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Final Report on the Charmey Workshop (Part V):**Appendix**

From the very beginning it had been agreed that there would be no presentations of prepared papers during the workshop. Instead, the organizers offered the opportunity to include into this final report any manuscript that had been written before or after the workshop. H. Tributsch was not able to attend the meetings and provided a text concerning his ideas on Toxic Chemical Waste Processing. The text of C. Gómez Camacho, who was present at Charmey, was written after the workshop and submitted for inclusion into the proceedings.

Feasibility of Toxic Chemical Waste Processing in Large-Scale Solar Installations**Helmut Tributsch***

A new strategy for processing toxic chemical waste in large-scale solar concentration installations is discussed in which photon energy, process heat as well as solar generated hydrogen are essential elements. It includes the following steps: Instead of burning chemicals at high temperature which produces many additional toxic products, they are hydrogenated using solar hydrogen and solar process heat to yield energy-rich mineral oil and natural gas type products. Non-utilizable and toxic waste materials are conducted through a high temperature chimney of incoming concentrated, UV upgraded, solar radiation, where they are broken down to environmentally compatible products. Concepts from irreversible thermodynamics are used to underline the advantage of the proposed strategy. This Solar Chemical Recovery and Annihilation Project (SCRAP) will require long-term research and development, especially in the fields of high temperature-high photon density photochemical plasmas, of solar laser technology and frequency multiplication for UV enhancement of solar radiation as well as on hydrogenation catalysis.

1. Introduction

Large-scale solar thermal installations suffer, like other solar technologies, from the disadvantage of being still too expensive and not competitive with other energy systems^[1]. This is unfortunately also true for solar thermal powered chemical processes such as reforming of natural gas and coal^[2], which in addition does not serve the idea of environmentally clean energy systems, which solar energy promises. In these cases the main problem is that conventional energy technologies are existing which are already more elaborated and more cost-efficient and that the long-term damage they are causing on the environ-

ment is not included in their market prize. It will be necessary to improve solar energy technology until later changed economic and political conditions will favour large-scale application.

On the other hand it would be desirable to develop solar technologies now which would not only be unique in their application but would also warrant major development efforts because they are needed. A proposal in this direction is based on the following considerations: Converting quantum energy directly into heat means wasting a significant advantage of solar energy since photons are very expensive to produce technically. Special attention should therefore be paid to technological processes in which both quantum and thermal energy could be used with advantage.

A serious international problem of our days and the future is the elimination of toxic chemical waste. Most of it cannot be



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eliminated at all, or is burned at high temperature with non-negligible emission of pollution. The presently practiced disposal of toxic chemical waste is expensive, a highly political issue, mostly only a temporary solution and frequently involves shipment of dangerous freight over long distance. Heat at elevated temperatures, which is used for burning toxic waste in presence of air, can also be produced by concentration of sunlight. But in addition solar radiation is also supplying a high flux

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of photons, which could much more easily break chemical bonds than thermal energy. Thermal energy turnover at 1000 °C is, for example, characterized by energy quanta (kT) of approximately 0.1 eV. Solar energy, however, before being degraded to heat, involves energy quanta up to 3.5 eV with a peak near 2 eV. The scientific feasibility of a solar strategy for the recycling and disposal of chemical waste is presently investigated in our laboratory. Because of the high complexity of the problems involved and the long-term aspect of technical development it appears to be reasonable to search discussion and controversy at an early stage of work.

2. The Solar Chemical Recovery and Annihilation Project (SCRAP)

The production of high temperatures (1000 °C to 2000 °C) in a central solar receiver is not a fundamental problem since we are talking in this project of a solar installation of a 100–200 MW size, which is at the limit of technical feasibility. The advantage and need for solar concentration of this magnitude will become clear from the discussion further below. However the question arises, whether burning of chemicals at high temperatures in presence of air is an environmentally attractive strategy. It is the burning of waste materials with air which is responsible for a considerable increase of volume and for many toxic and undesirable oxidation products including nitrogen oxides. Much more attractive would be a hydrogenation of chemical waste in closed reactors with hydrogen under pressure at high temperature, using catalysts. The advantage would be the formation of energy-rich products similar as they are found in natural gas and mineral oil. Hydrogenation of coal is known to work at well-defined conditions at temperatures between 200 and 500 °C in presence of special catalysts and of hydrogen under pressure. To hydrogenate toxic waste (including large varieties of industrial products, pharmaceuticals, and chemicals of everyday life, mostly in their plastic, glass or metal containers) it will be reasonable to envisage process temperatures between 1000 and 2000 °C. In presence of high-pressure hydrogen most chemicals will be converted into products identical and similar as recovered from mineral oil or natural gas. There will be gaseous, liquid and solid product components which will have to be subject to refining and processing. The necessary technology will have to be developed. Hydrogen, of course, should be produced from water in a parallel pathway utilizing solar energy. The preferred strategy should be to produce, by solar electrolysis, hydrogen in situ under pressure to minimize technical infrastructure.

Now the second important stage of solar processing of chemical waste material will come into play, which will necessitate a complete reconstruction of central solar re-

ceiver stations (Fig. V1). There will still be many chemical products which are either toxic or useless, but which cannot simply be discarded into the atmosphere of the environment. Examples are dioxines, nerve gases, and cancerogeneous products. Within the SCRAP concept they are transferred into a photochemical reaction chimney through which the incoming concentrated solar radiation is arriving. The chimney is constructed in such a way as to further concentrate radiation (principle of Winston collector^[3]) and has also the aim of providing a temperature gradient (from the bottom to the top) within the intensive beam of photons.

The aim of conducting waste chemicals into a photochemical reaction chamber is fragmentation of molecules. Fragmentation is to be expected because of the presence of both high temperature which leads to population of higher vibronic states of the molecules and because of the high density of photons which can break chemical bonds. A simple estimation shows that the

turnover to be expected may be of realistic dimensions. Taking 2 eV as the average energy of solar photons it can be estimated that a 100 MW central receiver installation will during one day collect up to $6 \cdot 10^{20}$ photons which corresponds to 10^7 einstein or mole-equivalents. Assuming that 100 photons are in the average needed to disrupt one molecule, and assuming molecular weights between 50 and 500, a maximum daily turnover between 5 and 50 tons of products could be expected only on the basis of quantum processes. The desintegration products could in part again be subject to hydrogenation. Since only a small fraction of non-utilizable toxic waste materials will have to be eliminated through the photon-chimney the total quantity of toxic chemicals processed daily through a SCRAP installation will be larger by at least one order of magnitude.

Simple thermodynamic arguments can be put forward for the advantage of photons for the degradation of toxic chemicals: The Planck formula for blackbody

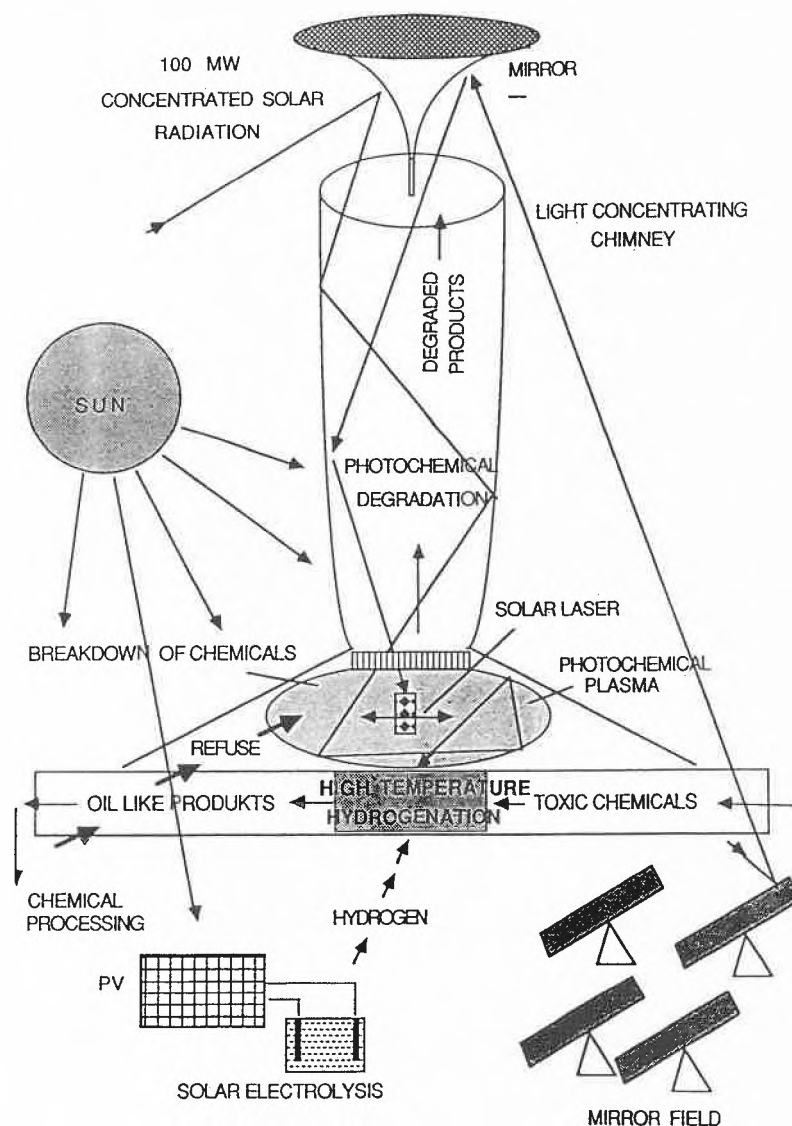


Fig. V1. Simplified scheme of large-scale solar installation for treatment of chemical waste (SCRAP).

radiation can be solved for the temperature which, using *Wien's* approximation for simplification, yields (ν : frequency, L_ν : spectral radiance, and since $c^2 L_\nu / 2h\nu^3 \ll 1$)^[4]:

$$T(\nu, L_\nu) = (h\nu/k)(\ln(2h\nu^3/c^2 L_\nu))^{-1} = \nu \ln L_\nu \quad (1)$$

This means that the temperature dependence is approximately linear in ν , but logarithmic in L_ν . This definition of the temperature T of radiation is thermodynamically correct in the sense that it describes the transported radiant energy δQ to the associated entropy δS for constant volume through $T = (\delta Q/\delta S)$. After being made diffuse the radiation is losing equilibrium contact with the source and increases its entropy. With internal equilibration, in contact with a heat bath, a decreased temperature and a further increased entropy is obtained.

The radiation temperature defines the direction of net energy flow, as for normal bodies in heat contact, or the energy flow in other irreversible processes like the decomposition of molecules. The consequence of relation (1) is that for the disruption of toxic chemicals much more advantage can be gained by increasing the frequency of quanta as compared to increasing their concentration. In other words: degrading direct concentrated solar light to scattered light with a lower formal temperature and further to thermal energy means sacrificing considerable advantages of solar energy. To use a quantitative example^[4], increasing the irradiance of 3 μm infrared quanta from 50 to 1000 W/m^2 means increasing the radiation temperature from approximately 350 to 450 K, but increasing irradiance of 0.5 μm visible quanta from 50 to 1000 W/m^2 means increasing it from 1500 to nearly 1800 K.

The deviation of chemical reactions from equilibrium is determined by their chemical affinity A_p which is proportional to the temperature and vanishing at equilibrium^[5].

$$A_p = kT \ln(K^{\text{eq}}/\prod_j \rho_j^{\nu_{jp}}) \quad (2)$$

(K^{eq} : equilibrium constant, Π_j : product over constituents j , ρ_j : concentrations of reactant j , ν_{jp} : stoichiometric coefficient of constituent j in reaction p).

For a simple non-equilibrium reaction of the type



the affinity A_p is, for example, described by

$$A_p = kT \ln(k_1 A_0 / k_2 B_0) \quad (4)$$

and the amount of energy ΔG per unit time involved in maintaining the steady state flux of formation of product B by^[5]

$$d(\Delta G)/dt = (k_1 A_0 - k_2 B_0) kT \ln(k_1 A_0 / k_2 B_0) \quad (5)$$

Both quantities (4) and (5) linearly increase with the effective temperature. Be-

cause of the much higher formal temperature produced, exposing toxic chemicals to an elevated concentration of solar photons is therefore much more disruptive than exposing them to the same energy in form of thermal quanta. Radical reactions, as initiated by photochemical mechanisms, also facilitate parallel chemical reaction pathways, which in irreversible chemical mechanisms has been shown to increase energy dissipation and the rate of product formation^[6]. In other words, under such conditions the system is traversed by a higher flux of matter.

A precondition for photochemical degradation is, of course, the possibility of quantum mechanical interaction. Thermally induced bond breaking in molecules will usually have the effect of shifting the absorption spectrum into the region of visible light. The consequence will be that the absorption probability for solar photons will increase, causing further disruption and degradation of the molecules. Also population of higher electronic states at elevated temperature will cause a spectral shift to lower energies. Since many small molecules permit the excitation of binding electrons (at ambient temperature) only with near-UV photons, it might be necessary to upgrade the UV portion of solar light. This is possible using a solar pumped laser with subsequent frequency multiplication. The feasibility of solar pumped lasers^[6,7] with more than 10% overall energy conversion efficiency has been experimentally demonstrated^[6]. There are already design studies for solar lasers for space applications with energy outputs in the 1 MW range^[8] for which the authors claim no major technical problems. 5 MW of solar light absorbed by a $t\text{-C}_6\text{F}_6\text{I}$ lasant are expected to produce a 1 MW laser beam.

The photochemistry of plasmas under conditions of combined high temperature and high photon density is virtually unknown but it is to be expected that no chemical compound will be able to withstand. One possible problem might be the subsequent recombination of fragments to yield new toxic compounds. This problem will have to be carefully analyzed. Possibilities to control it are adiabatic expansion (of gas confined behind a photon-transparent barrier, cf. Fig. V1) to reduce recombination, or photochemical disruption until a lower temperature is reached at the top of the reaction chimney. There are many complementary construction details imaginable to the simple photon chimney depicted in Fig. V1 for an improved utilization of solar quanta.

3. Discussion

The proposed technology for the recycling and elimination of toxic chemical waste involves severe technical and scientific challenges. Among these the degradation behaviour of molecules in high tem-

perature-high photon density plasmas is an unexplored research area. The integration of solar laser technology with frequency multiplication for the UV upgrading of solar light will, if this should be necessary, require additional efforts in laser technology. Further difficulties may be expected in material and process technology. However, the expected results warrant a major effort, especially since most of the solar process heat will not be consumed for hydrogenation but remain available for further energy conversion processes as they are presently practised and explored in central solar receiver systems. Conceptually, the suggested chemical waste processing technology may therefore in principle be practicable as a step preceding conventional solar thermal energy conversion.

Instead of being too much impressed by expected difficulties we should ask: What are the possible alternatives for the processing and disposal of toxic chemical waste? We know the limitations of present-day toxic chemical waste treatment, which usually involves combustion at high temperature and expensive storage. Solar energy provides the only possibility to combine process heat at elevated temperatures and high-intensity photon power to disrupt and convert molecules. What we are proposing is basically a scaled down sun into which to throw toxic waste. Solar processing of toxic waste can in addition be conceived as a non-continuous process which is a definite advantage for solar installations which are only functioning at the rhythm of sunshine.

Economic considerations appear to be in favour of the proposed long-term solar project (SCRAP). The prices to be paid for the disposal of chemical waste will increase and it is to be expected that even taxes will in the future be charged for materials needing special disposal and treatment. Side products would be recycled, useful chemicals and process heat. Most important, public opinion and political reasoning will be in favour of the envisaged technology and tolerate a higher level of funding which will also stimulate other developments in the field of solar energy conversion.

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