.org/wiki/Pollutant.
[118] https://en.wikipedia.org/wiki/Environmental_hazard.
[119] https://en.wikipedia.org/wiki/Oil_sands_tailings_ponds_(Canada).