

## Renewable and Sustainable Production of Practicable Fuel

J. A. Van Vechten\*, PureGeneration (UK) Ltd., Hillsboro, OR  
javanvec@msn.com

### Abstract:

The overall problems for the energy-climate crisis are logistics and transportation (L&T), i.e., matching the locations, times, and amounts of supply to the location, times, and amounts of demand. The solution is to produce, at renewable and sustainable (R&S) source points, a chemical fuel that is practicable to collect, transport, store, and to distribute to demand regions. The most economic new R&S source now available is that of ideally located wind turbines. With current technology, electricity from wind turbines could be used to make enough ammonia-based fuel to relieve almost all our need for fossil fuel. In particular, this paper presents the fuel potential of guanidine, guanidine-urea alloys, and guanidine-alcohol solutions that could serve as carriers for ammonia or hydrogen. The potentials of ammonia and methanol are also discussed. If the hydrogen for any of these fuels is produced by electrolysis of saltwater, the resulting NaOH byproduct can remove CO<sub>2</sub> from the atmosphere and allow for climate recovery. Meanwhile, the HCl byproduct can be used in local mining operations to produce valuable commodities, and/or it can be sequestered as chlorides. The sequestered chlorides, the carbonates, and the mined pits can be used to geoengineer hydroelectric facilities.

### Introduction:

#### *The Need for a Carbon-Negative Fuel*

It is becoming clear to increasing numbers of people that the world cannot continue to rely on fossil fuels, not just because they are non-renewable and unsustainable, but because their use is driving catastrophic environmental changes with vicious feedback effects. For example, the melting of ice reduces albedo (a measure of reflectivity) from about 80% to 5% for exposed water or about 30% for exposed land so that more energy is absorbed, further increasing the heating. As permafrost melts in polar regions, more area is covered with water, further decreasing albedo and releasing methane from the methane-ice [1]. Because methane is a much stronger greenhouse gas than is CO<sub>2</sub> and because there is so much of it in the methane-ice, its large-scale release would cause extinction of many species. Also, seawater is being acidified by the excess CO<sub>2</sub> [2]. If ocean acidification continues to the point that sea creatures can no longer make their carbonate shells and bones, then not only will the global warming accelerate, but our food web will collapse.

The challenge considered here is how to avoid catastrophe as a consequence of a century and a half of development based on non-R&S energy sources [3]. The solution will require a new energy economy and infrastructure, but most of the technologies needed are now available and adequate; developments remaining seem quite manageable.

This massive change will cost about as much as the Iraq War plus the bailout of the Banking System (several trillion dollars), but this will be an investment with lasting

value. The clear and present danger has not as yet motivated governments to drive the necessary change. However, because the energy economy is between 12% and 14% of GDP globally, there is an opportunity to make massive profits and create millions of jobs by engineering the solutions. Such economic incentives may bring about change where political reasoning has not.

#### *Sources of R&S Energy*

Available sources of solar, wave, and wind R&S energy each far exceed the amount now provided by fossil fuels. At this time wind is the technology that is being commercialized. Wind locations are rated by NASA and NREL as “poor, marginal, fair, good, very good, excellent, outstanding, or superb” depending upon average sustained wind velocity 50 m above ground [4]. Other factors that affect the quality of a site include wind turbulence, which produces torques on the rotor shaft that cause excessive wear, and the fraction of the time that wind velocity is within the range that the turbine can process. More than 27,000 MW of wind farms were constructed in 2008 [5], but almost all existing windfarms are at “marginal” to “good” locations, and are connected directly by a grid to customers willing to pay a high price for R&S electrical energy. It would be cheaper to generate wind electricity at a “superb” site and use it to make fuel there, so that neither a grid nor a grid connection is needed.

Even if it cost nothing to generate electrical energy sustainably, the problems of powering vehicles and of matching instantaneous local supply to instantaneous local demand would remain. The “intermittence problem” and the need to maintain a nearly constant grid voltage limit the direct contribution from wind to about 20% of our electrical energy, which is about 30% of total energy now derived from fossil fuels. This limit comes from the limited availability of gas turbines that can respond sufficiently rapidly to demand/supply fluctuations. Other electricity generators (coal, oil, nuclear, and hydroelectric) are all constrained, to one extent or another, by their ability to respond quickly.

To approach 100% replacement of fossil fuels, therefore, we will need to produce a fuel. When and where there is an excess of power on a grid, the fuel might be made there and then used at the same site when more power is needed. This is being explored as a means to strengthen electrical grids without new power-lines by building “Hydrogen Hubs,” although the fuel contemplated is ammonia [6]. Such opportunities are limited by the primary fuel supply.

Production of a practicable fuel will allow it to be produced cheaply at the “superb” wind locations, which are often the windward shores of islands at high latitudes, such as the Aleutians, Hebrides, Iceland, and Tierra-del-Fuego. These locations have strong wind with low turbulence much of the time, are very lightly populated so that land costs and siting objections are minimal, and permit the components to be delivered and erected from ships at minimal cost. Tropical storms and tornados do not reach high latitudes. Because fuel producing windfarms would be locally connected directly to DC electrolyzers, they would not need the expensive power electronic devices that are required for grid connections.

Consider briefly the cost of wind energy. The capital cost of a windfarm for a “fair” to “good” site is typically \$1/W. The cost for a windfarm for a superb site will be less because the rotors and towers will be shorter for a given sized generator. The power varies as the cube of wind velocity ( $v^3$ ), so a rotor designed for 80 km/h is 1/8 as long as a rotor for 20 km/h. For the same ground clearance the tower is correspondingly shorter. The shorter rotor blades can be engineered to process a wider range of  $v$ . This combines with the more constant winds at “superb” sites to imply a capacity factor of about 80% compared with a factor of about 30% at “fair” sites. The capital cost of the fuel generating windfarm without grid connection electronics should be no more than \$0.80/W. As the number of units manufactured increase greatly, the cost should drop further. While wind turbines at “good” sites with substantial wind turbulence are expected to last 20 years, turbines at “superb” sites without turbulence should last 40 years. At the end of its 40 year life the machine will need new bearings and rotors but the copper, magnets, steel, aluminum, concrete and other materials will be reused on site or recycled, so much of the initial value of a 5 MW turbine will remain. Still, investors will insist on recovering their investment in about 10 years, so we might take the capital cost to be \$400,000/MW<sub>y</sub>. There are 8760 hours in a year. Thus a 5 MW turbine at a “superb” site should generate 35,040 MWh of electrical energy. Thus the capital cost of the energy is about \$11.41/MWh. A leading manufacturer, Enercon, specifies 1 maintenance technician per ten 5 MW turbines so the maintenance cost should be about \$250,000/50 MW = \$5,000/MW<sub>y</sub>. This adds \$0.71/MWh to the cost for a total of \$12.12/MWh. Grid connected wind power is being sold (at a profit) for \$25/MWh for an “outstanding” site in North Dakota and offered at \$14/MWh at a “superb” site in Iceland; at a “fair” site the price is often \$120/MWh.

Consider briefly the magnitude of the energy market. According to Wikipedia, the World average power consumption in 2008 was 15 terawatts ( $15 \times 10^{12}$  W) and 80% to 90% of this came from fossil fuels, about 13 tW. (There are many good reasons to favor energy conservation to reduce this consumption level, but because the solution advocated here would remove CO<sub>2</sub> from the atmosphere and because this is an urgent need, it might be better to let all people buy as much R&S energy as they can afford. This also seems to be a political reality.) If the conversion of electrical energy to fuel is 54% efficient, which is what PureGeneration estimates, then 6 million 5 MW turbines are required to replace all fossil fuel. Their cost should come down with mass production, but at \$4 million each, this would cost the World \$24 trillion. 600,000 maintenance technicians would be permanently employed. The rule-of-thumb is that wind turbines should be spaced at 3 times the rotor diameter so as not to interfere with one-another. Although the rotors for the “superb” locations would be much shorter than those used at present sites, it might be prudent to space them at 200 m intervals so that there would be 25 turbines per km<sup>2</sup>. Then the World’s windfarms would extend over 240,000 km<sup>2</sup>. The superb sites of the Aleutians extend about 5,000 km, so if farms were 48 km wide, they could supply the World. (Of course, this would be neither practicable nor politically viable; there are too many other “superb” sites closer to important markets and belonging to other nations.)

The obvious fuel that can be produced from electrical energy is hydrogen from the electrolysis of water. Recent improvements in electrolyzers have dramatically reduced

the cost of this [7] from a sales price of \$2000/kW in 2003 to a low volume manufacturing cost of \$164/kW in 2007. However, the physical properties of elemental hydrogen imply overwhelming L&T problems [8]. The hydrogen must therefore be reacted into some practicable compound.

There are evident two practicable families of fuel; one is methanol based [9] and the other is ammonia based [6, 10-13]. Methanol is a high octane liquid that can fuel air-cooled race car engines. It can also be converted to dimethyl ether, which is a high cetane diesel fuel. It can be used in direct methanol fuel cells or reformed to provide H<sub>2</sub> for H fuel cells. However, it is so toxic that major auto makers refuse to consider it for general use. Furthermore, methanol production from electrical energy, CO<sub>2</sub>, and water still requires development, although this is a subject of ongoing research [7,9]. It is produced from wood and other biomaterials but these are not produced in sufficient amounts to replace all fossil fuel. (Note that a human diet of 2000 kcal/day equals 100 W and 1 metric horsepower is 750 W.) Methanol is now relatively expensive [13]. If a practicable method to produce methanol from electrical energy can be developed and its cost reduced, it would be possible to convert it to conventional hydrocarbon fuels that are less problematic and in common use [9].

In contrast, the technology to produce ammonia from electrical energy, air, and water is mature (electrolysis of water followed by the Haber-Bosch process).

Further, electrolysis of saltwater removes CO<sub>2</sub> from the atmosphere [14]:



The H<sub>2</sub> is then used for production of ammonia or methanol, and the NaOH is reacted with CO<sub>2</sub> to form baking soda or washing soda:



or



There are markets for both commodities, but demand is a tiny fraction of the quantity that would be produced if enough hydrogen were produced to replace 100% of fossil fuels, whether by methanol-based or ammonia-based fuels. The remainder could be heaped in arid locations or covered to sequester the carbon dioxide and to sculpt landscapes. An inexpensive alternative would be to disperse the NaOH into seawater to reverse ocean acidification, but one would need to take care not to harm sea-life.

There is an \$8 billion/y market for 40 million tonnes of HCl, which, if it were cheaper, might also capture part of the larger market for sulfuric acid. However, the amount of HCl produced replacing all fossil fuels would be orders of magnitude greater than present markets for hydrochloric and sulfuric acids combined. One would wish to avoid the

expense of transporting the HCl any great distance from the sites where it is produced, presumably the lightly inhabited shores at high latitudes. Many of these sites have steep hills and mountains. It is suggested that the acid be used in the mining and processing of rock and ore near the generation sites to obtain valuable commodities. (An Icelandic concern has begun processing olivine using imported HCl at current prices [15].)

Simple ammonia has been used as a transportation fuel since at least 1933 [10], fueled Belgian buses during WW2 and the X-15 airplane [11,12]. It can be used in both Diesel and spark-ignited engines. It can fuel solid-oxide fuel cells and gas turbines (with some modification from natural gas designs [16]). It can be cracked or electrolyzed to provide hydrogen for hydrogen fuel cells [17]. It is now arguably the lowest cost option [13]. (Almost all ammonia is now made from foreign natural gas that has too severe L&T problems to come to market as methane. For US corn growers it is shipped as ammonia despite the substantial L&T expenses. For all other customers it is converted to urea or other ammonium compounds. With the recent advances in electrolyzers it now seems that it would be less expensive to produce ammonia in the US Corn-Belt from wind even at less than “excellent” sites [18]. Ref. 13 used a current price for ammonia from natural gas delivered to point of use.)

A persistent objection to the use of ammonia as fuel has been concern over the production of NO<sub>x</sub>, but several studies show that these concerns are overblown [19]. There are two sources of N that might result in NO<sub>x</sub> – the N<sub>2</sub> in the air and the N in the compound. Because NO<sub>x</sub> formation is endothermic and ammonia burns at a lower temperature than the fuels it would replace, NO<sub>x</sub> formation from the air is much less for ammonia than for fossil fuels. NO<sub>x</sub> formation from the N in ammonia is a problem for certain operating conditions; incomplete burning of ammonia is a bigger problem that has sometimes been mistaken for NO<sub>x</sub> formation. These problems can be managed by proper control of the engine [19] or eliminated by cracking or electrolyzing the ammonia and burning the hydrogen [17].

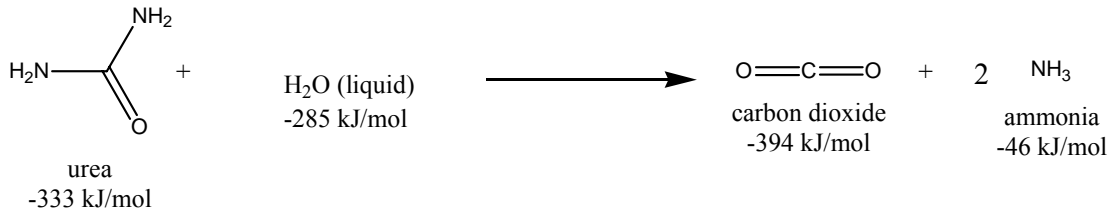
However, ammonia boils at -33°C at 1 bar so it must be pressured to 14 bar at room temperature to keep it in the liquid state. Its liquefaction requirements are similar to those of propane. Many special ships would need to be built to transport it to market from distant islands. It is highly toxic.

Solution:

Ammonia can be converted to relatively safe and convenient solids for transport, storage, and distribution and then converted back to ammonia at the time of use. Two options have been advanced; one is urea based [20,21] and the other is guanidine based [22,23].

More than 100 million tonnes per year of urea (CON<sub>2</sub> H<sub>4</sub>) are produced commercially by combining two units of ammonia with one of CO<sub>2</sub> and extracting one unit of water. Urea is a non-flammable, non-toxic solid with a melting point of 133°C. It can be converted back to ammonia by adding hot water (178 kJ/mole), which may come from oxidation of

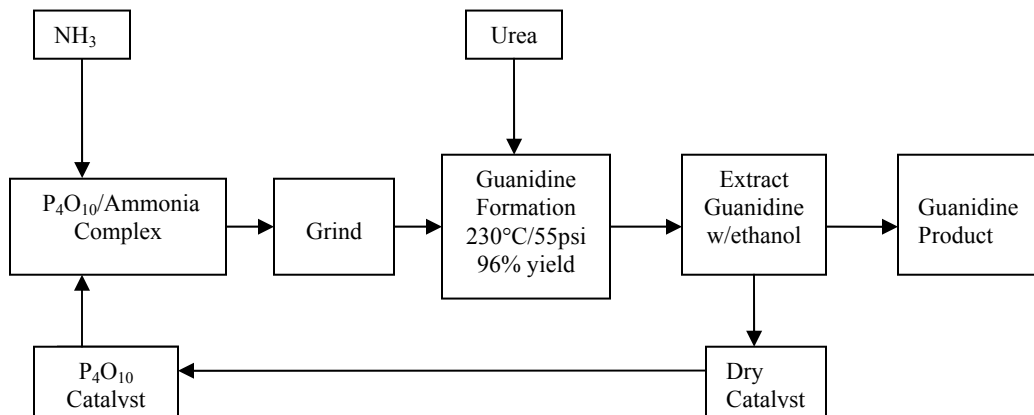
1/3 of the ammonia, with a catalyst. The ammonia releases 809 kJ per mole of urea when oxidized. Thus, its use as a sustainable and renewable fuel is being advocated [21].



$$\Delta H = +178 \text{ kJ/mol}$$

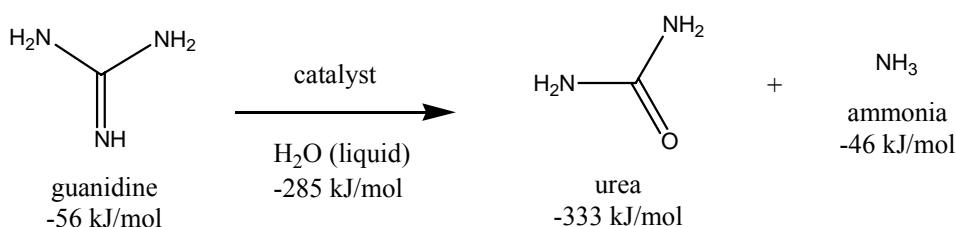
Problems with the use of urea as fuel include: a) its energy density and specific energy are lower than the Freedom Car benchmarks; b) while the solid phase is convenient for storage and transportation, one would want the molten phase for plumbing within an engine and 133°C is inconveniently high; and c) one might want to liquefy it by combining it with liquid, but its solubility is poor in ethanol and limited in water.

Guanidine (CN<sub>3</sub>H<sub>5</sub>) can be made by combining three units of ammonia with one unit of CO<sub>2</sub> and extracting two units of water [24, 25]. Guanidine is a highly alkaline and hygroscopic but non-flammable and non-carcinogenic solid with a melting point of +50°C.



Shaver Process to make guanidine [25].

Guanidine can be converted back to ammonia by addition of 4/9 of the water from the oxidation of the ammonia and less heat than required for urea. The first step of this conversion is exothermic, which is convenient for cold starting. Its energy density and specific energy substantially exceed the Freedom Car benchmarks [23]. Its melting point is convenient for plumbing engines. It is completely soluble in ethanol and in water. It can be alloyed with urea. It can be coated with urea. Up through the 1960s it was produced on an industrial scale, particularly as a precursor for melamine. Since melamine has gone out of fashion, its production has declined.



$$\Delta H = -38 \text{ kJ/mol}$$

First step of guanidine to ammonia conversion.

The production of 1 tonne of guanidine by electrolysis requires [23] 10 MWh of electricity. The 13 tW World rate of (fossil) fuel consumption would require  $2.1 \times 10^{10}$  t/y of guanidine for 100% replacement at 54% efficiency. A fixed cost estimated to be \$43 must be added to the cost of energy. If the electricity costs \$14/MWh, the total cost estimate is \$183/t. 1 t of guanidine provides the equivalent of 148 gallons of gasoline (148 GGE). Thus, the cost estimate for “superb” sites is \$1.24 / GGE. If the cost of electricity were \$25/MWh, as currently in North Dakota, the cost would be \$1.98 / GGE.

Consider the cost of transport to market. Spot rental rates for bulk carrier ships fluctuate wildly with supply and demand but \$10,000/d for a 50,000 t ship that can sail at 20 knots is reasonable. Suppose the ship spends 1 day loading, 1 day unloading, and 10 days sailing each way. Thus it can carry 50,000 t 8,800 km for \$240,000, assuming it sails back with no cargo. This adds \$4.80/t or \$0.03/GGE to the cost of the fuel. Transportation of  $2.1 \times 10^{10}$  t/y in this way would require  $4.2 \times 10^5$  voyages/y. If each ship makes 15 voyages per year, 2,800 ships are required. It may be practicable to convert existing oil-tankers to carry R&S fuels and thus to reduce transportation costs.

Should methanol, or urea, or guanidine be made with  $\text{H}_2$  from freshwater,  $\text{CO}_2$  from the atmosphere, and wind energy, then the fuel would be carbon neutral. Because the greenhouse gas level is now past the point that catastrophic climate change has begun, carbon neutrality is not enough; we must reduce the level of  $\text{CO}_2$  to that of the 19<sup>th</sup> century. As noted, this can be done by electrolysis of saltwater to provide the  $\text{H}_2$  with co-production of NaOH.

Transportation of HCl is so expensive that it is now generally made by saltwater electrolysis at sites where it will be used, so the “Hydrogen Hub” concept might serve present chlorine markets by electrolyzing saltwater (and by replacing ammonia storage in urban areas with guanidine storage).

The islands at high latitudes that are the best sites for the wind farms often have basaltic mountains and sometimes have exposed olivine on slopes. Many also have substantial amounts of ores but may not be economic to mine if materials such as acids need to be shipped in. HCl produced nearby as a byproduct of fuel production should be less expensive. The mining process could sculpt out a succession of pits connected by trenches on these slopes as the minerals in the rocks are mined to produce valuable

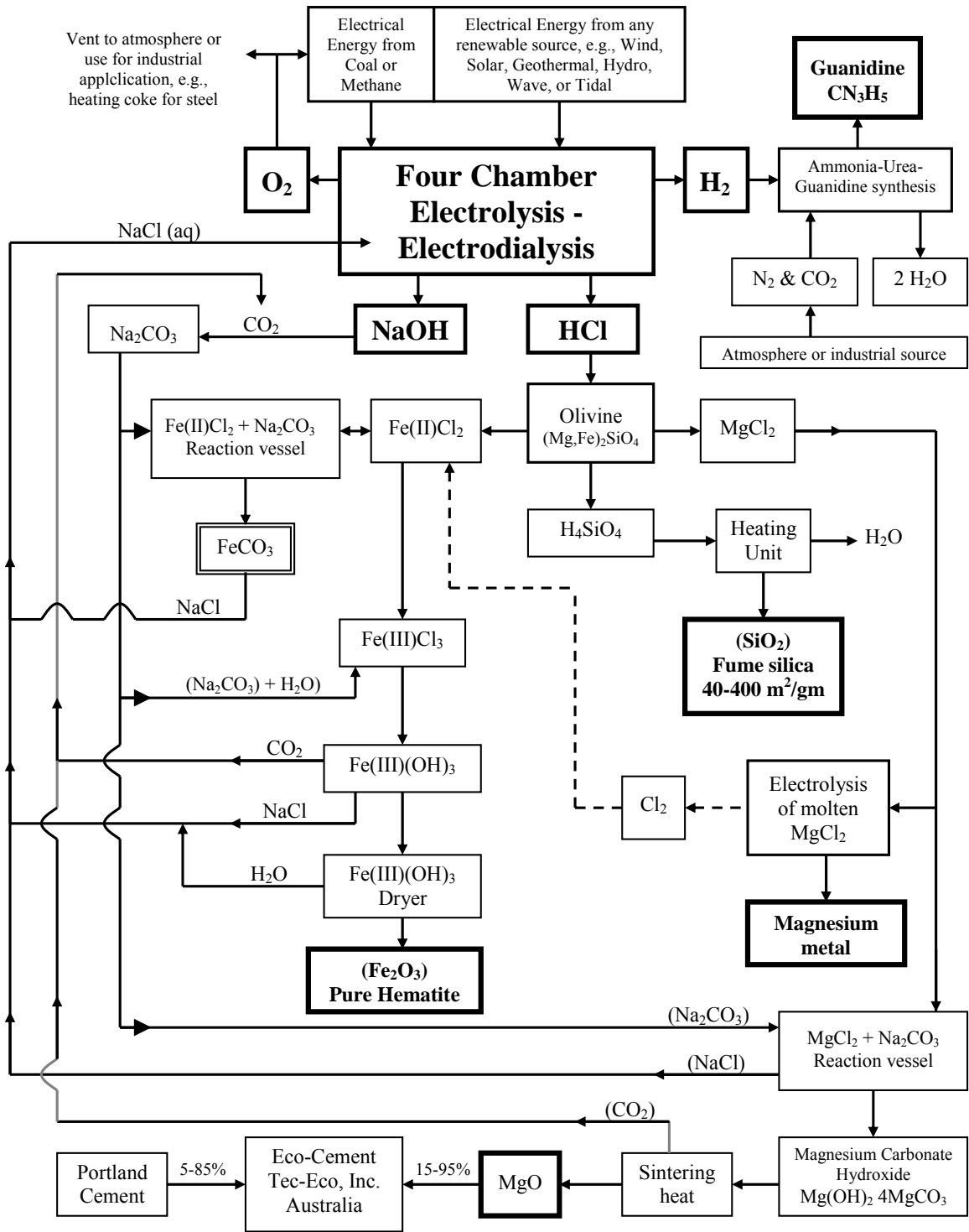
commodities. The material that is mined out and processed but not exported as an economic commodity could be heaped around the pits and trenches. This material would sequester chlorine from the conversion of various oxides to chlorides by the HCl. To this would be added the carbonates that sequester the CO<sub>2</sub> from the atmosphere. This would gradually produce hydroelectric facilities that would use the abundant precipitation at many of these sites.

The figure below illustrates a process for olivine that extends Gunnarsson's process for the production of fume silica [15,26], which has a surface to mass ratio of 40 to 400 m<sup>2</sup>/gm. The HCl first converts olivine, [Mg,Fe]<sub>2</sub>SiO<sub>4</sub>, to SiO<sub>2</sub> and H<sub>2</sub>O, and to MgCl<sub>2</sub> and FeCl<sub>2</sub>, which are not suitable for sequestration. The MgCl<sub>2</sub> and FeCl<sub>2</sub> can be reacted with the Na<sub>2</sub>CO<sub>3</sub> to form MgCO<sub>3</sub> and FeCO<sub>3</sub>, which are good for sequestration, and NaCl. A portion, adjusted to market conditions, of the chlorides can instead be processed to produce iron ore, electrolytic iron, magnesium metal, magnesium carbonate hydroxide, MgO, and Si using some of the electrical energy generated at these sites. Large amounts of MgO can be used to replace CaO in the making of cement, which would reduce a major contributor of CO<sub>2</sub> to the atmosphere [27]. It would also produce better cement that is less damaged by salt.

Processing of basalt could provide Al, K, and Ti commodities, as well as Fe, Mg, and Si.

However, the replacement of all fossil fuel would produce amounts of these oxides that would exceed their markets. The excess Al<sub>2</sub>O<sub>3</sub>, MgO, and SiO<sub>2</sub> might be used as aggregate to provide high albedo concrete for civil structures and pavements. Increasing urban albedo to about 80% would dramatically reduce the need for air conditioning and slow global warming. As noted above, transporting these very high albedo materials by sea would cost only about \$4.80 /t.

The mining option and geoengineering would provide for future hydroelectric power. Initially this would provide back-up power for the electrolyzers, but eventually enough hydroelectric power might be produced that the wind turbines would no longer be needed.



## Conclusions:

Renewable and sustainable electrical energy suffers from problems of logistics and transportation. These problems could be solved by using the electricity to produce an easily stored and transported chemical fuel. This paper argues that:

- Wind energy generated on high latitudes shores is the most practicable way to power fuel production.
- Including electrolysis of saltwater as a step in fuel production removes CO<sub>2</sub> from the atmosphere, reversing atmospheric effects of past fossil fuel combustion. The HCl byproduct of electrolysis can be used for local mining and to create future hydroelectric facilities.
- Methanol would provide fine fuel but needs breakthrough for production from electricity.
- Ammonia is fine fuel but has problems of logistics and transportation.
- Storing ammonia in the form of pure guanidine and mixes of guanidine, urea, and alcohol solve the L&T problems of ammonia.
- NO<sub>x</sub> concerns with ammonia, urea, and guanidine can be eliminated by electrolysis or cracking to hydrogen, or by proper control of engines.

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\* The author is one of the founders and board members of PureGeneration; he is a Professor Emeritus of Electrical Engineering at Oregon State U. and was formerly at IBM Research, Bell Laboratories, and US Naval Research Laboratory. PureGeneration is a for-profit UK corporation concentrating on the guanidine-based fuels, the sequestration of CO<sub>2</sub>, and the use of HCl for mining options discussed herein.

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[3] Cf., e.g., Paul Brown, *Notes from a Dying Planet, 2004-2006* (iUniverse, Bloomington, 2006); Tim Flannery *The Weather Makers* (Atlantic Monthly Press, New York, 2006).

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- [19] Cf., e.g., for spark ignited engines running on ammonia within emission limits in California, Ted Hollinger and Don Vanderbrook at <http://www.energy.iastate.edu/Renewable/ammonia/ammonia/2007/HEC.pdf> ; Ted Hollinger at [http://www.energy.iastate.edu/Renewable/ammonia/ammonia/2008/Hollinger\\_2008.pdf](http://www.energy.iastate.edu/Renewable/ammonia/ammonia/2008/Hollinger_2008.pdf) ; for Diesels see Aaron Reiter and Song-Charng Kong at [http://www.energy.iastate.edu/Renewable/ammonia/ammonia/2007/Kong\\_NH3.pdf](http://www.energy.iastate.edu/Renewable/ammonia/ammonia/2007/Kong_NH3.pdf) .
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