Reports

A High-Efficiency Power Cycle in Which Hydrogen Is Compressed by Absorption in Metal Hydrides

Abstract. *A high-efficiency power cycle is proposed in which molecular hydrogen gas is used as a working fluid in a regenerative closed Brayton cycle. The hydrogen gas is compressed by an absorption-desorption cycle on metal hydride ($FeTiH_x$) beds. Low-temperature solar or geothermal heat (temperature about 100°C) is used for the compression process, and high-temperature fossil fuel or nuclear heat (temperature about 700°C) supplies the expansion work in the turbine. Typically, about 90 percent of the high-temperature heat input is converted to electricity, while about 3 kilowatts of low-temperature heat is required per kilowatt of electrical output.*

Central power plants in operation at the present time convert only 30 to 40 percent of their thermal input to electricity. This low conversion reflects Carnot limitations as well as various irreversibilities in conventional Rankine or Brayton power cycles. Typically, about 60 percent of the reversible Carnot work is achieved in a practical cycle. The high-grade fossil and nuclear energy resources used in present power plants are limited and expensive. If the fraction of thermal energy converted to electricity could be substantially increased, scarce resources could be conserved and electrical generation costs reduced. It is clear that significant improvements are possible, and that the scientific and engineering communities should be encouraged to develop new power cycle concepts.

We have analyzed a new high-efficiency power conversion cycle which converts almost all, that is, ~90 percent, of the high-grade thermal input to electricity. In this cycle two thermal inputs are used: a high-temperature ($T \geq 300°C$) input, which can be supplied by a conventional nuclear reactor or fossil fuel combustor, and a low-temperature ($T \approx 100°C$) input, which can be supplied by low-temperature solar or geothermal energy. Such low-grade energy is virtually unlimited and should be available at many locations for relatively low cost. In principle, this low-grade heat could be used in a conventional power cycle but the resultant conversion efficiency is very low.

The proposed cycle is similar to the conventional regenerative Brayton cycle except that the gas, instead of being mechanically compressed, is compressed by an absorption-desorption cycle in a suitable chemical compound. In order that this "chemical compressor" be used, it is necessary that the compound be thermally cycled: a low-pressure absorption step rejects heat to the surroundings, and a high-pressure desorption step requires a heat input obtained from the low-temperature heat source.

In a conventional Brayton cycle, a large fraction of the turbine output is used to drive the mechanical compressor. As a result, with practical turbine temperatures only about 30 to 40 percent of the high-temperature heat can be converted to electricity. In the proposed cycle, all of the turbine output appears as electricity and only a small fraction (~10 percent) of the high-temperature heat input is not converted to electricity. The higher efficiency results from the fact that low-grade heat supplies the pumping work required by the compressor, whereas the small inefficiencies in the use of high-temperature heat result from the imperfect recovery of sensible heat in the regenerator.

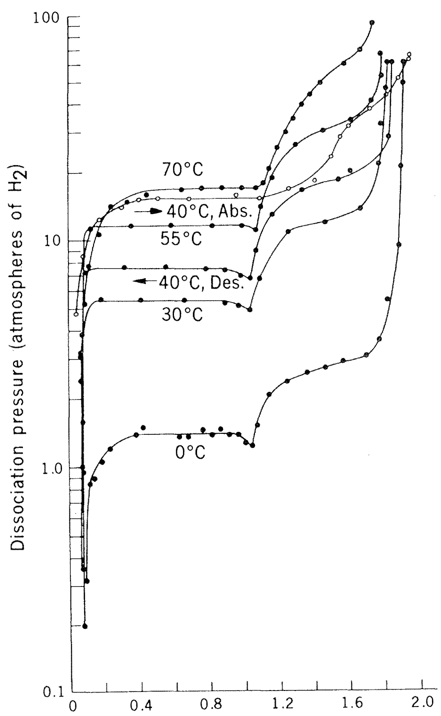

Fig. 1. Equilibrium dissociation pressure of $FeTiH_x$ as a function of temperature and composition [after (3)]; *Abs.*, absorption; *Des.*, desorption. The two curves for 40°C show the phenomenon of hysteresis for the absorption-desorption of H_2 in FeTi. [Courtesy of the American Chemical Society, Washington, D.C.]

A number of gases and absorptive materials can be used as the chemical compressor. The absorptive material can be a solid (for example, CO_2 gas absorbed in a molecular sieve) or a liquid (for example, CO_2 absorbed in ethanolamine). The best choice, however, appears to be H_2 gas absorbed in solid metal hydride particles. The density of hydrogen nuclei in a metal hydride approaches that in liquid hydrogen, the absorption-desorption rates are rapid, and useful pressures are readily obtained. Furthermore, H_2 gas has high thermal conductivity, which minimizes the regenerator cost and enthalpy loss; it is relatively inert to materials of construction; it does not decompose at high temperatures; and it is nontoxic, cheap, and can be handled safely.

We have also considered a high-efficiency Rankine cycle in which the working fluid condenses instead of being absorbed and desorbed in a solid or liquid. The condensed liquid is then evaporated at a higher pressure by the low-temperature thermal input ($T \sim 100°C$). The vapor is first heated by a regenerator and then by a high-temperature heat source, and finally it is expanded through a turbine. For a practical cycle, the vapor pressure at $T \sim 100°C$ should be at least 10 atm. This requirement eliminates water as a possible working fluid, but other fluids such as NH_3, C_3H_8, SO_2, or some of the Freons would be suitable; however, such cycles appear less attractive than the proposed hydrogen-hydride compressor cycle for several reasons. Partial condensation effects in the vapor limit the conversion efficiency to only about 50 to 60 percent of the high-temperature heat input. In addition, the working fluid may irreversibly decompose at high temperature or cause severe corrosion problems, or both. The thermal conductivity of the vapor is much less than that of H_2, and regenerator cost will be much greater than if H_2 is used.

Wiswall and Winsche (*1*) originally conceived of a cycle similar in nature to that described in this report. In their hydride engine scheme, H_2 was driven off a vanadium hydride (VH_x) bed by heat from a low-temperature source at $\sim 65°C$, then expanded through a turbine, and finally absorbed in another VH_x bed at 30°C. A high-temperature heat source was not used in this cycle, so that the overall efficiency was limited to a calculated 9.4 percent (90 percent of Carnot efficiency).

Iron titanium hydride ($FeTiH_x$), a more promising material for a H_2 compressor than VH_x, is being investigated as a means of storing H_2 in electric utility systems (2). In this application, H_2 would be produced by electrolysis during off-peak periods and used in fuel cells to generate electricity during peak periods. Figure 1 shows the equilibrium desorption pressure of H_2 above $FeTiH_x$ as a function of composition and temperature (3). The hydride compressor would operate in the lower plateau region shown in Fig. 1 ($0.1 \leq x \leq 1.0$), where the desorption pressure is essentially independent of composition. This region corresponds to a two-phase mixture of FeTi and FeTiH.

The hydride compressor would absorb H_2 at low pressure (P_0) and low temperature (T_A) while connected to the low-pressure H_2 circuit. The exothermic heat of absorption (ΔH_A) would be removed by heat exchange surfaces in the hydride bed and dumped to the ambient surroundings. After the desired hydrogen content of the hydride is reached (for example, $x \sim 0.6$), the bed would be isolated and heated to a higher temperature (T_D) and then connected to the high-pressure H_2 circuit (P_1). The absorbed H_2 would then be desorbed, with the endothermic heat of desorption ($\Delta H_D \simeq \Delta H_A$) supplied from a low-grade solar or geothermal source. After desorption ($x \simeq 0.1$) the metal hydride would be isolated and cooled to T_A, where it would be ready for another compression cycle. In an actual power plant a number of hydride beds would be used, with continuous flow through the high- and low-pressure H_2 circuits.

The inventory of FeTi in a hydride compressor, as well as its cost and size, may be affected both by H_2 absorption-desorption kinetics in FeTi and by the rate at which heat can be supplied to the bed. The heat supply rate can be optimized by suitable design, but the H_2 absorption-desorption kinetics are inherent to the material. The absorption of H_2 in FeTi is considerably slower than the desorption step. Accordingly, absorption rates were measured in a small test compressor, containing 3 g mole of FeTi, as a function of hydride composition and absorption pressure. These results are shown in Fig. 2.

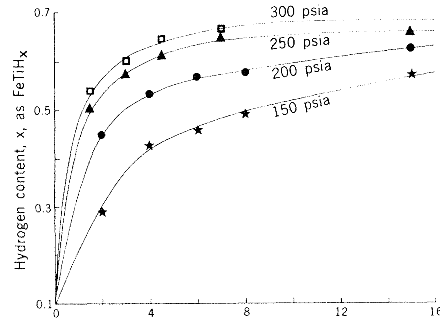

Fig. 2. Rate of absorption of H_2 in a $FeTiH_x$ compressor, as a function of H_2 pressure and hydride composition.

Absorption rates decrease monotonically as x increases and increase monotonically as P_0 increases. The absorption rates are quite rapid and permit large compression capacity at short cycle times in the range where x equals 0.5, that is, 6 to 8 minutes. These absorption rates are lower limits, since large temperature differences were observed between the FeTi bed and the coolant ($T = 16°C$), that is, ΔT of up to 30°C. Absorption rates should be considerably faster in beds with smaller ΔT between the FeTi particles and the coolant. In fact, for practical compressors, it is likely that absorption rates are limited by heat transfer and not by kinetics. Based on these experiments, the performance of this compressor would be quite attractive for a high-efficiency cycle. However, it should be possible to improve performance with better materials.

Figure 3 is a temperature-entropy diagram for the compressor and turbine portions of the proposed cycle. The two components can be easily connected by H_2 pipelines if the high- and low-temperature heat sources are physically separated.

Two efficiencies can be defined for the proposed high-efficiency cycle. The first, η_{HT}, measures the fraction of the high-temperature heat input, Q_{HT}, converted to electrical work, W_T, by the turbine expansion:

$$\eta_{HT} = \frac{W_T}{W_T + (C_p)_{H_2}\Delta T_R} = \frac{W_T}{Q_{HT}} \tag{1a}$$

$$W_T = \eta_T\,(N+1)\,\frac{\gamma}{\gamma - 1}\,RT_2 \times \left[1 - \frac{P_1}{P_0}^{\frac{1-\gamma}{\gamma(N+1)}}\right] \tag{1b}$$

where η_T is the mechanical efficiency of the turbine, $\gamma = C_p/C_v$ (the ratio of the heat capacity at constant pressure to the heat capacity at constant volume), R is the universal gas constant, and T_2 is the turbine inlet temperature. In Eqs. 1a and 1b the turbine expansion consists of $(N + 1)$ expansions and N reheats; for example, Fig. 3 shows a single expansion without any reheating. The enthalpy loss, $(C_p)_{H_2}\Delta T_R$ (ΔT_R is the temperature differential in the regenerator), of the low-pressure exit stream from the regenerator is the only inefficiency in the conversion of high-temperature heat to electrical work, and is much smaller than W_T.

Figure 4 shows η_{HT} as a function of T_2 ($600°K < T_2 < 1400°K$) and exhaust pressure, P_0, of 150, 200, 250, or 300 pounds per square inch absolute (psia) (1 atm = 14.6 psia). Other cycle parameters are held constant: turbine inlet pressure $P_1 = 750$ psia; $\eta_T = 0.90$; $\Delta T_R = 40°K$; $N = 1$; and $\gamma = 1.4$. The value of η_{HT} is very high, in the range of 80 to 90 percent, and is not very sensitive to a choice of cyclic parameters; η_{HT} could be increased with a smaller ΔT_R and

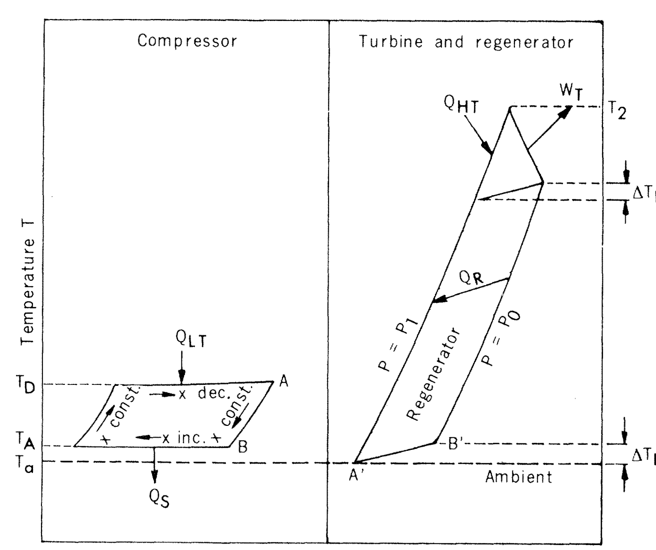

Fig. 3. Schematic diagram of temperature versus entropy for the high-efficiency cycle; A to A', high-pressure H_2 pipeline; B to B', low-pressure H_2 pipeline; Q_s, heat rejected from the hydride bed (Q_s is slightly less than the input Q_{LT}); Q_R, heat transferred in the regenerator.

larger N, but the gains may not be economically justified. Interestingly, η_{HT} is not very sensitive to T_2, which implies that high temperatures may not be necessary, particularly if materials problems are of concern. In this analysis, the turbine exhaust pressure is assumed to be equal to the absorption pressure in the hydride beds. In practice, the exhaust pressure will be slightly greater than the absorption pressure because of pressure losses in the piping system.

The second efficiency term, η_{LT}, measures the amount of low-temperature heat required for the compressor, per unit electrical output from the turbine. It is defined by

$$\eta_{LT} = \frac{W_T}{Q_{LT}} \quad (2)$$

and is also shown in Fig. 4 as a function of T_2 and P_0. The value of η_{LT} increases linearly with T_2, so there is a substantial incentive for a high value of T_2 to reduce the amount of low-temperature heat needed for the compressor. As an example, $\eta_{LT} = 0.3$ for $P_0 = 150$ psia and $T_2 = 1000°K$. This T_2 value should be achievable with a fossil fuel combustor or a high-temperature, gas-cooled reactor (HTGR). For these conditions, the high-efficiency cycle would produce about 0.3 unit of electrical work per unit input of low-temperature heat, whereas a standard power cycle would yield only about 0.1 unit of electrical work. With improvements in compressor performance, that is, lower P_0 and better recovery of sensible heat, η_{LT} could be increased to about 0.50 for the same cycle conditions.

One can compare the work output from the high-efficiency cycle with the reversible Carnot work (W_C) by using the same two thermal inputs. The ratio is:

$$\frac{W_T}{W_C} = \frac{\eta_{HT}}{\frac{(T_2 - T_a)}{T_2} + \frac{\eta_{HT}}{\eta_{LT}} \frac{(T_D - T_a)}{T_D}} \quad (3)$$

where T_a is the temperature of the ambient surroundings (~20°C), and T_D is the bed desorption temperature. The quantity η_{HT}/η_{LT} is the ratio of low-grade to high-grade heat inputs in the high-efficiency cycle. At $P_0 = 150$ psia and $T_2 = 1000°K$, the high-efficiency cycle yields about 60 percent of the Carnot work. Various irreversibilities, for example, H_2 overpressure for rapid absorption, hysteresis, and incomplete recovery of the sensible heat in the bed, account for the difference. This ratio would increase to 80 percent if improvements in compressor performance raise η_{LT} to 0.50.

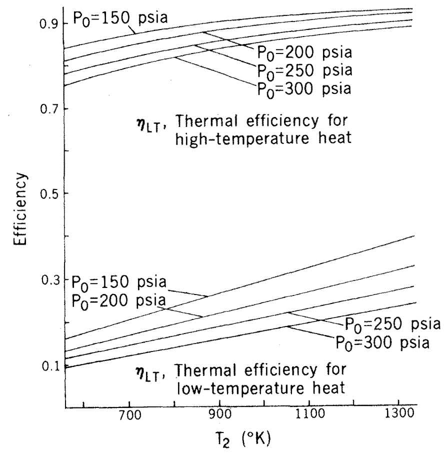

Fig. 4. Efficiency of utilization of high- and low-temperature heat in the high-efficiency cycle, as a function of T_2 and P_0 (P_1 = 750 psia; ΔT_R = 40°K; η_T = 0.9; Q_{LT} = 9 kcal per g mole of H_2; N = 1).

Overall, the proposed high-efficiency cycle achieves a performance relative to the Carnot cycle which is as good as or better than that achieved in conventional power cycles, even though it uses a substantial amount of low-temperature heat which would be difficult to use efficiently in a conventional cycle. What is more significant than the performance relative to the Carnot cycle is the almost complete conversion of expensive high-grade heat to electricity.

Savings of ~30 percent in electrical generation cost are projected for the proposed cycle. In calculating this saving we assume current fossil and nuclear fuel costs, current capital costs per kilowatt (thermal) for high-temperature heat sources (coal-fired plants or HTGR's), and an estimated \$15 per kilowatt (thermal) for the hydride compressor. The compressor cost is based on \$10 per kilowatt (thermal) for the heat exchange surface in the bed, 10 pounds (1 pound = 454 g) of FeTi per kilowatt (thermal) (derived from absorption experiments), and a projected cost of \$0.50 per pound of FeTi. Also assumed is a cost of \$20 per kilowatt (thermal) for the low-temperature heat source. This figure is probably a high estimate for low-grade geothermal heat and probably a low value for solar heat.

Virtually unlimited amounts of solar and geothermal heat should be available at many locations in the United States, particularly in the western states. At an average geothermal gradient of 30°C/km, useful temperatures are reached at a well depth of only 3 km. This heat source provides a much larger resource base of geothermal energy than a conventional power cycle would. A conventional cycle needs higher temperatures (~250°C) to be economical, necessitating deeper and more expensive wells or restriction in the use of geothermal energy to a limited number of locations where high geothermal temperature gradients exist.

The low-temperature heat sources, either geothermal wells or solar collectors, could be distributed over a fairly large area around a localized high-temperature heat source. The hydride compressors can be located at the sources of low-temperature heat. High- and low-pressure H_2 pipelines can couple the distributed low-temperature sources to the central high-temperature source. This procedure appears to be much cheaper than transmitting thermal energy by hot water, and it ensures that almost all (~95 percent) of the reject heat from the cycle will be dispersed over a large area. Estimated H_2 transmission costs are low, for example, about \$10 per kilowatt (electrical), even for a collection area of ~100 square miles (1 square mile = 2.6 km^2). The total reject heat per unit electrical output will be comparable to that from conventional or nuclear fossil plants, but the local effects will be much less. For most locations this reject heat will be dumped to the atmosphere through either wet or dry cooling towers. The costs of such cooling towers should be comparable to those for conventional plants. If the metal hydride is contained in tubes or sheets that are a part of the cooling tower structure, it appears possible to reject heat in dry cooling towers with acceptably small temperature differences.

The technologies required to implement the proposed hydride compressor cycle are being developed in ongoing R & D programs on H_2 storage by absorption-desorption in FeTi. The design of regenerator and turbine systems for the H_2 working fluid seems to be relatively straightforward and in many respects would be quite similar to the closed-cycle helium systems under development for nuclear reactors. The principal development area for the regenerator and turbine would appear to be in the selection of materials that will not embrittle in H_2 at the temperatures contemplated, that is, ~1000°K. The cycle described in this report could be implemented in both new and retrofitted central station power plants where suitable low-grade heat sources exist. The resultant conservation of fossil and nuclear resources, as well as the projected savings in the cost of the electricity generated, should be of great benefit.

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References and Notes

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A Human Syndrome Caused by Immotile Cilia

Abstract. *Four subjects who produced immotile sperm were studied. In three of the subjects, who had frequent bronchitis and sinusitis, there was no mucociliary transport, as measured by tracheobronchial clearance. Electron microscopy indicated that cilia from cells of these patients lack dynein arms.*

Evidence has been found for the existence of an inborn disease that is due to an immotility of the cilia. This disease has been studied in four men, but the condition may not be exceedingly rare. A study of this disease may contribute to a better understanding of the role of ciliary movement.

1) The four subjects produced spermatozoa that were living but immotile. The sperm tail appeared as in rigor—that is, straight, stiff, and with no motility. Electron microscopy indicates the spermatozoa to be relatively normal except that so-called dynein arms were not present (*1*). Dynein arms are structures that in normal cilia, flagella, and sperm tails form temporary cross bridges between adjacent ciliary filaments and that are believed to be responsible for generating the movements of cilia or sperm tails (*2*).

2) Three subjects have had, since childhood, chronic sinusitis and bronchitis, and frequent pneumonias, common colds, and ear infections.

3) Study of the tracheobronchial clearance in the three subjects reveals that there is no measurable mucociliary transport (*3*). The investigation was performed by having the subjects inhale, by mouth, a test aerosol of 6-μm particles labeled with technetium-99, and making external measurements of the radioactivity in the chest for 2 hours. The subjects were asked not to cough during this time span. Ordinary tracheobronchial clearance was nearly or totally absent, when no coughing occurred, but a reasonably good substitute for this clearance could be obtained by permitting the subjects to cough.

4) No ciliary motion could be seen in biopsy material obtained from the bronchial mucosa of one subject. In a portion of the biopsy sample that was processed for electron microscopy, the appearance of the cilia was abnormal. There was dense matrix material between the ciliary filaments. Very few dynein arms were seen, and these seemed shorter than in normal cilia.

5) Three of the subjects have situs inversus totalis; the fourth subject is brother to one of the other three affected men.

From the above five findings two tentative conclusions are drawn. The cells of the four men cannot synthesize normal dynein arms, or, if such dynein arms are formed, they cannot attach to the ciliary filaments; this causes immotility of spermatozoa and cilia. Visceral asymmetry is determined through the movements of cilia of some embryonic epithelial tissues.

There is some support for the first conclusion. The human sperm tail is a modified cilium. Ordinary cilia in ciliated epithelia are present at the following sites in the human body: the respiratory tracts, the paranasal sinuses, the Eustachian tube, the ependyma lining brain ventricles and spinal cord, and, in women, the oviducts.

In the spermatozoa of the four subjects, tail paralysis and a lack of dynein arms can be directly observed (Fig. 1). Similarly, the bronchial cilia seem to be immotile and to have an abnormal ultrastructure (Fig. 2). An evaluation of the detailed pattern of the ciliary machinery is difficult as a dense matrix fills most of the space within the cilium. There is, however, a clear space around the nine ciliary filaments in distal regions of the cilia, and the dynein arms are usually absent. Occasionally, a short dynein arm is present, particularly in the basal region, but the appearance is atypical. The morphology of these cilia differs from that of normal cilia in the human respiratory tract (*4*).

The respiratory tract, sinuses, and auditory ducts are sites of repeated infections in these men, as might be expected in a person with no mucociliary transport mechanism. Chronic bronchitis and sinusitis may cause, as a secondary phenomenon, a particular anatomical lesion in the bronchi which is called bronchiectasis. The condition has been found in those two of the present subjects who have been examined in this respect.

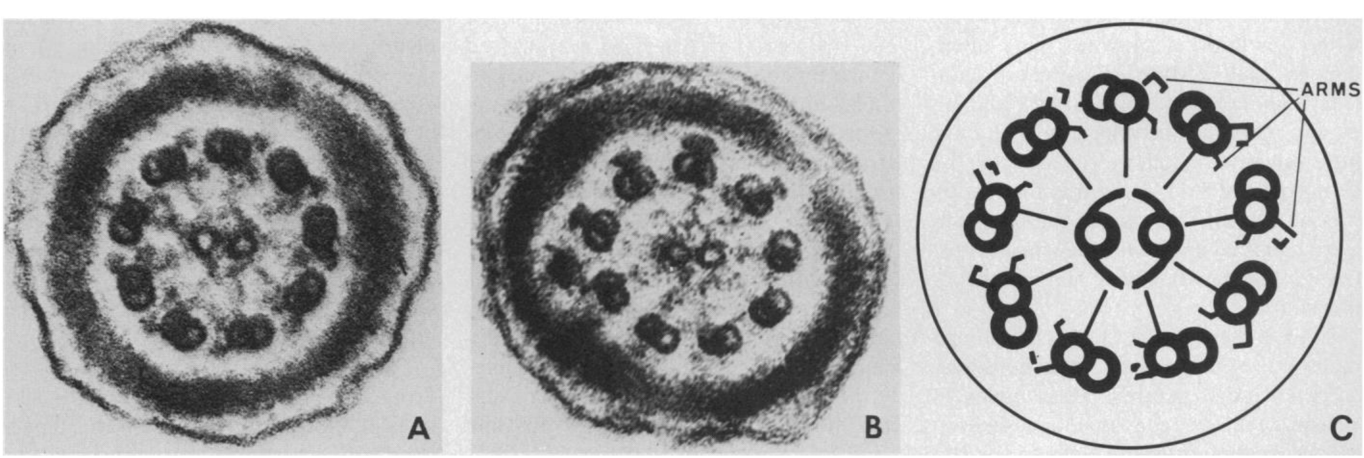

Fig. 1. Electron micrographs of cross sections through the sperm tail and a schematic drawing showing the location of the dynein arms. (A) The tail of an ordinary, motile spermatozoa has nine microtubular doublets; on each of the doublets there are two dynein arms (× 128,000). (B) The sperm tail of patient L.P. is devoid of the dynein arms. The pattern is indistinguishable from that of three patients previously described (*1*) (× 128,000). (C) Drawing of the sperm tail or ciliary cross section.