

*The CCEMC Grand Challenge: Innovative Carbon Uses*

**HUMASORB®-L for Removal of CO<sub>2</sub>, NO<sub>x</sub> GHGs, along with SO<sub>x</sub> and Trace Metals from Fossil Fuel Combustion Gases and Recycling into a Value Generation HUMASORB®-CS, a Stable Multipurpose Water Filter**

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## Executive Summary

HUMASORB<sup>®</sup>, a technology selected for the Alberta Grand Challenge award, was evaluated for its applicability for CO<sub>2</sub> recycle for target application in Alberta. The HUMASORB<sup>®</sup> technology is a unique and innovative approach for CO<sub>2</sub> capture using ARCTECH's proprietary liquid absorbent, HUMASORB<sup>®</sup>-L and converting it into HUMASORB<sup>®</sup>-CS solid water filter for removing multiple contaminants from wastewater. HUMASORB<sup>®</sup>-L is a coal-derived organic humic liquid product for removal of greenhouse gases (GHG) from flue gases. Its added advantage is that it also removes precursor nitrous oxides (NO<sub>x</sub>), which have a ~200 times higher GHG potential than CO<sub>2</sub>, as well as SO<sub>x</sub> and toxic trace metals which result from combustion of fossil fuels, especially coal and oil. Removal of these multiple contaminants from combustion gases are accomplished by passing the gas through HUMASORB<sup>®</sup>-L absorber. It also can be deployed as a low cost treatment in a standalone tower reactor and/or it offers a practical and cost effective approach for retrofitting the existing liquid reagent based SO<sub>x</sub> scrubbers commonly utilized for flue gas treatment.

The HUMASORB<sup>®</sup> technology offers an economic value generation approach for recycling of the largest GHG CO<sub>2</sub>, and direct environmental benefits for mitigating adverse impacts due to climate change, the primary focus of this Grand Challenge. Furthermore there are multiple collateral environmental benefits which will result from the technology. These are: 1. Along with capture of CO<sub>2</sub>, the technology captures environmentally polluting SO<sub>x</sub>, NO<sub>x</sub>, and toxic metals from combustion gases. 2. The resultant marketable product HUMASORB<sup>®</sup>-CS will be a cost effective product and effective approach for the removal of environmental contaminants from wastewaters and permanent sequestration of CO<sub>2</sub>. 3. The potential use of ARCTECH MicGAS<sup>™</sup> Coal Biotechnology for producing HUMASORB<sup>®</sup>-L and other products from the abundant humic-rich coal resources in the Alberta coal fields will result in mitigating environmental concerns from the current approaches of use of Alberta's coal resources.

The main objective of this project was to advance applicability of ARCTECH's HUMASORB<sup>®</sup> technology for carbon capture and utilization (for removing GHG, other contaminants and recycling).

This HUMASORB<sup>®</sup> project is an innovative approach of utilizing both capture and recycling of CO<sub>2</sub> into value generating product. This project was highly successful and resulted in valuable outputs including the main conclusions described below.

- HUMASORB<sup>®</sup>-L successfully captured and absorbed CO<sub>2</sub> as well as SO<sub>x</sub>, NO<sub>x</sub>, metals, and particles/soot from flue gas generated by coal burning and cylinder gas. Total amount of CO<sub>2</sub> absorbed was comparable as 47.66 g and 45.99 g per 200 mL of HUMASORB<sup>®</sup>-L for both cylinder gas and flue gas from coal burning, respectively. These are equivalent to 0.902 kg and 0.87 kg per gallon of HUMASORB<sup>®</sup>-L. Overall about 1,000 gallon of HUMASORB<sup>®</sup>-L will be required to capture 1 ton of CO<sub>2</sub> under current experimental conditions.

- Absorbed CO<sub>2</sub> in HUMASORB®-L was present in carboxylic, bicarbonate, and carbonate forms. The mass balance of absorbed CO<sub>2</sub> in the spent HUMASORB®-L as a carboxylate, bicarbonate, and carbonate was calculated to be 47.1: 35.3: 17.6, respectively. This is consistent with the result of Fourier Transform Infrared Spectroscopy (FTIR) analysis. FTIR analysis of HUMASORB®-L before and after CO<sub>2</sub> absorption verified that the CO<sub>2</sub> is bound with humic molecule as carboxylates as well as carbonate and bicarbonate.
- HUMASORB®-L was productively converted to a value added water filter, HUMASORB®-CS, by cross-linking and immobilization of spent HUMASORB®-L with a cross-linking agent to make an insoluble product. N<sub>2</sub>-BET surface area of HUMASORB®-CS from spent HUMASORB®-L was 0.9222 m<sup>2</sup>/g and stable at wide range of pH conditions without re-releasing of captured CO<sub>2</sub>. The dominant final fixed form/species of absorbed CO<sub>2</sub> in solid phase of HUMASORB®-CS was identified by high resolution X-Ray powder diffractometer as calcium carbonate. Thus, after captured by HUMASORB®-L adsorbent, CO<sub>2</sub> was converted to the stable carbonate form and permanently stored in the final product of HUMASORB®-CS.
- HUMASORB®-CS from spent HUMASORB®-L after CO<sub>2</sub> absorption is effective in treating metals of concern from wastewater.
- In 2015 the Government of Alberta established the Tailings Management Framework for the Mineable Athabasca Oil Sands to support faster reclamation of fluid fine tailings. In the Lower Athabasca Region, about 976 million cubic meters of fluid tailings are contained within tailings ponds, with a net cumulative footprint of about 220 km<sup>2</sup> including dykes, berms, beaches, and in-pit ponds in 2013. Thus, oil sand operations present an opportunity to use HUMASORB®-CS for wastewater treatment. By applying HUMASORB®-CS technology to oil sands water no longer used for recycle, the water can be remediated faster supporting more progressive aquatic reclamation options than that of straight passive reclamation. HUMASORB®-CS offers a cost-effective active treatment process with low energy intensity that can facilitate faster remediation and reclamation of process-affected waters.
- In the US, on September 30, 2015, the Environmental Protection Agency (USEPA) has finalized the Coal Solids Residues (CSRs) Rule for power plant effluent limitations. It sets the first federal limits on the levels of toxic metals in wastewater discharges from steam electric power plants. This new rule has stringent requirements for the discharge of arsenic, mercury, selenium, and nitrogen in wastewater streams from flue gas desulfurization, and requires zero-discharge of pollutants in ash transport water and mercury control wastewater. It also strictly limits arsenic, mercury, selenium, and total dissolved solids in coal gasification wastewater. Thus, the application of HUMASORB®-CS for the cleanup of wastewater generated from power plants has considerable potential and can be readily-deployed.
- The stability study of spent HUMASORB®-L on soil to determine the potential use of spent HUMASORB®-L as a soil amendment shows that the absorbed CO<sub>2</sub> in spent HUMASORB®-L was re-released by contacting soil with pH as low as of 5.6. This result

reveals that HUMASORB®-CS is better than spent HUMASORB®-L as a soil amendment for the utilization of recycling of captured CO<sub>2</sub>.

- HUMASORB® technology could address the large CO<sub>2</sub> emissions from coal plants and insitu oil sands operation. Insitu GHG footprint is largely due to natural gas combustion for steam, in mines lots of it is from the mine fleet and other dispersed activities for which it will be difficult to apply this technology. The HUMASORB® technology approach of capturing GHG emissions from the largest sources as well as meeting the large needs of cost effective treatment of its wastewaters, will allow the Province of Alberta to meet its objectives of GHG reduction while enabling the meeting of other important environmental needs with a creative and value generating approach. ARCTECH technology will overcome these challenges that Canadian oil sands industries are confronting.
- The economic viability of HUMASORB®-L fitted flue gas scrubbers is assured by the sale and utilization of HUMASORB®-CS product. For every mega tonne of CO<sub>2</sub> captured, over 3.58 billion pounds of HUMASORB®-CS is produced that will be sufficient for the treatment of 716 billion gallons of complex wastewater. It will be achieved by using as polishing an existing treatment system which do not fully comply with lower levels of contaminants now required by regulations with HUMASORB®-CS and/or as a subcomponent of existing treatment system. Based on a market research analysis in 2011 by the McIlvaine Company of Chicago for ARCTECH, water treatment costs can range anywhere from USD \$5 to USD \$122 per 1000 gallons; HUMASORB®-CS should be economical even at the lower cost basis of USD \$5 per 1000 gallons and thereby create direct economic impact of USD \$3.6 billion per megatonne of CO<sub>2</sub> captured. Also, HUMASORB®-CS, because of its abilities to capture multiple contaminants simultaneously as well as its physical granular form, is well suited for deployment as passive sub-surface barrier for containment of contaminants in the groundwater or leaching from solid wastes such as municipal solid waste and coal ash ponds.
- Widespread adaptation of HUMASORB® technology will be easy due to the technology's scalability and replicability. It is a "bolt-on" solution for installation with the standard scrubbing systems in use by thermal-electric power plants and oil sands operations. The size and build of the scrubbing columns can be readily adjusted to fit a particular facility's operating conditions without loss to carbon capture efficiency. Even where a HUMASORB®-L system is the first scrubber to be fitted to a stack, the simplicity and adaptability of the technology ensures that a reliable engineering solution can be achieved whether a facility is old and conventional or state-of-the-art.
- Since the requirements of its use at the target sites of coal power plants and oil sands operations are similar and subject to uniform mandates, it is expected that the replication of the technology will be rapid without requiring to prove its performance at each new site. So it is envisioned that it will be deployed commercially upon introduction.
- Demo test of this technology is needed over a two year cycle period. Thereafter ARCTECH expects to establish business operations in Alberta for both replicating the use of the technology as well as for manufacturing of HUMASORB® products and servicing

its use. It is envisioned about three to five years' time will be required for full commercialization of the technology in Alberta.

- The United States Patent and Trademark Office (USPTO) allowed ARCTECH application on December 23, 2014 covering application of CO<sub>2</sub> capture and recycling entitled “Methods of Filtering Multiple Contaminants, Mitigating Contaminant Formation, and Recycling Greenhouse Gases Using a Humic and Fulvic Reagent”. Also allowed the Patent Cooperation Treaty (PCT) for securing worldwide patents. United State Patent issued ARCTECH Patent on April 21, 2015 (Patent No.: US 9,011,577 B2).

## 1. Project Description

HUMASORB<sup>®</sup>, a technology selected for the Alberta Grand Challenge award, was evaluated for its applicability for CO<sub>2</sub> recycle for target application in Alberta. The HUMASORB<sup>®</sup> technology is a unique and innovative approach for CO<sub>2</sub> capture using ARCTECH's proprietary liquid absorbent, HUMASORB<sup>®</sup>-L and converting it into HUMASORB<sup>®</sup>-CS solid water filter for removing multiple contaminants from wastewater. HUMASORB<sup>®</sup>-L is a coal-derived organic humic liquid product for removal of greenhouse gases (GHG) from flue gases. Its added advantage is that it also removes precursor nitrous oxides (NO<sub>x</sub>), which have a ~200 times higher GHG potential than CO<sub>2</sub>, as well as SO<sub>x</sub> and toxic trace metals which result from combustion of fossil fuels, especially coal and oil. Removal of these multiple contaminants from combustion gases are accomplished by passing the gas through HUMASORB<sup>®</sup>-L absorber. It also can be deployed as a low cost treatment in a standalone tower reactor and/or it offers a practical and cost effective approach for retrofitting the existing liquid reagent based SO<sub>x</sub> scrubbers commonly utilized for flue gas treatment.

Today almost 9.6 trillion gallons of wastewaters are produced in Canada by fossil fuel, municipal, industrial and mining operations. The wastewaters are increasingly being required to be treated for recycling and/or remediated to high standards prior to discharge to the environment. The HUMASORB<sup>®</sup> technology offers an opportunity to creatively address these two large needs to reduce GHG emissions and to treat wastewater with an economic value proposition.

HUMASORB<sup>®</sup> is one of the organic humic products of the MicGAS<sup>™</sup> Coal Biotechnology ([www.arctech.com](http://www.arctech.com)). This technology converts coals into clean methane rich biogas or liquid fuels and non-energy organic humic products for food production, waste water treatment, and waste recycling. It results in the complete utilization of coal with zero waste. The MicGAS<sup>™</sup> Coal Biotechnology approach of using coals for production of energy results in zero to about 15 tonnes of CO<sub>2</sub> equivalent reduction from each tonne of coal. This reduction in CO<sub>2</sub> equivalent is attributed to the use of lower CO<sub>2</sub>-producing methane gas made from coal, along with the increased biomass resulting from the use of the humic acid in improving soil fertility and establishment of biomass even in impaired soils and desert lands ([www.ihccs.org](http://www.ihccs.org)).

HUMASORB® product in liquid form designated as HUMASORB®-L and in solid form (1-2 mm beads) is designated as HUMASORB®-CS. HUMASORB®-L has multiple functional groups comprised of carboxylic, hydroxyl, and enolic acids embedded in a carbon matrix. It has multiple adsorption, chelation, and ion exchange properties and thus is able to bind multiple organic and inorganic chemicals from various media. It is then amenable to cross-linking along with contaminants bound into a solid HUMASORB®-CS. The HUMASORB® product because of multiple binding sites has been successfully developed into a water filter for removal of multiple contaminants.

The HUMASORB® technology offers an economic value generation approach for recycling of the largest GHG CO<sub>2</sub>, and direct environmental benefits for mitigating adverse impacts due to climate change, the primary focus of this Grand Challenge. Furthermore there are multiple collateral environmental benefits which will result from the technology. These are: 1. Along with capture of CO<sub>2</sub>, the technology captures environmentally polluting SO<sub>x</sub>, NO<sub>x</sub>, and toxic metals from combustion gases. 2. The resultant marketable product HUMASORB®-CS will be a cost effective product and effective approach for the removal of environmental contaminants from wastewaters and permanent sequestration of CO<sub>2</sub>. 3. The potential use of ARCTECH MicGAS™ Coal Biotechnology for producing HUMASORB®-L and other products from the abundant humic-rich coal resources in the Alberta coal fields will result in mitigating environmental concerns from the current approaches of use of Alberta's coal resources.

The main objective of this project was to advance applicability of ARCTECH's HUMASORB® technology for carbon capture and utilization (for removing GHG, other contaminants and recycling).



## **2. Outcomes and Learnings**

The system optimization of HUMASORB<sup>®</sup> technology has been established in bench scale for removing GHG, other contaminants and recycling spent HUMASORB<sup>®</sup>-L that absorbed CO<sub>2</sub> into HUMASORB<sup>®</sup>-CS.

The CO<sub>2</sub> composition in the treated outlet gas from the absorbent was analyzed by gas chromatograph with thermal conductivity detector (TCD) (GOW-MAC Series 580 fitted with a 10'x 1/8" OD stainless steel column packed with 100/120 mesh Carboseive S-II (Supelco Co.)). The change of pH by the reaction was measured before and after reaction. The amount of CO<sub>2</sub> absorbed in the absorbent was calculated based on the inlet and outlet CO<sub>2</sub> composition and total amount of feed gas. The endpoint of the reaction was determined based on the point at which the outlet CO<sub>2</sub> composition was close to the initial value, i.e., concentration of input gas. Carbonate, bicarbonate, total acidity, phenolic functional group and carboxylic functional group of spent HUMASORB<sup>®</sup>-L were also analyzed to identify possible chemical reaction, species of absorbed CO<sub>2</sub> on humic molecule, and carbon distribution and/or mass balance to the final product of HUMASORB<sup>®</sup>-L.

For evaluation of HUMASORB<sup>®</sup>-L for absorption of CO<sub>2</sub> from flue gas, the experiment was conducted by generating flue gas by burning coal in a tube furnace and passing flue gas through the HUMASORB<sup>®</sup>-L filled in reactor. A batch-typed Pyrex cylindrical reactor (55 mm diameter and 420 mm height) was used for HUMASORB<sup>®</sup>-L absorbent. 200 mL of HUMASORB<sup>®</sup>-L absorbent and glass beads for better absorption of gases by increasing contact time and providing uniform distribution of input gas were placed in the reactor.

### **Conversion of Spent HUMASORB<sup>®</sup>-L into HUMASORB<sup>®</sup>-CS and Applicability for Wastewater Treatment**

HUMASORB<sup>®</sup>-CS was produced by cross-linking and immobilization of spent HUMASORB<sup>®</sup>-L with cross-linking agent to make insoluble product. Surface area property of the prepared HUMASORB<sup>®</sup>-CS was analyzed by N<sub>2</sub>-BET adsorption using a Micromeritics ASAP 2020 instrument (Micromeritics Instrument Corporation) at the Advanced Materials Characterization Lab of the University of Delaware. N<sub>2</sub>-BET surface area of HUMASORB<sup>®</sup>-CS from spent

HUMASORB<sup>®</sup>-L1 was 0.9222 m<sup>2</sup>/g, which is identical with the surface area of regular HUMASORB<sup>®</sup>-CS (0.9556 m<sup>2</sup>/g).

To identify the final fixed form/species of absorbed CO<sub>2</sub> in solid phase of HUMASORB<sup>®</sup>-CS, Bruker D8 XRD (Bruker Corporation), a versatile, sensitive, and high resolution X-Ray powder diffractometer was used at the Advanced Materials Characterization Lab of the University of Delaware. The monochromatic Cu K $\alpha$ 1 line is isolated by the Vario monochromater at the X-Ray tube.

Stability of the HUMASORB<sup>®</sup>-CS product was determined at various pHs ranging from 3 to 12 adjusted by either sodium hydroxide or nitric acid. 7.5 g of HUMASORB<sup>®</sup>-CS beads were placed in 25 mL water with a head space of ~10 mL. CO<sub>2</sub> was monitored at different days for 1 month and confirmed that CO<sub>2</sub> was not released even at low pH of 3 (Figure 1(a)).

Also no physical change/deformation of HUMASORB<sup>®</sup>-CS was observed after 1 month of contact time (Figure 1(b)). The bead shape of HUMASORB<sup>®</sup>-CS maintains its form and stability in the different pH solutions, even in high pH of 12. This observation means that HUMASORB<sup>®</sup>-CS from spent HUMASORB<sup>®</sup>-L is insoluble in water at a wide range of pH values. These results indicate that HUMASORB<sup>®</sup>-CS, as determined under the conditions of this study, is outstandingly stable without any deformation and that it sequesters the captured CO<sub>2</sub> without re-releasing to the atmosphere.

Meanwhile, stability of spent HUMASORB<sup>®</sup>-L on soil was also conducted for the potential use of spent HUMASORB<sup>®</sup>-L as a soil amendment. Captured CO<sub>2</sub> in the spent HUMASORB<sup>®</sup>-L which comes into contact with soil could be degraded and released to the atmosphere. The stability study of spent HUMASORB<sup>®</sup>-L was conducted to determine the nature and extent of any degradation. 1, 5, 10, and 25% (v/v) of spent HUMASORB<sup>®</sup>-L were added to the 75mL (~100 g) of soils with pH of 5.6 placed inside of glass head space vials and capped with butyl rubber stopper and aluminum open top hole cap, then purged by helium for about three minutes. After one day, the headspace gas was analyzed for the CO<sub>2</sub> by GC. Regardless of different loading of spent HUMASORB<sup>®</sup>-L to the soils, a strong CO<sub>2</sub> peak was observed, which indicates that absorbed CO<sub>2</sub>

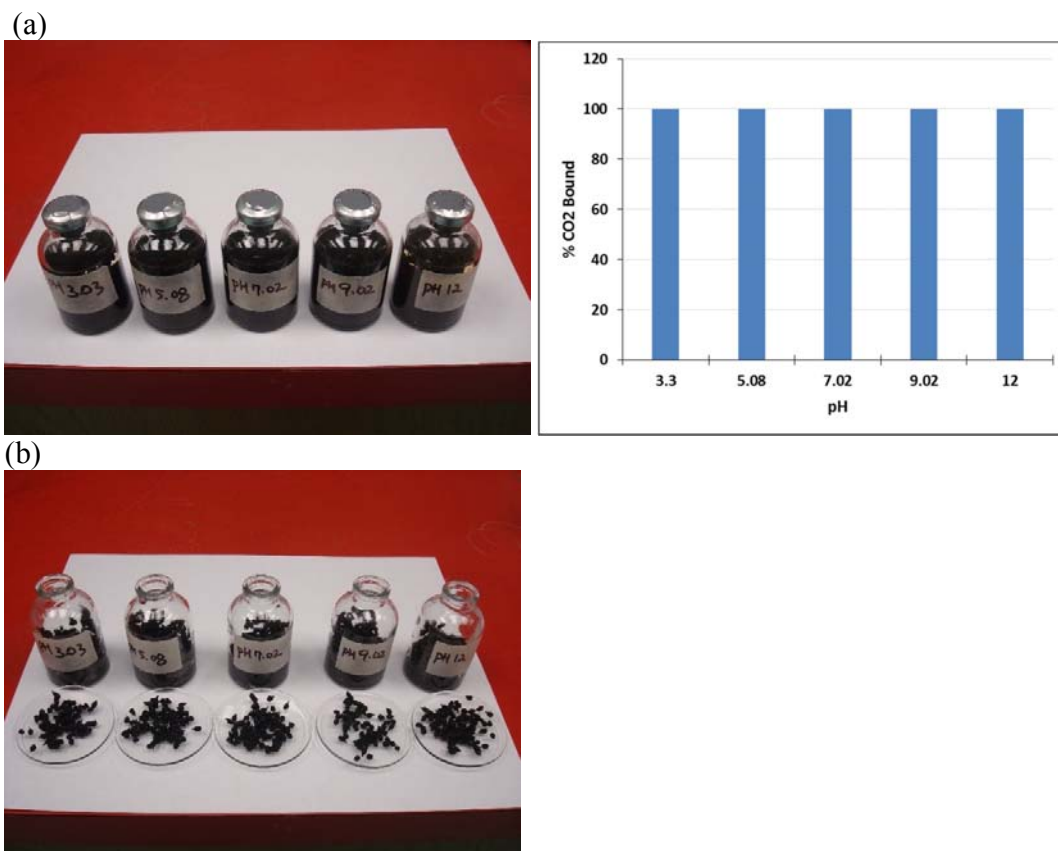


Figure 1. HUMASORB<sup>®</sup>-CS Made from Spent HUMASORB<sup>®</sup>-L Exhibited Stable at Various pHs without Releasing Captured CO<sub>2</sub>; (a) CO<sub>2</sub> Bound Completely on HUMASORB<sup>®</sup>-CS and (b) No deformation of HUMASORB<sup>®</sup>-CS.

in spent HUMASORB<sup>®</sup>-L was re-released due to the contact with low pH soil. This result reveals that the HUMASORB<sup>®</sup>-CS pathway is better approach than spent HUMASORB<sup>®</sup>-L as a soil amendment for the utilization of recycling of captured CO<sub>2</sub>.

Removal of contaminants by HUMASORB<sup>®</sup>-CS that was formulated using spent HUMASORB<sup>®</sup>-L1 after CO<sub>2</sub> absorption was evaluated by contacting with simulated waste streams that contain multi-metals, including toxic Resource Conservation and Recovery Act (RCRA) regulated metals (As, Cd, Cr, Pb, Hg, Se, Ag), Cu, and Zn. Two batch of multi elements artificial solution were prepared to minimize any possible precipitation during preparation. The first batch of solution was prepared by using ICP standard solution of Ag, Cd, Cr, Cu, Pb, and Zn and pH was adjusted to 5.5. The second batch of solution was prepared by using ICP standard solution of As, Hg, and

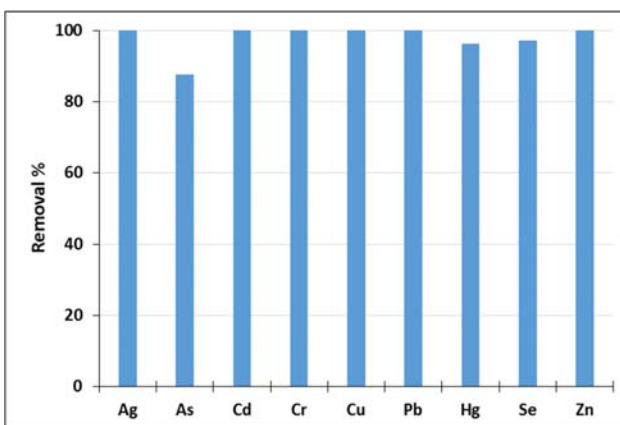
Se and pH was adjusted to 5.83. The initial concentration of each metal would be 5 ppm if no precipitation occurred. Hg was salted out due to precipitation during initial solution preparation, thus single element of Hg was prepared separately again (pH = 2.65). After contact time of two hours at 100 rpm with solid/liquid loading of 30%, solid/liquid was separated by centrifuge and liquid portion was filtered through 0.45  $\mu\text{m}$  membrane filter before analysis.

Ag, Cd, Cr, Cu, Pb, and Zn were removed below detection limit by HUMASORB<sup>®</sup>-CS. Removals of As, Hg, and Se were 87.64, 96.28, and 97.2 %, respectively (Table 1). Note that selenium removal will be affected by the oxidation states. Selenium is generally present in four different oxidation states in environment as selenate (VI), selenite (IV), elemental selenium (0), and selenide (II-), also selenium can be complexed with other chemicals. Selenate, the most oxidized form of selenium and the most abundant in the coal mine discharge wastewater, is the most difficult to treat. Thus, it is important to identify the condition of oxidation states. The selenium used in this study was soluble compound as Se(0), CAS#: 007782-49-2, in the matrix of water with dilute nitric acid. The result shows that HUMASORB<sup>®</sup>-CS from spent HUMASORB<sup>®</sup>-L after CO<sub>2</sub> absorption is effective of treating metals of concern from contaminated sites and wastewater. Overall metal removal by HUMASORB<sup>®</sup>-CS produced from spent HUMASORB<sup>®</sup>-L exhibited similar result as that of ARCTECH's regular HUMASORB<sup>®</sup>-CS for metal removal from wastewater.

Table 1. HUMASORB<sup>®</sup>-CS Made from Spent HUMASORB<sup>®</sup>-L after CO<sub>2</sub> Absorption Effectively Removed Toxic Metals from Contaminated Water

Metal	Initial, mg/L	Final, mg/L	Removal, %
Ag	3.904	ND	100
As	5.355	0.662	87.64
Cd	5.27	ND	100
Cr	3.26	ND	100
Cu	3.585	ND	100
Pb	3.93	ND	100
Hg	5.02	0.186	96.28
Se	5.255	0.147	97.2
Zn	4.793	ND	100

ND: Not Detected



Feasibility tests were conducted using HUMASORB® for removal of Barium and Strontium from actual field-sourced frac wastewater that has high Ba and Sr concentration. The frac water currently being produced from shale gas wells is used for production of natural gas from the deep shale rock formation. Presently the returned frac water containing several toxic metals and organics is trucked from the gas well sites for disposal. Generally major components of produced water are hydrocarbons, salts, metals, production chemicals and naturally occurring radioactive material (NORM), though the properties and quantities are vary by site.

Frac water is generally held in lined pits and transported to off-site disposal facilities. The primary disposal option for this frac water is underground re-injection in a Class II injection well. However, re-injection wells are often located further from the original well site, requiring transportation to a re-injection site. Therefore, at many places the frac water is transported for treatment to a local municipal sewage treatment plant. Reuse of frac water is limited due to its high Total Dissolved Solid (TDS) content since current hydraulic fracturing procedures or fluid additives are not operable at this high TDS content.

Following Table 2 presents the result of HUMASORB® treatment for the frac wastewater. The removal efficiency is excellent, >99.99 %, for both contaminants for reaction time of ten minutes. HUMASORB® has been proven to treat real world samples and allows the recycling of the treated water.

Table 2. Frac Water Treatment by HUMASORB® Technology

	Ba, ppm	Ba removal%	Sr, ppm	Sr removal%
Frac water	1694		3742.2	
HUMASORB® Treated	0.237	99.99	0.494	99.99

Metal removal by HUMASORB®-CS is due to unique binding properties of humic acid in the HUMASORB®-L CO<sub>2</sub> absorbent. Humic acid possesses multiple functional groups comprising of carboxylic, hydroxyl, and enolic and its carbon matrix, which impart it multiple adsorption, chelation, and ion exchange properties and thus the ability to bind multiple organic and inorganic chemicals from various wastewater streams. Moreover, metals are bound to the carbon skeleton

of humic substances through heteroatoms such as nitrogen, oxygen or sulfur. The most common metal binding occurs via carboxylic and phenolic oxygen, but nitrogen and sulfur also contribute. HUMASORB<sup>®</sup>-CS has high cation exchange capacity between 2 to 5 meq per gram. However, note that service life of HUMASORB<sup>®</sup>-CS will vary by the concentration of contaminants in wastewater. Following Figure 2 shows the conceptual view of metal ions attached to humic acid in HUMASORB<sup>®</sup>-CS. The properties of HUMASORB<sup>®</sup>-CS are useful for the removal of toxic metals attributed from its properties of high cation exchange capacity and ability to chelate metals.

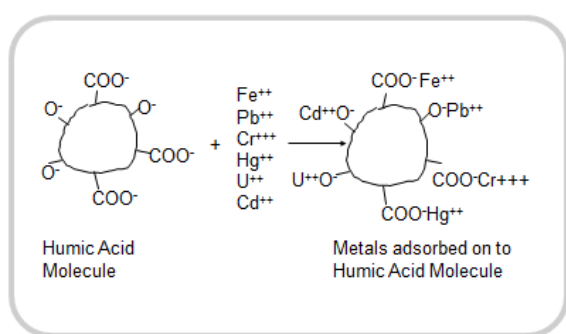


Figure 2. Conceptual View of Metal Ions Attached to Humic Acid.

### 3. Scientific Achievements

The United States Patent and Trademark Office (USPTO) allowed ARCTECH application on December 23, 2014 covering application of CO<sub>2</sub> capture and recycling entitled “Methods of Filtering Multiple Contaminants, Mitigating Contaminant Formation, and Recycling Greenhouse Gases Using a Humic and Fulvic Reagent”. Also allowed the Patent Cooperation Treaty (PCT) for securing worldwide patents. United State Patent issued ARCTECH Patent on April 21, 2015 (**Patent No.: US 9,011,577 B2**).

### 4. Deployment Approach of HUMASORB<sup>®</sup> Capture and Recycling Technology System

HUMASORB<sup>®</sup>-L is a liquid based scrubber technology and can be retrofitted to existing wet scrubbers. It is based on a unique coal-derived absorber which removes SO<sub>x</sub>, NO<sub>x</sub>, Hg and other toxic metals and even CO<sub>2</sub> from coal combustion flue gas all in single step to satisfy recent more stringent mandataries.

Currently, the majority of the scrubbers in use today are wet scrubbers and use almost half and half of spray and tower systems (Figure 3). The most common scrubbing solution is based on limestone forced oxidation technology. The scrubber systems are primarily made of fiber glass resin but a small number use alloy steel or C-276 clad flue. A spray nozzle, packed towers, or an aspirator will be installed to increase removal efficiency by increase contact time and the surface area.

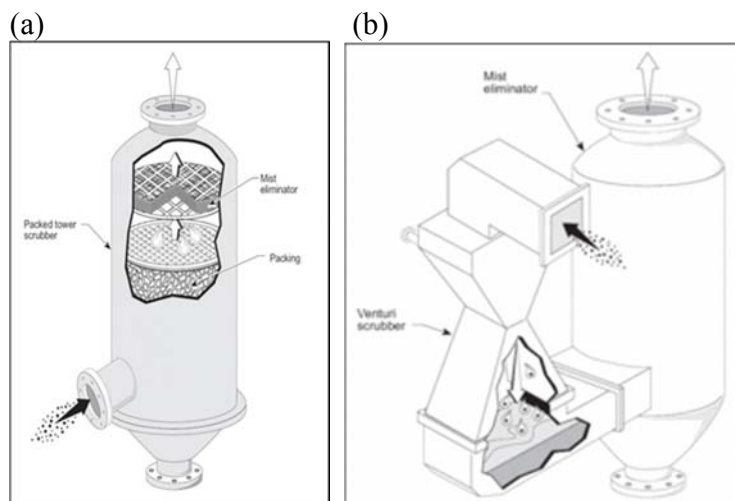


Figure 3. Examples of Wet scrubbers: (a) Packed Bed Tower and (b) Venturi Scrubber.

HUMASORB<sup>®</sup>-L system can be deployed as a low cost treatment in a standalone tower reactor and/or it offers a practical and cost effective approach for retrofitting the existing liquid reagent based SO<sub>x</sub> scrubbers commonly utilized for flue gas treatment.

HUMASORB<sup>®</sup>-CS can be readily-deployed into existing power plant ash ponds to protect the surrounding environment. An example of use of HUMASORB<sup>®</sup>-CS for filtering toxic contaminants leaching out from ash ponds and HUMASORB<sup>®</sup>-CS feasibility test result for contaminant of toxic chemicals from ash pond leachate are presented in Figure 4 and Table 3.

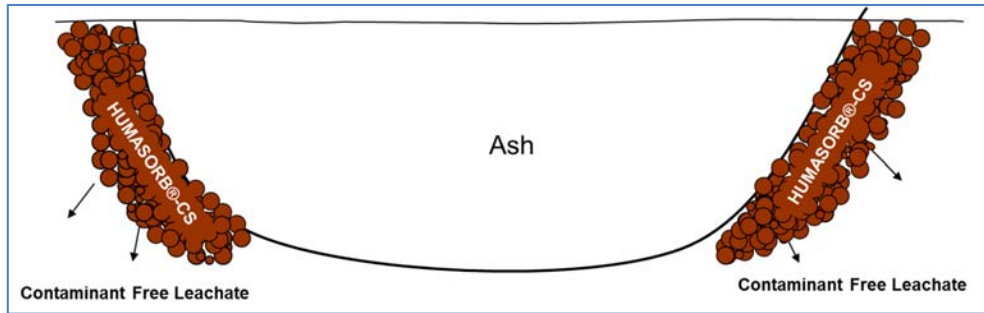


Figure 4. A Schematic of Envisioned Installation of HUMASORB®-CS for Containment of Leachate from Existing Ash Pond.

Table 3. HUMASORB®-CS Feasibility Test for Contaminant Removal of Toxic Chemicals from Ash Pond Leachate

Toxic Metals (mg/L)	Ash Pond Leachate (mg/L)			HUMASORB Treated (mg/L)			TCLP Hazardous Waste Limit, mg/L
	pH3	pH5	pH6.5	pH3	pH5	pH6.5	
As	1.163	1.135	1.580	nd	nd	nd	5.0
Ba	1.220	0.608	0.680	0.011	0.006	0.003	100.0
Cd	0.193	0.183	0.183	nd	nd	nd	1.0
Cr	0.090	0.090	0.095	nd	nd	0.006	5.0
Hg	nd	nd	nd	nd	nd	nd	0.2
Pb	1.055	1.118	1.028	nd	0.052	0.037	5.0
Se	1.165	1.215	1.585	nd	nd	nd	1.0
Ag	nd	nd	nd	nd	nd	nd	5.0
Cu	9.023	nd	nd	nd	nd	nd	
Fe	0.683	nd	nd	nd	nd	nd	
Ni	2.315	1.258	0.193	0.045	0.072	0.011	
Tl	1.345	1.208	1.288	nd	nd	0.045	
Zn	1.003	0.143	nd	nd	nd	nd	

nd: Not Detected

It offers a cost effective approach to retrofit the scrubbers on existing power plants as well as control leachates from coal ash ponds with several advantages:

- Retrofit existing scrubbers without requiring high capital investment
- Comply with existing mandates on ash ponds with use of a recycled product for cost effective control of release of toxic metals from ash ponds and waste waters at power plants.
- Retain the use of lowest cost coal Btu with long term assured supply contracts and remain competitive with low cost gas.



## **5. Applicability for Target Oil Sands Processing Plant and Power Plant Sites and Techno-Economic Analysis for Deployment in Alberta**

**Oil Sand Processing Plant:** The Province of Alberta has the largest fossil fuel resources of coal, oil sands, oil and gas in Canada. The use of these fossil fuels results in large amounts of GHG, especially CO<sub>2</sub>. Coal power generation plants and oil sands operation sites emit almost 76 % of the total GHG emissions in Alberta.

Oil sand is a naturally occurring sandstone that contains mixture of sand, clay or other minerals, water, and bitumen, which is a heavy and extremely viscous oil. Bitumen must be treated before it can be used by refineries to produce fuels such as gasoline and diesel. Bitumen is so viscous that at room temperature it acts much like cold molasses (Alberta Energy<sup>a</sup>).

The production of Alberta's oil sands, the third-largest proven crude oil reserve in the world, is expected to increase from 1.9 million barrels per day in 2012 to 3.8 million barrels per day in 2022 (Alberta Energy<sup>b</sup>) and 5.2 million barrels per day by 2030 (Canadian Energy Research Institute, 2014). Open-pit mining and in situ extraction are two different methods of producing oil from the oil sands. About 20% of oil sands are recoverable through open-pit mining and 80% of oil sands reserves (which underly approximately 97% of the oil sands surface area) are recoverable through in situ technology (Canadian Association of Petroleum Producers, 2015).

Canadian oil sands operations have several challenges to overcome including GHG emission, land and forest disturbance, water consumption and pollution, and tailings ponds. Oil sands operations inherently release more greenhouse gases than other forms of oil production since they require lots of energy for mining and separation of oil from the sands, as well as extraction of the oil. In 2010, the total oil sands operations sector, which includes oil sands in situ extraction, oil sands mining and upgrading, and associated cogeneration facilities, had highest GHG emission (38.2%) in Alberta, and accounted for 6.8% of total Canadian greenhouse gas emissions, and for 0.15% of global greenhouse gas emissions (Alberta Energy<sup>c</sup>).

The demand for water for oil sands mining is so large that a mining operation requires about 2–4.5 m<sup>3</sup> of water (net figures) to produce one m<sup>3</sup> of synthetic crude oil (upgraded bitumen) (Griffiths, 2006). In 2011, oil sands operators used approximately 170 million m<sup>3</sup> (1.1 billion bbls) of water and oil sands mining uses three times as much fresh water as conventional oil production (Grant, et al., 2013). In 2013, the total volume of fine fluid tailings in Alberta was 975.6 million m<sup>3</sup> and the total area occupied by oil sands tailings ponds and associated structures (such as dikes) was 220 km<sup>2</sup> or 54,363 acres (Alberta Environment and Parks Oil Sands Information Portal, 2015).

Thus, HUMASORB<sup>®</sup> technology is applicable to the large CO<sub>2</sub> emissions from coal plants and oil sands operation. The HUMASORB<sup>®</sup> technology approach of capturing GHG emissions from these sources as well as meeting the needs of cost effective treatment of its wastewaters, will allow the Province of Alberta to meet its objectives of GHG reduction while enabling the meeting of other important environmental needs with a creative and value generating approach. ARCTECH technology will overcome these challenges that Canadian oil sands industries are confronting.

Furthermore, in 2015 the Government of Alberta established the Tailings Management Framework for the Mineable Athabasca Oil Sands to reduce tailing pond and regulate the use of water from the Athabasca River (Alberta Government, 2015). The water used during oil sands mining is stored in tailing ponds, which allow sand and waste to separate, disposal of coarse and fine tailings, and most importantly storage of water for recycling. In the Lower Athabasca Region, about 976 million cubic meters of fluid tailings are contained within tailings ponds, with a net cumulative footprint of about 220 km<sup>2</sup> including dykes, berms, beaches, and in-pit ponds in 2013 (AESRD, 2014). Thus, oil sand operations present an opportunity to use HUMASORB<sup>®</sup>-CS for wastewater treatment. By applying HUMASORB<sup>®</sup>-CS technology to oil sands water no longer used for recycling, the water can be remediated faster supporting more progressive aquatic reclamation options than that of straight passive reclamation. HUMASORB<sup>®</sup>-CS offers a cost-effective active treatment process with low energy intensity that can facilitate faster remediation and reclamation of process-affected waters.

The Province of Alberta possesses many sites available for the disposal of “spent” HUMASORB<sup>®</sup>-CS and its safe containment as sequestered carbon, such as Westar Landfill in Medicine Hat and

the Municipal District of Big Lakes in High Prairie. Unlike gaseous CO<sub>2</sub> storage by underground injection (i.e. traditional Carbon Capture and Storage), HUMASORB®-CS can be disposed in a secure landfill or simple holding facility as a non-volatile, solid waste.

**Power Plant:** The Province of Alberta utilizes more than 20 coal-fired plants for electricity generation that combined produce over 50 million tonnes CO<sub>2</sub> of air emissions per annum (Doluweera *et al.*, 2011; Environment of Canada, 2010). The individual facilities can be large and significant emitters of GHG and noxious pollutant gases. For instance, the Sundance Thermal Generating Station (Parkland County), owned by TransAlta Corporation, operates at 15.11 million MW-h capacity and is the single largest CO<sub>2</sub>-emitter in Alberta at over 15.8 million tonnes CO<sub>2</sub> annually. The Sundance facility also generates over 30,000 tonnes SO<sub>2</sub> and 25,000 tonnes NO<sub>x</sub> per year (CEC, 2011). Furthermore, two plants owned by ATCO Power, Sheerness Thermal Generating Station (near Hanna) and the Battle River Generating Station (of Forestburg), are of 5.89 and 5.08 million MW-h per year capacity, respectively, and generate emissions of 5.9 and 5.3 million tonnes CO<sub>2</sub> per year, respectively (CEC, 2011). Additionally, these two power plants together produce over 50,000 tonnes SO<sub>2</sub> and 20,000 tonnes NO<sub>x</sub> per year (CEC, 2011). These power plants are potentially good targets of flue gas streams as suitable sites for the application of HUMASORB® technology for mitigating CO<sub>2</sub> emissions along with SO<sub>x</sub> and NO<sub>x</sub> removal. For example, following Table 4 shows required HUMASORB®-L, produced amount of HUMASORB®-CS, and cost and revenue for the reduction of 1 megatonnes of CO<sub>2</sub> over 30 years or approximately 35,000 tonnes of CO<sub>2</sub> per year on the Sheerness Thermal Generating Station. Cost analysis for the input material (HUMASORB®-L) compared to the final value added product (HUMASORB®-CS) shows that revenue is much higher than cost, even 1.7 times higher at the lowest selling price of \$1 per pound of HUMASORB®-CS.

Table 4. Case Analysis for Alberta Based Coal Power Plant - Sheerness Thermal Generating Station

	Sheerness Thermal Generating Station	Note
Electricity Generation, MW-h per year	5,892,719	
CO <sub>2</sub> Emission, tonnes per year	5,927,674	
CO <sub>2</sub> emission Rate, kg/MW-h	1,006	

CO <sub>2</sub> Reduction, tonnes per year	35,000	Based on one megatonne of CO <sub>2</sub> reduction over 30 years
HUMASORB <sup>®</sup> -L Needed, gallon per year	38,500,000	
HUMASORB <sup>®</sup> -L Cost @\$1.84/gallon HS-L, \$ per year	70,840,000	
Spent HUMASORB <sup>®</sup> -L, gallon per year	42,350,000	Spent HUMASORB <sup>®</sup> -L volume increases approximately 1.1 times of input HUMASORB <sup>®</sup> -L
HUMASORB <sup>®</sup> -CS Production, tonnes per year	54,210	Accounts for captured CO <sub>2</sub>
Revenue: HUMASORB <sup>®</sup> -CS selling @ \$1/lb , \$ per year	119,511,700	
Revenue: HUMASORB <sup>®</sup> -CS selling @ \$2/lb , \$ per year	239,023,400	

Alberta produces large quantities of quality marketable coals in excess of 36 million tonnes per year for power generation and other uses (Alberta Energy: Coal). The province's thermal generation plants of the Interior Plains rely on lower-BTU subbituminous coals from local mines for their feedstock (Gentzis and Goodarzi, 1994). The burning of coals with lesser heating value entails the consumption of more coal mass to generate the same amount of power compared to, for instance, the combustion of the bituminous coals. So bituminous coals are sourced from the Outer Foothills (Gentzis and Goodarzi, 1994; CEC, 2011). Moreover, the necessity of burning greater quantities of subbituminous coal increases a plant's burden in scrubbing regulated contaminants from the flue gases. HUMASORB<sup>®</sup> technology can be readily retrofitted into existing flue gas scrubber systems, thereby minimizing costs to the power plant while upgrading the pollution controls and the use of abundant subbituminous Alberta coals available near the power plant.

In the US, on September 30, 2015, the Environmental Protection Agency (USEPA) has finalized the Coal Solids Residues (CSRs) Rule for power plant effluent limitations. It sets the first federal limits on the levels of toxic metals in wastewater discharges from steam electric power plants. This new rule has stringent requirements for the discharge of arsenic, mercury, selenium, and nitrogen in wastewater streams from flue gas desulfurization, and requires zero-discharge of pollutants in ash transport water and mercury control wastewater. It also strictly limits arsenic, mercury, selenium, and total dissolved solids in coal gasification wastewater. Thus, the application of HUMASORB<sup>®</sup>-CS for the cleanup of wastewater that generated from power plant has considerable potential and can be readily-deployed.

**Market Evaluation for HUMASORB®-CS:** Alberta possesses the transportation infrastructure to move both liquid and solid, coal-derived humic products economically from production sources to the user markets domestically, across the region, and overseas. The provincial government maintains an extensive highway system and Highway 36, in particular, is a high load corridor that cuts through the heart of the Short Grass County trading area that is associated with some coal mines and power generation plants of interest (Transportation in Hanna, 2006), as well as connects to the USA-Canadian land port at the border crossing of Coutts, Alberta and Sweetgrass, Montana by way of Highway 4. The roadways command high financial priority as a lynchpin of the province's economic lifeline, with the Transportation Ministry having spent nearly CAD \$2 billion over the 2012-2013 period alone with over half of the funds devoted to highway development and preservation (Alberta Transportation, 2013). Furthermore, railways from Calgary and Edmonton allow access to the major seaports of Prince Rupert and Vancouver, which lie within 800 miles of south-central Alberta (Transportation in Hanna, 2006).

HUMASORB®-CS product has the potential to contribute value to all major areas of Alberta's economy that generate contaminated wastewater: municipal, manufacturing, mineral extraction, and especially power generation (Table 5). The effective treatment of wastewater is of particular importance to the health of Alberta's water bodies and associated wildlife habitats as surface water bodies are the primary points of wastewater discharge in the province and neighboring territories (Table 6). Metals contaminants of concern for Alberta surface waters (Surface Water Quality, 1999) that are effectively removed by HUMASORB®-CS filtration of wastewater are shown in the previous section as well as previously-reported research conducted by ARCTECH (HUMASORB™ Final Report to U.S. DOE, 2000). Moreover, the product has proven effective in removing organic contaminants such as acetone, greases, PCBs, phenol, phthalate, toluene, and xylene (HUMASORB™ Final Report to U.S. DOE, 2000). HUMASORB®-CS can be readily-integrated into existing wastewater treatment facilities at the "tertiary" treatment stage for the removal of trace metals and residual organics immediately prior to discharge and has the potential for direct application in storm water drainage systems and settling ponds. Additionally, HUMASORB®-CS can be deployed as a sub-surface barrier for groundwater contaminated sites.

Table 5. Major Sources of Wastewater Discharge in Canada, 2009 (Statistics Canada<sup>a</sup>, 2012)

<b>Discharge sources</b>	<b>Millions cubic meters wastewater</b>	<b>Millions gallons wastewater</b>
Municipal	6,371	1,683,040
Manufacturing	3,451	911,658
Mineral extraction	620	163,787
Thermal-electric power generation	25,838	6,825,677
Total	36,280	9,584,162

Table 6. Prairie Provinces vs. all-Canada Water Discharge (Millions of Cubic Meters) in Thermal-electric Power Industries, 2009 (Statistics Canada<sup>b</sup>, 2012 and Statistics Canada<sup>c</sup>, 2012)

	Public & municipal utilities	Surface water bodies	Tidewater	Groundwater	Other	Total discharge
<b>Prairie Provinces<sup>1</sup></b>	0	<b>1,765.4</b>	0	0	1.9	1,769.1
<b>All Canada</b>	4.1	<b>24,435.1</b>	1,396	0	0	25,838.4

<sup>1</sup>Includes Alberta, Manitoba, and Saskatchewan

Other potential market use of the HUMASORB<sup>®</sup>-CS product is wastewater treatment. It will be achieved by using as polishing an existing treatment system which do not fully comply with lower levels of contaminants now required by regulations with HUMASORB<sup>®</sup>-CS and/or as a subcomponent of existing treatment system. Thermal-electric power generation companies alone in Alberta and the neighboring Prairie Provinces provide the largest target market sector with per annum surface-water discharge rates in excess of 467 billion gallons (Statistics Canada<sup>b</sup>, 2012). Following Table 7 lists the overall market potential data for various geographies for the environmental market sectors. Projected market potential for the Alberta, Canada, U.S, and foreign were then compared to the amount of production of HUMASORB<sup>®</sup>-CS per year basis are given below. The projected single-plant annual production rate of nearly 119.5 million lbs of HUMASORB<sup>®</sup>-CS per 35,000 tonnes CO<sub>2</sub> recycled is sufficient to satisfy 23.9 billion gallons of wastewater treatment demand at application rate of 5 lbs of HUMASORB<sup>®</sup>-CS per 1000 gallons of wastewater. If its application is considered for Alberta alone, it will only treat 13.20% of Alberta's municipal wastewater or 45.96% of Alberta's manufacturing industries wastewater.

Table 7. Potential Demand for HUMASORB®-CS Product for Environmental Market Sector in Potential Target Markets

	Wastewater Produced (Billion Gallons/yr) <sup>a</sup>	HUMASORB®-CS Required (Million lbs/yr) <sup>b</sup>	Projected HUMASORB®-CS Production (Million lbs/yr)	Projected Wastewater Treated (Billion Gallons/yr) <sup>b</sup>	HUMASORB®-CS Application %
Alberta, Municipal	181	905	119.5	23.9	13.20
Alberta, Manufacturing Industry	52	260			45.96
Canada	9,584	47,920			0.25
United States	90,510	452,550			0.03
Pacific Region	27,342	136,708			0.09

a. Source:

<http://www.statcan.gc.ca/pub/16-201-x/2012000/longdesc-ct002-eng.htm>  
<http://www.statcan.gc.ca/pub/16-401-x/16-401-x2012001-eng.pdf>  
[http://publications.gc.ca/collections/collection\\_2010/ec/En11-2-2006-eng.pdf](http://publications.gc.ca/collections/collection_2010/ec/En11-2-2006-eng.pdf)  
<http://www.fao.org/nr/water/aquastat/data/query/results.html>

b. Application rate: 5 lbs of HUMASORB®-CS/1000 gallons

The high volumes of wastewaters available for treatment outside Alberta and worldwide further ensures a strong market for HUMASORB®-CS and could allow Alberta to serve as an exporter of HUMASORB®-CS based on domestic vs. foreign demand, and hence going prices, for wastewater treatment products. For instance, great demand for wastewater treatment in underdeveloped economies may render the export of HUMASORB®-CS from Alberta a more profitable alternative to domestic sale and use. The economic viability of HUMASORB®-L fitted flue gas scrubbers is assured by the sale and utilization of HUMASORB®-CS product. Based on a market research analysis in 2011 by the McIlvaine Company of Chicago for ARCTECH, water treatment costs can range anywhere from USD \$5 to USD \$122 per 1000 gallons; HUMASORB®-CS should be economical even at the lower cost basis of USD \$5 per 1000 gallons and thereby create direct economic impact of USD \$119.5 million per 35,000 tonnes of CO<sub>2</sub> captured and recycled.

HUMASORB®-CS is a durable product that can withstand the climate of Alberta whether in storage or when actively applied in the field. The effectiveness of HUMASORB®-CS as a water filter is not expected to be reduced by cold temperatures due to its adsorbent, non-reactive nature. The cross-linked beads do not dissolve or otherwise degrade in long-term contact with water over wide ranges of solution pH and can also withstand prolonged exposure to high temperatures as shown by its successful deployment in Egypt (ARCTECH Project #9916 Report 7, 2005).

HUMASORB®-CS has been shown to emerge intact from multiple freeze-thaw cycles (unpublished data). Furthermore, as a recalcitrant, aromatic-backboned solid matrix with new, extensive cross-linking, HUMASORB®-CS should be less biodegradable than soil humic substances, so breakdown by microorganisms, insects, or other life forms is not expected over the application period. Carbon in HUMASORB®-CS is therefore effectively sequestered upon manufacture. The long-term sequestration of both GHGs and toxic contaminants with HUMASORB® technology offers an approach to meet today's aspirations of total lifecycle, long-term solutions as have been embodied by the Iroquois Indians per their 7<sup>th</sup> Generation Principle to consider impacts of decisions of today on the 7<sup>th</sup> generation expected to be 140 years from now.

## **6. Design for Scale up Demo Test Unit**

This section describes design for a mobile treatment unit to build a scale up demo test unit for obtaining site specific data and design at the target site in Alberta. Based on the demo tests data, pilot plant design is established to build or retrofit target user's existing gas treatment system as a next stage.

HUMASORB® demo test unit is comprised of two major sections, the CO<sub>2</sub> absorption section and the HUMASORB®-CS formulation section, with one auxiliary section. In addition this mobile test unit will be placed inside of 40ft container. Construction materials for the reactors and tanks will be stainless steel, carbon fiber or polyethylene. Schematic HUMASORB® Process Flow Diagram is shown in following Figure 5 and design specification is presented in Table 8.

Design basis for this demo test unit are: each absorption column contains 90 gallon of HUMASORB®-L (60% of reactor volume) and flue gas flow will be kept at 45 gpm. CO<sub>2</sub> in the flue gas is assumed 12 ~ 15 mole or volume %.

*Direct Contact Cooler:* The flue gas from Fossil Fuel plant is cooled down in a direct contact cooler. First, the flue gas is drawn into the direct contact cooler. Then, cooling water is sprayed through the fine nozzles. Flue gas cools to 55 °C on direct contact with the water and then flows towards the blower suction. In the case of biogas, it directly goes to blower suction bypassing the



direct contact cooler. The flow rate of the flue gas/biogas is measured by the gas flow meter before entering the absorption reactor.

*CO<sub>2</sub> Absorption Reactors:* This mobile demo test units have multi absorption reactors working in series (three in series and one backup). When the HUMASORB<sup>®</sup>-L absorbent in the first reactor becomes near saturated, i.e. CO<sub>2</sub> concentration has reached the breakthrough point, the second reactor is connected. After that, when the outlet concentration of CO<sub>2</sub> is reached to the target breakthrough concentration, the third reactor is connected and the first reactor is disconnected for replacing the absorbent. The spent HUMASORB<sup>®</sup>-L has been transferred to the storage tank for the HUMASORB<sup>®</sup>-CS formulation.

*HUMASORB<sup>®</sup> Formulation Reactor:* Spent HUMASORB<sup>®</sup>-L is transferred to HUMASORB<sup>®</sup>-CS Formulation Reactor (R5) fitted with mixer for mixing with two cross-linking chemicals. This reactor is equipped with a mixer and a discharge pump. In this reactor different chemicals will be added to make the solid HUMASORB<sup>®</sup>-CS. The contents of this reactor will then be directed to the HUMASORB<sup>®</sup>-CS Pelletizer reactor (R6).

*HUMASORB<sup>®</sup>-CS Pelletizer Fitted with Nozzle:* HUMASORB<sup>®</sup>-CS formulation solution from R5 is metered through spray nozzles designed to produce about 2-3 mm droplets. These droplets will be dropped into HUMASORB<sup>®</sup> Pelletizer (R6) with adjustable pulley and frame system mounted on top of the reactor. This reactor is also equipped with a mixer. After curing, HUMASORB<sup>®</sup>-CS pellets will be separated from solution by screening in the catch basin. The catch basin is equipped with a sump pump that will function both for recirculating the solution and discharging the solution when required.

*HUMASORB<sup>®</sup>-CS Slow Curing & Dryer:* HUMASORB<sup>®</sup>-CS pellets that are still wet and spongy will be allowed to cure further and are dried in low temperature dryer operated at ~60 °C. The dryer is a rectangular unit that can fit multiple trays inside. It is integrated with a heater/fan combination that can circulate heated air inside the dryer. There is a vent at the top of the dryer to discharge the spent and cooled air from the unit.

*Auxiliaries:* This section has a gas monitoring unit for the measurement of CO<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub> and Hg concentration of inlet and outlet gases. A flair will be installed for biogas upgrade case.

Demo test of this technology is needed over a two year cycle period. Thereafter ARCTECH expects to establish business operations in Alberta for both replicating the use of the technology as well as for manufacturing of HUMASORB<sup>®</sup> products and servicing its use. It is envisioned about three to five years' time will be required for full commercialization of the technology in Alberta.

## Multi-Purpose HUMASORB® Process Flow Diagram

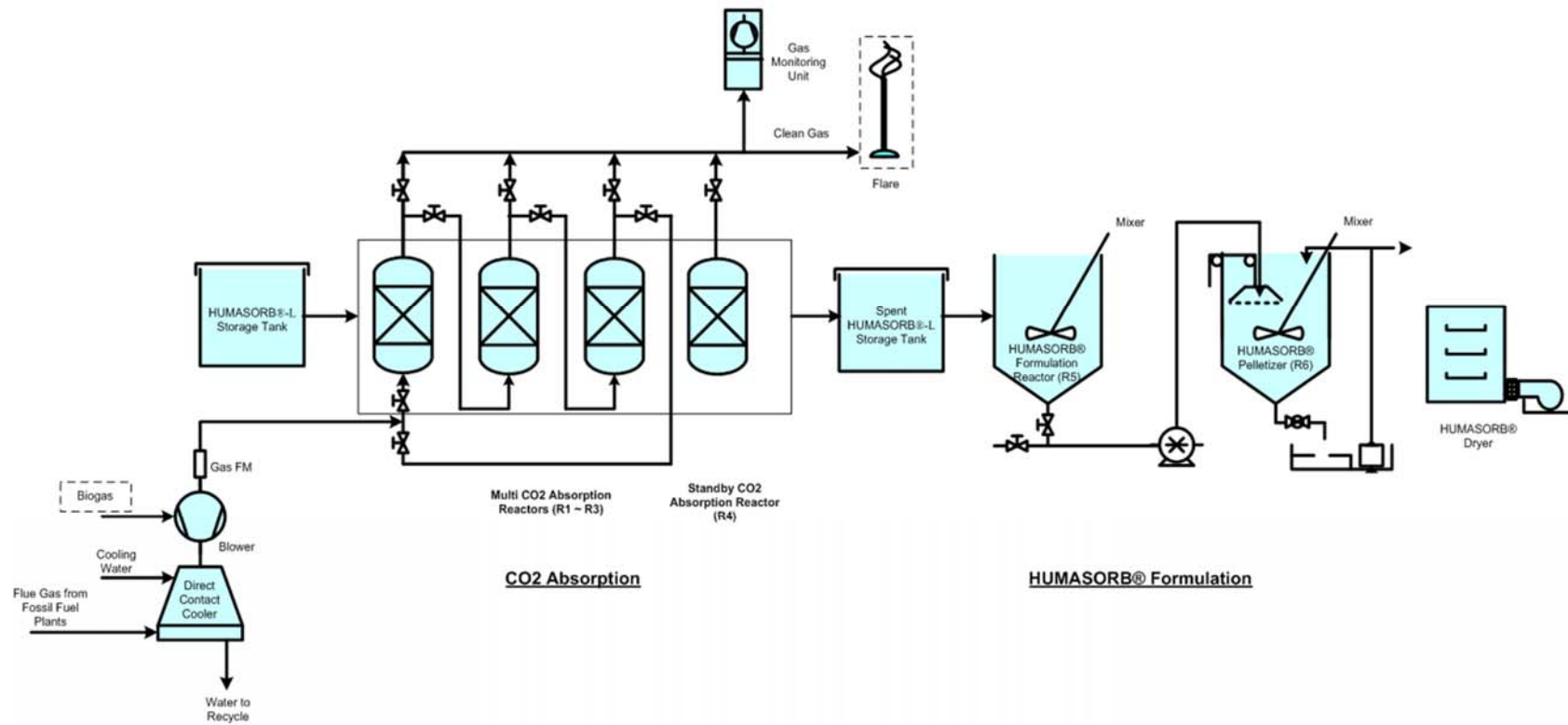


Figure 5. Flow Diagram for Multi-Purpose HUMASORB® Process.

Table 8. Design Specification of HUMASORB® Demo Test Unit

Description	Type/Size (Dia x Ht., Inches)	Capacity, Gallon	Vol. per inch of straight Ht., Gallon	Material	Design Temp
Section I					
HUMASORB®-L Storage Tank	C/42 x 60	350	6.00	PE	-
Direct Contact Cooler	24 x 36 x 24 (LxWxH)				
Blower		Flow range: up to 15 CFM; Discharge pressure: Max 10 psi		S	116 °C Max
CO2 Absorption Reactor	CBT/24 x 72	150	1.95 (Vol. of conical bottom=3.0)	SS	-
Section II. HUMASORB®-CS Formulation					
Spent HUMASORB®-L Storage Tank	C/42 x 60	350	6.00	PE	-
HUMASORB®-CS Formulation Reactor	CB/42 x 60	250	6.11 (Vol. of conical bottom=13.5)	PE	140 °C
HUMASORB®-CS Pelletizer Tank	CB/42 x 60	250	6.11 Vol. of conical bottom=13.5)	PE	140 °C
Pump	Self priming	Capacity : 42 gpm @ 30 feet height		SS	-

C: Cylindrical, CBT: Conical Bottom and Top, CB: Conical Bottom, S: Steel, SS: Stainless Steel, PE: Polyethylene

## 7. Overall Conclusion

This HUMASORB® project conducted by ARCTECH demonstrates an innovative approach of utilizing both the capture and recycling of CO<sub>2</sub> into value generating products. This project was highly successful and resulted in valuable outputs including the main conclusions described below.

- HUMASORB®-L successfully captured and absorbed CO<sub>2</sub> as well as SO<sub>x</sub>, NO<sub>x</sub>, metals, and particles/soot from flue gas generated by coal burning and cylinder gas. Total amount of CO<sub>2</sub> absorbed was comparable as 47.66 g and 45.99 g per 200 mL of HUMASORB®-L for both cylinder gas and flue gas from coal burning, respectively. These are equivalent to 0.902 kg and 0.87 kg per gallon of HUMASORB®-L. Overall about 1,000 gallon of

HUMASORB®-L will be required to capture 1 ton of CO<sub>2</sub> under current experimental conditions.

- Absorbed CO<sub>2</sub> in HUMASORB®-L was present in carboxylic, bicarbonate, and carbonate forms. The mass balance of absorbed CO<sub>2</sub> in the spent HUMASORB®-L as a carboxylates, bicarbonate, and carbonate was calculated to be 47.1: 35.3: 17.6, respectively. This is consistent with the result of Fourier Transform Infrared Spectroscopy (FTIR) analysis. FTIR analysis of HUMASORB®-L before and after CO<sub>2</sub> absorption verified that the CO<sub>2</sub> is bound with humic molecule as carboxylates as well as carbonate and bicarbonate.
- HUMASORB®-L was productively converted to a value added water filter, HUMASORB®-CS, by cross-linking and immobilization of spent HUMASORB®-L with cross-linking agent to make an insoluble product. N<sub>2</sub>-BET surface area of HUMASORB®-CS from spent HUMASORB®-L was 0.9222 m<sup>2</sup>/g and stable at wide range of pH conditions without re-releasing of captured CO<sub>2</sub>. The final fixed form/species of absorbed CO<sub>2</sub> in solid phase of HUMASORB®-CS was identified by high resolution X-Ray powder diffractometer to be the most abundant was calcium carbonate. Thus, after capture by HUMASORB®-L adsorbent, CO<sub>2</sub> was converted to the stable carbonate form and permanently stored in the final product of HUMASORB®-CS.
- HUMASORB®-CS from spent HUMASORB®-L after CO<sub>2</sub> absorption is effective in treating metals of concern from wastewater.
- In 2015 the Government of Alberta established the Tailings Management Framework for the Mineable Athabasca Oil Sands to support faster reclamation of fluid fine tailings. In the Lower Athabasca Region, about 976 million cubic meters of fluid tailings are contained within tailings ponds, with a net cumulative footprint of about 220 km<sup>2</sup> including dykes, berms, beaches, and in-pit ponds in 2013. Thus, oil sand operations present an opportunity to use HUMASORB®-CS for wastewater treatment. By applying HUMASORB®-CS technology to oil sands water no longer used for recycle, the water can be remediated faster supporting more progressive aquatic reclamation options than that of straight passive

reclamation. HUMASORB®-CS offers a cost-effective active treatment process with low energy intensity that can facilitate faster remediation and reclamation of process-affected waters.

- In the US, on September 30, 2015, the Environmental Protection Agency (USEPA) has finalized the Coal Solids Residues (CSRs) Rule for power plant effluent limitations. It sets the first federal limits on the levels of toxic metals in wastewater discharges from steam electric power plants. This new rule has stringent requirements for the discharge of arsenic, mercury, selenium, and nitrogen in wastewater streams from flue gas desulfurization, and requires zero-discharge of pollutants in ash transport water and mercury control wastewater. It also strictly limits arsenic, mercury, selenium, and total dissolved solids in coal gasification wastewater. Thus, the application of HUMASORB®-CS for the cleanup of wastewater that generated from power plant has considerable potential and can be readily-deployed.
- The stability study of spent HUMASORB®-L on soil to determine the potential use of spent HUMASORB®-L as a soil amendment shows that the absorbed CO<sub>2</sub> in spent HUMASORB®-L was re-released by contacting with soil with low pH of 5.6. This result reveals that HUMASORB®-CS pathway is better approach than spent HUMASORB®-L as a soil amendment for the utilization of recycling of captured CO<sub>2</sub>.
- HUMASORB® technology could address the large CO<sub>2</sub> emissions from the coal plants and insitu oil sands operation. Insitu GHG footprint is largely due to natural gas combustion for steam, in mines lots of it is from the mine fleet and other dispersed activities for which it will be difficult to apply this technology. The HUMASORB® technology approach of capturing GHG emissions from the largest sources as well as meeting the large needs of cost effective treatment of its wastewaters, will allow the Province of Alberta to meet its objectives of GHG reduction while enabling the meeting of other important environmental needs with a creative and value generating approach. ARCTECH technology will overcome these challenges that Canadian oil sands industries are confronting.

- The economic viability of HUMASORB®-L fitted flue gas scrubbers is assured by the sale and utilization of HUMASORB®-CS product. For every mega tonne of CO<sub>2</sub> captured, over 3.58 billion pounds of HUMASORB®-CS is produced that will be sufficient for the treatment of 716 billion gallons of complex wastewater. It will be achieved by using as polishing an existing treatment system which do not fully comply with lower levels of contaminants now required by regulations with HUMASORB®-CS and/or as a subcomponent of existing treatment system. Based on a market research analysis in 2011 by the McIlvaine Company of Chicago for ARCTECH, water treatment costs can range anywhere from USD \$5 to USD \$122 per 1000 gallons; HUMASORB®-CS should be economical even at the lower cost basis of USD \$5 per 1000 gallons and thereby create direct economic impact of USD \$3.6 billion per megatonne of CO<sub>2</sub> captured. Also, HUMASORB®-CS, because of its abilities to capture multiple contaminants simultaneously as well as its physical granular form, is well suited for deployment as passive sub-surface barrier for containment of contaminants in the groundwater or leaching from solid wastes such as municipal solid waste and coal ash ponds.
- Widespread adaptation of HUMASORB® technology will be easy due to the technology's scalability and replicability. It is a "bolt-on" solution for installation with the standard scrubbing systems in use by thermal-electric power plants and oil sands operations. The size and build of the scrubbing columns can be readily adjusted to fit a particular facility's operating conditions without loss to carbon capture efficiency. Even where a HUMASORB®-L system is the first scrubber to be fitted to a stack, the simplicity and adaptability of the technology ensures that a reliable engineering solution can be achieved whether a facility is old and conventional or state-of-the-art.
- Since the requirements of its use at the target sites of coal power plants and oil sands operations are similar and subject to uniform mandates, it is expected that the replication of the technology will be rapid without requiring to prove its performance at each new site. So it is envisioned that it will be deployed commercially upon introduction.
- Demo test of this technology is needed over a two year cycle period. Thereafter ARCTECH expects to establish business operations in Alberta for both replicating the use of the

technology as well as for manufacturing of HUMASORB® products and servicing its use. It is envisioned about three to five years' time will be required for full commercialization of the technology in Alberta.



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