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Boron as a storage medium for solar energy

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Abstract

The use of Boron as an energy storage medium in the framework of solar energy systems development is suggested, highlighting its potential advantages. The issue which is considered here is mainly that of reducing the energy waste connected with power transfer from areas of high solar energy productivity to highly industrialized areas, such as those of Europe, where the energy is needed. Both the production and transfer of Hydrogen or the build up of power lines give rise to an energy loss which can be up to 50% of the produced energy. A cycle is described in which Boron is used as a means to store and transport solar energy from a production site to the location where the energy stored in Boron will be used. This cycle would solve the long range transport and long term storage problem, which are two critical issues of a prospective solar energy economy. We describe how the use of Boron could indeed be a solution to the problem which is both energetically favorable and environmentally safe.

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1. Introduction

The power from the Sun, as electromagnetic radiation, on each unit surface of the Earth perpendicular to the Sun direction, is, outside the atmosphere, about 1,36 kW/m², with a peak power centered in the middle of the so-called visible region (wavelength 500 nm) [1]. This is the ultimate energy source for the Earth, since wind power, waves power and even energy stored in Carbon and oil, all comes from the Sun. Energy source independent from the Sun are geothermal energy and nuclear energy. Unfortunately, nuclear energy from fissile elements presents severe risks and cannot be considered a long lasting energy source [2]. Maybe worst, the process to obtain energy from Hydrogen nuclear fusion is not, at the present time, a practical and efficient technology. It can be quite effectively defined as perpetually 30 years away, because of breakthroughs announced with monotonous regularity and

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regularly dismissed. Geothermal power is cost effective, sustainable and environmentally friendly and recent technological advances have expanded the range of viable resources. But, despite Earth's geothermal resources be in principle adequate to supply humanity's energy needs, only a very small fraction may be profitably exploited. Geothermal energy must therefore be considered an help and not the solution of the mankind energy supply problem [3,4].

The widespread knowledge about these facts, together with the recognition that fossil fuels will not last forever [5] and that a Carbon-free economy would be a much better choice for the environment, has spurred in the last decades the development of solar energy [6]. Moving from a fossil fuels to a solar energy economy would get rid of most of the problems connected with pollutant emission of harmful substances and greenhouse gases [7]. Not to mention the problems connected with political conflicts caused by their volatile prices.

One of the most interesting options to obtain energy from the Sun is to build large plants where light from the Sun is collected and used to directly obtain electric energy or fuels like Hydrogen. As regard the better choice of solar energy production sites, the potential importance of desert areas is widely recognized. There are, for instance, very good reasons for the localization of solar power plant at places like the south coasts of the Mediterranean sea (see figure 1). Large unused areas with less cost and no competition with other uses like agriculture or nature maintenance; sun shining nearly every day of the year. The latter is particularly important for the success of processes using Concentrated Solar Power, which is more dependent on purity of atmosphere and the amount of sunny days than on the amount of solar radiation reaching the ground (which is higher at low latitudes). South Mediterranean regions present very low cloudiness in summer and also low in winter.

The main problem to be addressed for a large scale solar energy production in desert areas is how to store and transport the energy from production to the utilization areas. None of the current solutions can be considered fully satisfactory. As regard electric energy, the drawback is the relevant cost of a power line plus the energy loss over long distances. The overall losses between the power plant and consumers is estimated to be above 6% [8]. Unfortunately, this is computed for an average distance between plant and consumers in the range of 100-200 km. The longer the distance, the greater the losses. Furthermore, an energy storage system must still be used if any excess produced energy has not to be lost.

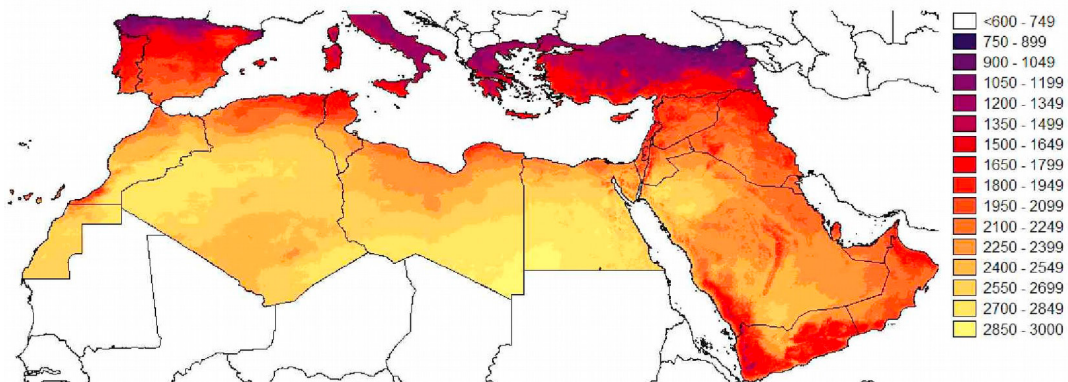


Figure 1. Annual direct normal irradiance in the Mediterranean region in the year 2002 in (kWh/m²/yr).

An international foundation, the Desertec Foundation [9], has been established, with the mission to promote the large-scale production of solar and wind power in the desert regions of the world. Among other projects, a solar plant (160 MW electric power) has been financed and built by this foundation in Ouarzazate, Morocco, to produce electric energy which was in origin to be transferred to Europe by High Voltage Direct Current (HVDC) transmission. Despite its apparent simplicity and economic convenience, this project is facing many problems, mainly due to the high costs of realizing HVDC transmission lines (those already existing, like the submarine power line below Gibraltar strait cannot stand the extra power produced by the new solar plants). As a consequence, the Foundation is now more concerned with the needs of countries of North Africa and the forecasts are that imports to Europe will not take place on a large scale until after 2030.

The alternative method currently envisaged is that to store and transport energy into Hydrogen [10]. Three

alternative routes are possible to transport Hydrogen [11]. 1) In gaseous form with a pipeline, which is an expensive investment and can be justified only by very large amounts of Hydrogen production. 2) In liquid form. Then a cooling down to about 20 kelvin is required, followed by an heating at destination. The liquefaction process is energy intensive, with an energy consume of more than 30% of the energy stored in Hydrogen. With a critical temperature of 32 K, above which Hydrogen is a gas regardless of the applied pressure, liquid Hydrogen containers are open systems to prevent overpressures. Considering therefore an Hydrogen evaporation of about 2% per day during transportation and the energy request for the gassification once at destination, a 50 % loss of the stored energy is easily computed [12,13]. 3) Metal hydride storage. Several metal based compounds, such as LiB, LaNi₅ or Mg₂Ni absorb Hydrogen in a reversible manner [14], yielding hydrates (LiBH₄, LaNi₅H₆ or Mg₂NiH₄). Usually, Hydrogen can be stored and released with a temperature and/or pressure change and, in some cases, Hydrogen density in hydrides can be higher than that of liquid Hydrogen. But, despite much research, which is still in progress, a system sufficiently cheap to produce, with high Hydrogen storage density and that bind Hydrogen with low binding energy (less than 20–25 kJ/mol H₂) is still lacking [15].

Another possibility would be to store the energy into hydrocarbons, which have in many cases an high energy density per unit mass and volume. But since there is a growing concern about the environmental risks of the use of hydrocarbons, this cannot be the preferred solution. So the issue is still open and new solutions are to be found.

2. Boron solution

Boron might be part of the solution. This light element can be regarded as a promising energy source. The general idea is that of using concentrated sunlight to extract metals from their oxides and has been originally proposed by several authors, mainly as a possible alternative to fossil fuels in the automotive [11,16,17]. In the following, the concept of Boron utilization will be reviewed and discussed, in which Boron is used as a means to store and transport solar energy from a production site to the location where the energy stored in Boron will be used. This cycle will ease the long range transport and long term storage problem, which are two critical issues of a prospective low Carbon economy. More precisely, what is suggested is that the energy from the Sun obtained from large plants located in desert areas be stored in Boron trough Boron oxide reduction. Then Boron will be transported to large industrializes areas where the energy stored will be turned into electric energy or mechanical power or eventually used to produce Hydrogen. The energy release process yields Boron oxide, which will then brought back to the solar plant to be again reduced to Boron, closing the cycle.

Producing electricity from Boron and subsequently distributing it to the users also require a power transmission system, which has losses. Yet these losses in the transmission system from the high voltage grid through step-down transformers to the users are lower than those due to thousands km long power line from a solar plant in a desert area to a Northern Europe industrialized area (It is something like 100-200 km against 2-3 thousands km.). Therefore the Boron cycle is competitive in this respect to direct electric energy production.

A candidate solution should present low risks during handling and transportation. In this respect, Boron is surely promising. Both Boron and B₂O₃ are harmless substances, simple to handle and transport. If, for instance, a container ship transporting Boron or B₂O₃ would sink, there would not be any ambient disaster, unlike the case of a petrol tanker ship. Boron and B₂O₃ would sink with the ship and stay harmless on the sea bottom (B₂O₃ in effect would slowly dissolve. But as far as the sea already contains, dissolved, large amounts of boric acid, nothing dangerous would happen with a little more). They could even be rescued.

As regard fire risks, Boron ignition in air is very hard to happen and a piece of it could be heated to red incandescence in air without burning. Boron combustion in (pure) Oxygen is without any release to the ambient. When Boron and Oxygen react, B₂O₃ is the only reaction product. Nothing else, except energy. Oxidation of Boron was investigated for the last decades in literature as theoretical and experimental studies [18,19,20]. Those studies showed that the surface interaction between Boron and Oxygen determines and delays the reaction rate because of B₂O₃ formation which is covering the surface of the Boron particles. Removal of this B₂O₃ layer is the crucial part of the complete combustion of Boron. According to Glassman et al. [21], the Boron ignition process starts with the injection of Boron into a hot oxidizing gas medium. Boron is covered with a very thin oxide layer. During the vaporization of the oxide layer Boron goes into a heterogeneous oxidation process which produces Boron oxide and heat. With the increase of the temperature to a certain value, the rate of oxide vaporization exceeds the production of

oxide layer and the ignition eventually occurs [22].

In summary, it can be stated that there are no serious risks with handling and storing Boron. Neither there are with Boron Oxide (a white, glassy solid, almost always found in nature in the amorphous form) which, being an oxide, is even safer than Boron both for handling and storing.

Boron is a light metal and its energy release per unit mass is higher than that of gasoline. Noteworthy, Boron combustion is also Oxygen sparing. 1 Gjoule release requires less Oxygen than Carbon or gasoline and produces less ashes [11,23]. The ashes (Boron oxide) are solid at room temperature: do not disperse into the environment, can be easily collected and, as already stated above, re-used.

As regard Boron availability, it must be recalled that Boron does not appear on Earth in elemental form but as a compound. Although it is a relatively rare element in the Earth's crust, representing only 0,001% of the crust mass, it can be highly concentrated by the action of water, in which many borates are soluble. Its main uses, as Boron trioxide, are in borosilicate glasses, ceramics and refractory objects; as elemental Boron: pyrotechnic flares and neutron absorber. In small quantities Boron is essential for the cell walls of plants.

In the world, Turkey and USA have important Boron mines. In terms of total reserve basis, Turkey has a share of 72%. Other Boron mines are in Argentina, Chile, Russia. Total world Boron reserves on the basis of B₂O₃ content are 370 million tons proven; 800 million tons probable and possible, as a total of 1170 million tons.

If 10% of the Boron reserves were devoted to solar energy applications, an energy release through combustion of $(1,17 \cdot 10^{11}) \text{ kg} \times (5 \cdot 10^6) \text{ J/kg} = 5,85 \cdot 10^{17} \text{ J}$ could be obtained ($5 \cdot 10^6 \text{ J/Kg}$ is the energy released in combustion with pure Oxygen by 1 Kg Boron). If the Boron recycle could take about 1 month, a continuous thermal power of $2,3 \cdot 10^{11} \text{ watt}$ or 0,23 TW would be possible. So, for instance, there is surely enough Boron on Earth to satisfy the overall electric energy needs of the whole Europe or North America.

It must be also considered that the use of Boron as an energy carrier would not only be an important step for the exploitation of solar energy but will also promote a close cooperation between highly industrialized areas and other regions, such as those of north Africa. During the second High Level Meeting of the Africa-EU Energy Partnership that took place in 2014 in Addis-Ababa [24], the priorities for the energy collaboration between the two continents have been defined. Access to reliable, environmentally and economically sustainable energy in a world of constantly decreasing resources is one of the priority challenges for the 21st century. Two targets, to be reached by 2020, seem to be of the highest priority: to bring access to modern and sustainable energy services to majority of Africans, and double the capacity of cross-border electricity interconnections, thus increasing trade in energy while ensuring adequate levels of generation capacity [25].

Table 1. Energy release of Boron oxidation compared with that of other relevant cases. Data refers to single mol and weight unit oxidation. Since gasoline is a mixture of several chemicals, in the last line of the table it is reported the enthalpy variation of a compound representative of the mixture behavior.

Reagents	Products	$\Delta H_{573 \text{ K}}$ (kJ/mol reagent)	$\Delta H_{573 \text{ K}}$ (kJ/g reagent)
C(s)+O ₂ (g)	CO ₂ (g)	-394	-32.8
2H ₂ (g)+ O ₂ (g)	2H ₂ O(g)	-245	-121
2Al(s) + 1,5 O ₂ (g)	Al ₂ O ₃ (s)	-838	-31
2B(s) + 1,5 O ₂ (g)	B ₂ O ₃ (s)	-635	-58.8
C ₈ H ₁₈ (l)+12,5 O ₂ (g)	8CO ₂ (g)+9H ₂ O(g)	-270	-2.4

Although the basic properties of Boron are known from long ago, only recently, as a consequence of several facts, time has become ripe for a possible use of this element as an energy vector: a continuous reducing price of pure Oxygen; development and testing of many concentrated solar energy plants all around the world; a general interest for the production of large scale amounts of solar energy; a growing literature about Boron and Boron oxide reactions; awareness of initially underestimated problems with other energy vector transportation systems.

3. Energy release

Elements like Aluminum, Boron, Magnesium, Zinc and others, chemically react with Oxygen exothermally, that is burn with it. Some of them very energetically [26]. In particular Boron is interesting, having the highest volumetric heating value because of very strong bond strength of Boron with Oxygen. Metal oxidation yields amounts of energy comparable to that of hydrocarbons. In the case of rockets, for instance, where Oxygen as well as the fuel must be lifted, it is advantageous to use metals rather than other fuels. But why to choose Boron for solar energy storage and transportation? Mainly because it represents the best compromise between energy density, handling and transport risks, availability, oxidation and reduction needs, environmental safety.

In particular, Boron trioxide, with a formation enthalpy of about -1270 kJ/mol, represents a fairly deep chemical well. This means a considerable energy release during oxidation, which, in turn, implies a rather difficult deoxidation process. The Aluminum oxide formation enthalpy is even larger in modulus: about -1680 kJ/mol, and the reduction process correspondingly more difficult. At the opposite, metals like Magnesium have a too low enthalpy well (e.g. -363 kJ/mol for Mg).

3.1 Pure Oxygen combustion

A thin Boron rod won't burn in air, even if put in a flame. Only when put in pure Oxygen under pressure it will burn, with a maximum flame temperature of more than 4600 K. In this case, Boron combustion yields B_2O_3 and nothing else, according to the following equation:



At these very high combustion temperatures, the process could easily leads to fouling of the internal surfaces of a combustion chamber. In air it would also produce Nitrogen oxide pollutants. A better solution is probably the use of fine Boron particles and especially nanoparticles, which burn faster and more completely at lower temperatures with no gas phase combustion. The particles oxidize fast enough and never reach the peak combustion temperature. The advantage is that if the temperature is sufficiently high to achieve a good energy efficiency but not so high that ceramic materials such as Alumina (Al_2O_3) or Zirconia (ZrO_2), usually expensive, are required to contain the combustion, less expensive materials such as steel can be used for the combustion chamber.

In any case, using Boron we are forced to a burning process without emissions. Boron is too scarce to be released in the atmosphere and combustion in air would not be environmentally safe, because of Nitrogen oxide formation and Boron oxide release which, in turn, could yield acid rains. The fuel must be put into a closed chamber with pure Oxygen and the combustion ashes must not be dispersed into the ambient but collected to be used again. This in turn requires the development of a combustion vessel specifically engineered for this purpose. In fact, pure Oxygen systems pose significant fire and explosion risk to equipment and personnel if a loss of Oxygen containment occurs [27]. Vessel walls, components and piping must be designed carefully in order to withstand the operation conditions. Broadly speaking, the combustion vessel will comprise a heat exchange system, Boron oxide collector, Boron inlet system, Oxygen inlet system plus a number of control systems. This apparatus should be able to withstand the operation temperatures and pressures for periods of the order of thousands of hours.

Combustion in pure Oxygen is usually more expensive than air combustion mainly because of the cost of pure Oxygen, which is about 10-15 % in terms of energy, plus the cost of the more demanding materials due to the higher flame temperatures. But much of these costs are compensated if the treatment of the pollutants produced by air combustion is taken into account. Another disadvantage is the reduced heat transfer due to the flow of less gas (roughly speaking 1/5 of the air required for the same amount of fuel), compensated by an higher thermodynamic efficiency due to higher flame temperatures and to reduced volumetric requirement, again leading to improved efficiency.

As mentioned in section 2, the first suggestions regarding the use of Boron as a fuel were concerned with automotive systems [11,16,17]. Boron could be oxidised on-board of vehicles, replacing gasoline. Two oxidation routes can, in principle be implemented: combustion according to (1) or reaction with water to produce Hydrogen, to feed a fuel-cell engine or even an internal combustion engine. According to us, both have at present time some difficulties. As regard direct combustion, the first problem is the need of a portable and sufficiently pure Oxygen

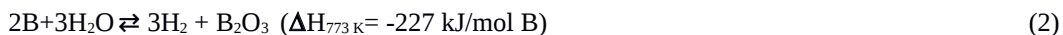
supply.

The problem with automotive applications is mainly the price of such vehicles. Both an Oxygen reservoir or an Oxygen supply device based on air separation are expensive, especially on board of a vehicle. The cost of developing a small size, robust, maintenance free solution is high and it is hardly imagined that an industry would invest on such a system. Not to mention the costs of a filling station infrastructure and that of a small size combustion engine. A better solution, with much lower development costs, would be therefore to burn Boron in an industrial plant in order to produce electric energy (or Hydrogen). What is prohibitively expensive or dangerous on a car becomes affordable in a plant because of large scale production costs reduction. For instance, in a plant a pure Oxygen supply would not be nor an economic neither a weight problem. An Oxygen supply unit inside the plant would provide Oxygen and the maintenance required for the combustion chamber could be easily performed without the drawbacks of a car.

3.2 Hydrogen production

It is worth mentioning the use of Boron to produce Hydrogen to either Fuel Cells or internal combustion engines because this alternative to combustion could even become the most attractive and extensively used in the long term. As mentioned in section 1, key obstacles to achieving a widespread use of Hydrogen are storage and transportation, especially for automotive use. One interesting approach to overcome these problems is based on hydrolysis, that is reaction of a substance with water to produce Hydrogen. Intensive efforts are currently performed to enhance the Hydrogen release kinetics in these processes and to decrease the reaction temperatures. The reason is obvious: Hydrogen content in water is high; water is liquid at ambient temperature and very abundant. All the problems linked with Hydrogen storage and handling are therefore solved. Several compounds have been considered as candidates for hydrolysis reactions: among them Boron and Nitrogen based compounds [28,29].

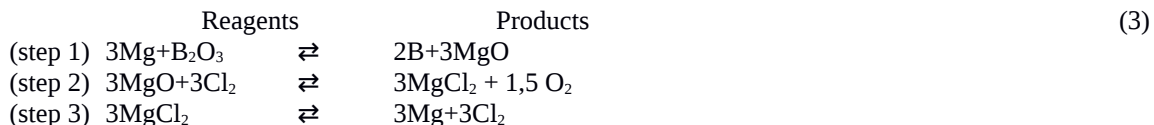
Boron hydrolysis is one of the most interesting possibilities because the energy release of this reaction is of 25 kJ/g (B), higher than that of any other possible candidate metal, such as Al, Mg, Fe [11]. The process is through Boron reaction with water (steam at $T > 700$ K) to produce Hydrogen [30,31] according to the following:



The reaction must be optimized, controlling the steam concentration and temperature. Further research on catalysts for enhanced kinetics and efficiency must be carried on. Nevertheless, this represents an interesting alternative to the direct use of solar energy to produce Hydrogen. A key advantage is that Boron hydrolysis gets rid of the Hydrogen transportation losses mentioned in the introduction.

4. Boron oxide reduction

Boron can be obtained from its compounds by different methods, such as chemical reduction, thermal decomposition, non-aqueous electric reduction. In the following, some processes to obtain Boron from Boron oxide are outlined. Those presented can implement the reaction in closed cycles. This means that no chemical waste is produced, at least in principle, and the net result of the chemical reactions is just Boron oxide reduction to Boron. Most of the methods are, at present, limited by the purity level of the produced elemental Boron. Furthermore, the simpler and most obvious method, direct dissociation of B_2O_3 is not feasible, since reaction temperatures higher than 3000 K are necessary. Production of Boron at lower temperatures can be achieved with the addition of metals reducing agents. In the production of large amounts of elemental Boron the use of Mg as reducing agents is the most common and promising method [32]. A closed cycle using Magnesium as reducing agents is reported below:

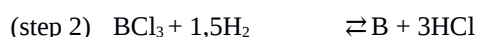


This closed reduction cycle and all the others mentioned below, require energy in the form of heat absorbed by the

products (although some step can be exothermic). This is in fact the energy which is stored in the Boron and that will be released in the oxidation process. Therefore a reduction facility should be realized, which uses solar energy to provide the heat needed in the endothermic steps of the cycle. In the Mg cycle, temperatures of the order of 1500 K are needed. The required energy and temperature for the several steps can be obtained from various degrees of concentrated solar energy [33]. A solution can be, for instance, to locate concentrating mirrors near the reduction reactor in order to provide the necessary energy concentration.

Solar reactors able to reach temperatures above 1000 K are already existing, mainly build for the purpose of hydrolysis. A few were built for the study of solar reduction of metal oxides like Alumina and ZnO and proved that they are able to keep a reaction vessel at temperatures in excess of 1800 K [34]. More common are linear concentrating solar power collectors where the incoming radiation is focused by mirrors on a pipe filled with molten salt such as Sodium Nitrate (NaNO_3) and Potassium Nitrate (KNO_3) mixtures. These salts melt above 500 K with operative temperatures in the range: 530-800 K [35]. The receiver tube fluid, which is heated by the sunlight concentrated on it by the mirrors, is then used to create super-heated steam that spins a turbine that drives a generator to produce electricity. The same system could be readily modified to provide heat for some of the steps of a Boron cycle. The goal is to avoid or reduce to a minimum any other kind of energy supply. This would represent an optimum employment of the solar energy, more efficient than direct electric energy production.

Higher Boron purities with respect to those obtainable from (3), could be achieved using Boron halogenides in the following cycle:



The use of Boron trichloride needs high temperatures, where the compound becomes highly corrosive. Alternatively, Bromine could be used, which is easier to reduce by Hydrogen, but has the disadvantage of toxicity of the bromide.

Different candidate cycles to separate the MgO from the Boron and recycle the Mg could be carboreduction of Mg oxide or methanoreduction of Mg oxide or even reaction with HNO_3 . These cycles have the disadvantage of Carbon oxides release into the atmosphere. The inconvenience could be limited if Carbon of non fossile origin were used. Then also the Carbon balance would be zeroed. One additional option is the carboreduction of the Boron oxide with Carbon as a reducing agent under vacuum conditions directly to produce Boron. Several other paths to B_2O_3 reduction were proposed for instance by G. Cowan [23], again with the net result of Boron oxide reduction.

The energy expense of Boron production ought also include the transportation costs of Boron from solar production site to energy release site and those of Boron oxide back to the solar site. These costs will reasonably be of the same order of those relative to coal transport, since Boron and Boron oxide will be carried by the same media.

5. Conclusions

In summary, solar energy storage in Boron and its subsequent release could effectively be an important step towards the development of a renewable energy based society. As regard the energy storage step in a Boron cycle, many possible paths has already been studied in the laboratory and the most promising of them schematically illustrated in the previous section. They all accomplish Boron oxide reduction absorbing thermal energy. For them all research is still required to overcome problems like products purity or efficiency of the process or the need of high temperatures in some of the steps. But in principle there are no obstacles which could not be overcome in a short time and which hinder the possibility to turn one of these cycles into an industrial process.

The reduced Boron, which is solid at ambient temperature, could be easily transported from production to utilization sites by means of ordinary transport means such as trucks, trains and container ships. This is surely one of the most appealing properties of Boron. No new infrastructures or capital investments are needed for Boron (or B_2O_3) transportation. Being harmless, Boron does not require particular care in handling and storing.

The energy release could follow two different paths. Combustion in pure Oxygen or Hydrogen production through reaction with water. In order to be without emissions and because of the relative scarcity of Boron, the

combustion process must be in a closed chamber in pure Oxygen. A specifically developed combustion chamber is therefore required, together with an Oxygen supply. Both are available at the current technology level. Hydrolysis yield Hydrogen, which in turn can be used as fuel both in combustion engines or in fuel cell engines. Whichever will be the energy release process, Boron oxide is obtained. It can be brought back to the solar plant with the same transport means used for Boron. At the plant, Boron is again obtained with the use of solar energy, closing the cycle.

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