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HIGH-TEMPERATURE NUCLEAR REACTORS AS AN ENERGY SOURCE FOR HYDROGEN PRODUCTION*

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Abstract

Application of current high-temperature reactor technology to hydrogen production is reviewed. The requirements and problems of matching a thermochemical hydrogen production cycle to a nuclear heat source are discussed. Possibilities for extending the temperature of reactors upward are outlined. The major engineering problem is identified as the development of a high-temperature process heat exchanger separating the nuclear heat source from the chemical process.

INTRODUCTION

The mounting intense pressure of the U.S. energy problem will result in the discovery and utilization of nearly all of the oil and gas reserves to furnish the bulk of energy demand for many years. However, a major energy deficit is inevitable by the 1990 to 2000 time period; therefore the nation will look increasingly to coal and nuclear energy to correct this deficit. These will supply energy primarily to generate electrical power while the oil and gas will be used primarily for heating, industrial and transportation uses. The major problem to appear in the 1990-2000 time period will be the fact that electricity cannot readily be substituted for these latter needs due to reasons of practicality and cost.

Production of synthetic fuels from coal will receive great emphasis, however this either makes poor utilization of the coal or requires massive supplies of hydrogen. A method of producing a substitute fuel using a nuclear heat source is desired to augment production of synthetic fuels from coal during the 1990-2000 transition period and ultimately as a source of nearly all non-electrical energy. If this substitute fuel is hydrogen then it can serve multiple functions - as a chemical feedstock for efficient coal liquefaction and gasification, ammonia production, metal ore reduction, as a primary fuel, and ultimately as an efficient source of electricity using turbines. The supply of hydrogen is virtually unlimited in the form of sea water and is essentially replaced as water vapor upon combustion. The switch to hydrogen for energy needs would return the carbon atom to its natural role in the biological life cycle and would provide for the use of the remaining supply of fossil fuels as feedstock to the expanding organic chemical industry. The hydrogen itself is not an energy resource, but rather a particularly convenient intermediate medium for storing and transporting energy. The energy resource is nuclear fuel.

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The use of nuclear fuel as a primary energy source has already proven economically competitive for the production of electricity, principally because of the low cost of nuclear fuel. For efficient dissociation of hydrogen from water, a high-temperature energy source will be needed because the process is fundamentally Carnot-limited. With further development of the high-temperature gas-cooled reactor (HTGR) as a primary nuclear energy source, a plant complex producing hydrogen and electricity could be developed for future long-range energy needs.[1]

Unless substantial increases in uranium reserves are discovered then some reliance on breeder reactors will be desired to avoid the excessive land despoilation which would be associated with recovery of very low grade uranium ore. A minor fraction of breeder reactors can supply the fuel required for HTGR converter reactors in order to obtain a net high utilization of the total uranium and thorium mined. An alternative may be the utilization of uranium from sea water.

HIGH-TEMPERATURE REACTORS FOR PROCESS HEAT

In the U.S. HTGR technology has been developed to produce helium at temperatures up to 1080 K (1480°F) for the commercial generation of electricity. The HTGR core design is a cluster of prismatic graphite blocks in which holes are spaced alternately for coolant passage and fuel elements. The cylindrical fuel elements are a carbonaceous matrix containing small uranium dicarbide (UC_2) spheres which are coated with three layers of pyrolytically deposited carbon and a single layer of silicon carbide to prevent the escape of fission products. The refractory design of this fuel form along with the low-cost refractory core are the principle features that permit high temperature operation without significant fission-product contamination of the primary coolant.

In Europe high temperature reactor technology has also been developed for commercial generation of electricity by the construction of the Westfalen Power Station in the Federal Republic of Germany. The reactor in this facility is designed to heat helium to 1023 K (1381°F). The core design is based on that of the experimental AVR (pebble bed) reactor which consists of a pile of spherical graphite fuel elements (about the size of tennis balls) contained in a cylindrical graphite shell. The fuel elements contain a fuel form similar to that of the HTGR except the UC_2 kernel is replaced by UO_2. The principal feature of this core design compared to the HTGR is that the fuel elements are more readily cycled through the reactor.

Consideration has been given for the use of both these reactor types in process-heat applications. For the HTGR a modification in the fuel-loading scheme would permit an increase in the outlet helium temperature to 1156 K (1620°F) without increasing the maximum fuel temperature. It has been suggested that with such a modification the HTGR could be used for the production of hydrogen by supplying the heat for the steam-methane reforming reaction. In both Japan and the Federal Republic of Germany, programs are underway for the development of high-temperature reactors to produce helium at 1270 K (1830°F). The West German effort is directed toward supplying heat for coal gasification (using the water-gas reaction) although emphasis is initially on the generation of electricity by direct cycle helium turbines. The Japanese program is directed primarily toward the production of hydrogen for the direct reduction of iron ore.

Nuclear reactors have been developed to operate at higher temperatures than that of HTGR's. The nuclear rocket propulsion reactors, developed in the Rover program, were designed and operated to heat hydrogen to temperatures up to 2600 K (4200°F) for periods up to 10 hours. The UHTREX reactor, originally conceived as a process heat source, was designed to heat helium to 1590 K (2400°F) and operated at fuel temperatures in excess of 1920 K (3000°F) for 30 days prior to project cancellation. Both of these reactors used the same fuel technology (pyrocarbon-coated UC$_2$ "beads") as that for the HTGR, but the core geometries were more finely divided than that of the HTGR, providing for smaller temperature differences between the fuel and the coolant, and the fission-product release requirements were less restrictive than for commercial power application.

There is little doubt that with further fuel technology development and with a different reactor core design, an HTGR-type reactor could be developed to heat helium to temperatures up to 1367 K (2000°F). Possibly helium temperatures as high as 1600 K (2400°F) could be attained. However, two disadvantages of nuclear heat make the application to the variety of high-temperature processes economically uncertain.

One disadvantage is that the environment in most process equipment is corrosive and must be separated from the reactor core by a physical barrier, i.e., a heat exchanger. This implies design constraints on the process equipment and requires that fuel temperatures in the nuclear core be significantly higher than that of the process. Actually, the direct circulation of the nuclear reactor coolant through process heat exchangers may be unacceptable because of safety implications. If an intermediate heat exchange loop is necessary for this reason, the nuclear fuel temperatures would be even higher.

The other disadvantage is the relatively low thermal power requirement of most processes for economic nuclear reactor size, possibly with the exception of large steel plant complexes. Because the capital cost of a reactor system scales roughly as the square root of power level, one is led to very large reactor sizes because of economic considerations. The AEC currently limits the size to 3600 MW$_t$ until more experience is gained, however even larger sizes may come in the future. Few process heat applications lend themselves to such large size units and smaller units will certainly incur a cost penalty. Also, most high-temperature process industries include multiple parallel process streams (usually three or four). This implies that (very high temperature) multiple coolant loops from the nuclear reactor to process vessels would be necessary, which is another expensive requirement; and a nuclear reactor shutdown would force a shutdown of the entire plant, which is an operational constraint that may be unacceptable, certainly undesirable. For hydrogen production however, the plant will be necessarily large, eliminating the size factor disadvantage for other process heat applications. The other disadvantage, that of providing a high-temperature process heat exchanger, is of course not mitigated, but at least one will be concerned with only <u>one</u> process, that of the "yet-to-be" discovered hydrogen production process, rather than the multiplicity of process heat applications.

REQUIREMENTS FOR THERMOCHEMICAL HYDROGEN PRODUCTION

The thermochemical production of hydrogen from water is basically a problem in high temperature chemistry. Thus, it is useful to examine the problem from the viewpoint of the high temperature chemist in order to understand not only the theoretical limitations on the efficiency of the process as related to reaction temperatures, but also to identify ideal values of the enthalpy and entropy changes required for any series of reactions considered for the decomposition process. These are determined by the number of reaction steps and the maximum temperature available from the heat source. From this knowledge of optimum enthalpy and entropy changes, and knowledge of the characteristic entropy changes associated with different types of reactions, one can select specific reaction types for evaluation.

In principle the thermochemical cycle consists of two or more reaction steps, proceeding as follows:

$$MO_X + H_2O \rightarrow MO_{X+1} + H_2 \qquad (1)$$

$$MO_{X+1} + (\text{heat}) \rightarrow MO_X + 1/2\ O_2 \qquad (2)$$

where M is a metal ion or complex radical. The ideal thermal efficiency of the above cycle is:

$$\eta = \frac{\Delta H^\circ}{\Delta G^\circ} \frac{(T_2 - T_1)}{T_2}$$

where ΔH° and ΔG° are respectively the heat and work for the dissociation of water at standard temperature (25°C) and pressure (1 atm) and T_1 and T_2 are respectively the temperature of steps (1) and (2). To approach this efficiency the actual work (or free energy) for each step should be minimized, and the total work should be near zero. Because $\Delta G = \Delta H - T\Delta S$ (where ΔS = entropy change), these conditions may be approached if the step (1) entropy change is negative and the reaction exothermic at T_1; and, correspondingly, the entropy change in step (2) is positive and the reaction endothermic at T_2.

The important feature of the thermochemistry of these reactions is the very large entropy change for the addition of an oxygen atom to the reactant MO_X. For the two-step cycle these entropy changes would be more than double that for typical reactions involving the addition of an oxygen atom to a condensed phase at reasonable temperatures (1100 to 1200 K). Therefore, it is apparent that simple two-step cycles will not be found and that practical thermochemical cycles will require additional reactions. It is also apparent if only one additional reaction is involved at the high and low temperature, these additional reactions must exhibit large entropy changes. Consequently, these additional reaction steps should incorporate a gaseous reactant.

Other than the obvious advantage in efficiency of operating at as high a T_2 as practicable, the following observations are made:

- The smaller the temperature interval between T_2 and T_1 (in general, for lower T_2), the larger (more positive) the total change in entropy required for the high-temperature decomposition reactions.

- With smaller values of $T_2 - T_1$, the low-temperature reactions are more exothermic (negative entropy change), high-temperature reactions are more endothermic (positive entropy change), and heat efficiencies for the production of hydrogen are lower.

- If the thermochemical decomposition process involves more than one heat cycle (with different T_2's) the overall efficiency will be lower than the value computed for the maximum T_2. Therefore, intermediate reaction steps with significantly lower values of T_2 or significantly higher T_1's should be avoided.

- Thermochemical reaction cycles with optimum entropy and enthalpy values for a particular set of temperature conditions will not be practical for lower temperatures and will not give significantly higher efficiencies if conducted at higher temperatures. Therefore, to the extent that nature permits, the thermochemical process should be tailored to match the temperature available from the heat source.

FUTURE DEVELOPMENT OF NUCLEAR HEAT AND HYDROGEN PRODUCTION PROCESS

Assuming one had a practical thermochemical hydrogen cycle that was compatible (in temperature) with current high-temperature reactor and materials technology, the technology development for commercial application should be relatively straightforward. However, in the U.S. the competition for such a process will be that of hydrogen produced from coal, for which the energy cost will be approximately the same as synthetic pipeline gas. It is likely that the hydrogen production cost from a thermochemical process will be higher. Therefore, the thermochemical process will not be developed commercially until the price of coal increases to the point that hydrogen from coal costs more than thermochemical hydrogen It is anticipated that this must occur within the next few decades. This implies that there is sufficient time for the development of a new high-temperature reactor-fuel technology extending the temperature up to possibly 1600 K as discussed previously. Such a fuels technology development might include the following:

- Using a fuel-element geometry that provides direct thermal contact between the fuel body and the helium coolant.
- Incorporating the coated-particle fuel directly into the graphite matrix of the element.
- Using a modified coated particle which will survive fuel element graphitization temperatures. This will result in an improvement in the thermal conductivity of the fuel element of at least a factor of five. The modified coated particle may be made by replacing the SiC layer with a ZrC layer.

- Possibly modifying the coated particles to allow a modest increase in particle operating temperature.
- Modifying the reactor flow rate and power-profile design to further decrease the temperature difference between the fuel particle maximum and the helium exit gas.

However, the principal engineering problem beyond the discovery of a practical, high-temperature thermochemical hydrogen process will be the design of the high-temperature process heat exchanger. Current materials engineering technology limits temperature levels to ∿ 1050 K for process equipment made of production field materials such as the Ni-Cr alloys. Use of production superalloys such as Udiment 700, Rene 41, and TD-nickel could permit operating temperatures up to ∿ 1400 K. At higher temperatures non-production refractory alloys would be necessary. Possibilities are molybdenum (TZM) or Nb-W alloys. The principal materials engineering problems with these alloys are the requisite means of fabrication, such as forming, machining, and welding and the means of corrosion protection such as cladding. The major design problems are the effects of temperature and pressure cycling on the fatigue strength.

Once the thermochemical hydrogen process is discovered at the bench scale, process engineering data, specifically chemical reaction kinetics, product yield, and heat transfer characteristics, will be needed prior to design of demonstration plants and will significantly reduce the cost of experimental pilot plants. Necessary materials engineering data are mass transport and structural strength of process equipment materials operated at the actual energy and momentum transport conditions of the process in question.

REFERENCE

1. LA-5456-MS, "Nuclear Heat and Hydrogen in Future Energy Utilization," L. A. Booth and J. D. Balcomb, November 1973.