conditions, probably as periglacial dune sands in this area, which flanks the once glaciated Cantabrian Mountains. Transport into the cave was unquestionably by water action, and it is significant for correlation that deposition ceased abruptly around 10,200 ± ∽250 years ago (according to Fig. 3), at the close of the Pleistocene. Subsequently, no further sediments were deposited in this area of the cave, and the sands underwent a lengthy period overgrowth under the aegis of a long-term *p*H change. These factors imply that the sands were relatively undisturbed in the postdepositional period and could, therefore, be expected to preserve the original orientation of magnetic particles. Sources of remanent magnetization could not be positively identified, but by correlation with other SEM data (*5*) blebs on Tito Bustillo sand grains appear to be goethite and indicate that some detrital iron minerals appear as coatings on such grains. Because of the restricted bacterial action in deep caves with rapidly accumulating deposits, it is thought that limited chemical diagenesis occurred and that remanent magnetism, therefore, reflects the secular field at the time of deposit.

Additional paleomagnetic dating of cave sediments (*6*) appears to verify the suitability of such materials for this technique. As more reference curves become available, the technique can be extended to cover increasingly greater time periods, periods that are not now adequately covered in the archeological record. This dating method has several advantages over other chronological techniques: paleomagnetic determinations can be made rapidly, and they require no intrusive elements—organic or otherwise—in the strata being investigated.

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References

1. F. J. H. Mackereth, *Earth Planet. Sci. Lett.* **12**, 332 (1971); ———, K. M. Creer, R. Thompson, L. Molyneux, *ibid.* **14**, 115 (1972).
2. R. Thompson, *Nature (Lond.)* **242**, 182 (1973). Figure 2 of this report is modified from Thompson's figure 1.
3. A. Leroi-Gourhan, *Sci. Am.* **218**, 58 (Feb. 1968).
4. E. K. Ralph, H. N. Michael, M. C. Han, *MASCA Newslett. (Mus. Appl. Sci. Cent. Archaeol. Univ. Pa.)* **9** (No. 1) (1973), pp. 1–20.
5. D. Krinsley and J. Donahue, *Geol. Soc. Am. Bull.* **79**, 743 (1968).
6. J. S. Kopper and K. M. Creer, *Caves Karst* **15**, 13 (1973).

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Water Salination: A Source of Energy

Abstract. *The thermodynamically reversible mixing of freshwater and seawater at constant temperature releases free energy. Salination power as a resource is comparable with hydroelectric power in magnitude; U.S. freshwater runoff could yield over* 10^{10} *watts. The energy flux available for natural salination is equivalent to each river in the world ending at its mouth in a waterfall 225 meters high. An osmotic salination converter could possibly operate at 25 percent efficiency. This energy source is renewable and nonpolluting. Although its full utilization would destroy estuarine environments, it might be practical for specialized purposes.*

The quest for new energy sources has heightened recently with world political and economic developments. Along with a growing realization of the need for more energy has come a simultaneous realization that the energy sources must be clean and renewable. These requirements suggest that naturally occurring geophysical energy fluxes be tapped. Direct solar energy conversion, the utilization of tidal, geothermal, wind, and hydroelectric energy fluxes (*1*), and even the energy available from the nonequilibrium state of the oceans (*2*) have been proposed as energy sources. Yet there is one large natural energy flux which, though readily available, I have not seen mentioned as a resource, namely, salination of water or the energy released from the mixing of freshwater with seawater.

That energy in fact can be extracted from the mixing of freshwater and seawater is best illustrated by considering the reverse process—energy is required to extract freshwater from seawater. The reversal of any desalination process should, in theory, release energy. Rather than present a full thermodynamic argument, I derive the amounts of energy involved through a heuristic approach (*3*). Let a volume V_1 of pure water mix irreversibly at constant temperature T with a volume V_2 of solution with an osmotic concentration of C_2, resulting in a solution of volume $(V_1 + V_2)$ and concentration $C_2V_2/(V_1 + V_2)$. Consider the osmotically active particles of solute as a "gas," initially with $N = C_2V_2$ moles of particles confined in volume V_2. After mixing, the "gas" has expanded isothermally to a volume $(V_1 + V_2)$ with an entropy increase $\Delta S = NR \ln (1 + V_1/V_2)$, where R is the gas constant. If the expansion were to proceed, instead, reversibly at constant temperature T, it would release energy $\Delta W = T \Delta S$. Normally, V_2 is much larger than V_1; the oceans act as an infinite reservoir of constant concentration. Hence,

$$\Delta W = NRT(V_1/V_2) = (RTC_2)V_1$$

Since seawater has an osmotic concentration of approximately 1 osmole/liter, each liter of freshwater added to the ocean would release 22.4 liter-atm of energy. In more practical units, a freshwater flow of 1 m^3/sec could provide 2.24 megawatts of salination power.

Substantial amounts of power are available from this source. The total surface runoff of water in streams and rivers into the oceans from the coterminous United States corresponds to a flow rate of 5.3×10^4 m^3/sec, which could release 120×10^9 watts, several times the present U.S. water power consumption, and almost equal to the total U.S. hydroelectric potential (*4*). The Mississippi River alone accounts for about one-third of the total runoff. A salination power plant using only 10 percent of the flow at an overall efficiency of 25 percent would deliver 1000 megawatts.

The salination energy is readily converted to mechanical or electrical energy. The proportionality constant, $P_0 = RTC_2$, between the energy released and the volume of water used has units of pressure, being in fact the osmotic pressure of seawater. An osmotic converter is illustrated in Fig. 1; other thermodynamic conversion schemes would work equally well. In the apparatus shown, freshwater is separated from seawater by a semipermeable membrane under a pressure head, P, which need not actually be a water column. If P is infinitesimally smaller than P_0, an infinitesimal volume of water, dV, will flow into the pressure chamber, spill off the top of the column, and release $P\,dV = (RTC_2)dV$ energy in the resultant waterfall. A conventional waterwheel and generator can then be used to produce electricity at an efficiency of nearly 100 percent (*5*). The tremendous energy flux available in the natural salination of freshwater is graphically illustrated if one imagines that every stream and river in the world is terminated at its mouth by a waterfall 225 m high, the height of a seawater column that develops 22.4 atm of pressure.

Not all the energy of salination is available in a practical device. The actual water flux depends on the difference between the hydrostatic and osmotic pressures across the membrane. The machine described above would operate infinitely slowly. Maximum power is obtained at 50 percent efficiency (*6*), at a pressure head of $P_0/2$. If the membrane is at all permeable to solutes, energy will be lost by the irreversible mixing of salt which flows into the freshwater, a loss which can be expressed as a reduction in the effective osmotic pressure (*7*). Membranes developed for reverse-osmosis water desalination programs, though designed to operate at higher hydrostatic pressures than 11 atm, could be used for salination energy conversion. Current membranes have a water permeability coefficient on the order of 10^{-6} mole cm^{-2} sec^{-1} atm^{-1}, which yields a flow of 2 ml/sec or a power output of 2 watts at a pressure 11 atm per square meter of surface (*8*). With a solute permeability of 10^{-5} cm sec^{-1}, the reverse solute flux is less than 0.1 percent of the forward water flux.

Two other factors limit the operating efficiency of a practical osmotic salination converter. First, sediments and solutes, carried in by the input stream or diffusing across the membrane, will accumulate in the freshwater chamber. These can be flushed away if part of the input stream is diverted, as shown in Fig. 1. The system efficiency will be reduced by the fraction of the input stream diverted. More important, membrane water flux will dilute the solution in the pressure chamber. The salt must be replenished somehow. One scheme is illustrated in Fig. 1, where seawater is pumped into the pressure chamber at a constant rate. This pump must work against a hydrostatic pressure gradient, but the necessary power can be completely reclaimed, in theory, as this pumped water flows through the waterwheel. Since this cyclical process will have an efficiency of less than unity, the pump rate must be limited and power will be lost in two ways in addition to pump losses. First, a limited pump rate allows substantial dilution of the chamber fluid, and, as a result, the salination process is incomplete. Second, the lowered osmotic pressure results in a lower transmembrane water flux, reducing the power output, though not the energy per volume of water used. For a pumping efficiency of 95 percent, it can be shown that the concentration, hence the operating pressure and membrane flux, should drop 17 percent, reducing the overall efficiency of conversion to 51 percent (*9*). Taking into account also the 50 percent energy loss necessary to maximize power output in even an ideal converter, the overall system efficiency will be 25 percent, yielding 0.5 megawatt of power per cubic meter per second of input flow.

Is such a scheme feasible? Reverse-osmosis desalination membranes can be formed and installed for less than 10¢ per square foot ($1.07 per square meter) (*10*), which, given a lifetime of 1 year, would yield electricity at 5¢ per kilowatt-hour. Desalination plants can provide water at less than 50¢ per 1000 gallons (13¢ per cubic meter) including operating and maintenance expenses and the amortization of capital (*11*). Such a plant operating in reverse should theoretically provide electricity at less than 20¢ per kilowatt-hour. Thus, continuing improvements in membrane technology (*12*), as well as possible improvements resulting from the designing of membranes specifically for salination, might well make such power economically attractive within a decade.

Salination power is almost completely benign to the physical environment. The energy extracted does not seem to play any significant role in any natural process. Furthermore, no deleterious substance, including heat, is added to the output stream. Like hydroelectric power, though, the impoundment of water would cause massive destruction of the biotic environment. Furthermore, the separation of freshwater and seawater and the elimination of brackish water environments would be catastrophic. These effects could be mollified by stepwise salination, creating a series of brackish water ponds of increasing salinity, interconnected by countercurrent-exchange "fish ladders." Even so, the mere absence of tidal swash would make this artificial impoundment a mere shadow of the richness of a natural estuary.

But are there not special situations where such power might be practical? Diversion of a portion of streamflow might provide sufficient power for supplemental or specialized purposes, or for isolated regions. Many freshwater outflows are already canalized and flow directly into the ocean with no true estuarine habitat. Could the storm and sanitary sewer outflow of a metropolitan area provide the power necessary for sewage treatment, water processing, or refuse reclamation?

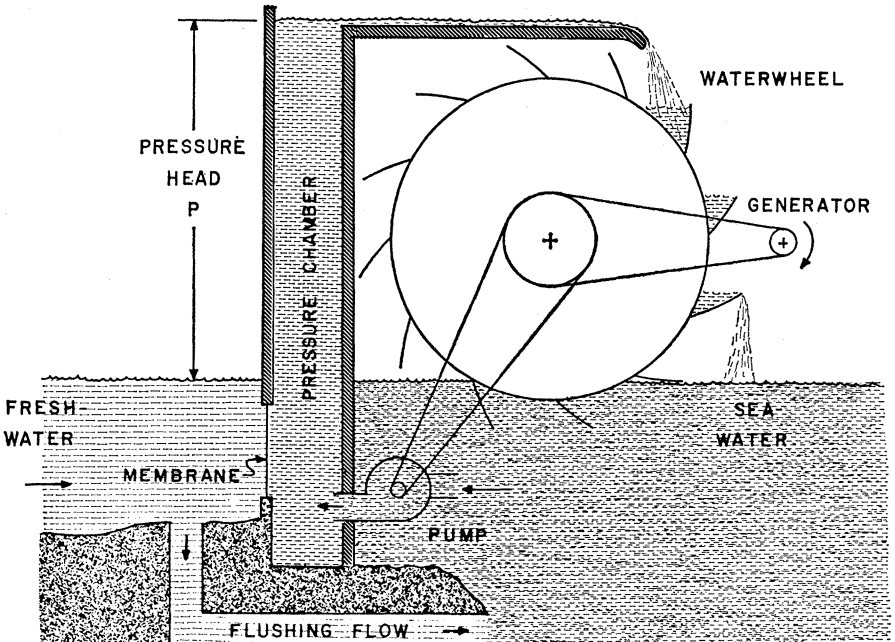

Fig. 1. Diagram of an osmotic salination energy converter, to extract power from the natural flow of freshwater into the sea. See text for details of operation.

Note added in proof: In a recent exchange of letters, Gregor (*13*) and Levenspiel and de Nevers (*14*) speculate on this concept. Gregor fails to account for membrane packing densities now obtainable (*10, 11*).

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References and Notes

1. M. King Hubbert, in *Resources and Man: A Study and Recommendations by the Committee on Resources and Man of the National Academy of Sciences–National Research Council* (Freeman, San Francisco, 1969), p. 502; *Sci. Am.* **224** (No. 3), 60 (1971); A. L. Hammond, W. D. Metz, T. H. Maugh II, *Energy and the Future* (American Association for the Advancement of Science, Washington, D.C., 1973); H. H. Landsberg and S. H. Schurr, *Energy in the United States* (Random House, New York, 1968); see also the special energy issue of *Science* (19 April 1974).
2. W. D. Metz, *Science* **180**, 1266 (1973); D. F. Othmer and O. A. Roels, *ibid.* **182**, 121 (1973); O. Levenspiel and N. de Nevers, *ibid.* **183**, 157 (1974).
3. Numerical values given here are approximate but sufficiently accurate for the purpose. In this derivation ideal solutions are assumed. See R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (Butterworth, London, rev. ed. 2, 1965), p. 242; B. F. Dodge and A. M. Eshaya, *Adv. Chem.* **27**, 7 (1960); L. A. Bromley, "Properties of Seawater and Its Concentrates and Related Solutions at Temperatures up to 400°F" [Office of Saline Water, U.S. Department of Interior Research and Development Progress Report 747 (1972)].
4. D. K. Todd, *The Water Encyclopedia* (Water Information Center, Port Washington, N.Y., 1970).
5. C. M. Summers, *Sci. Am.* **224** (No. 3), 149 (1971).
6. The power output is given by the product of the hydrostatic pressure, P, and the membrane water flux, which itself is proportional to $(P_0 - P)$. Hence power is proportional to $P(P_0 - P)$. Maximum power is obtained at $P = P_0/2$, and each cubic meter of water releases only half the theoretical energy of the reversible process.
7. A. J. Staverman, *Trans. Faraday Soc.* **48**, 176 (1952); O. Kedem and A. Katchalsky, *J. Gen. Physiol.* **45**, 143 (1961).
8. S. Sourirajan, *Reverse Osmosis* (Academic Press, New York, 1970); R. C. Riley, C. E. Milstead, H. K. Lonsdale, K. J. Mysels, "Improved Reverse Osmosis Membranes" [Office of Saline Water, U.S. Department of Interior Research and Development Progress Report 729 (1971)]; M. Clawson and H. H. Landsberg, *Desalting Seawater* (Gordon & Breach, New York, 1972).
9. An ideal system will operate at a pressure head of $P_0/2$, with seawater (concentration C_0) in the pressure chamber, and a membrane water flux of F_0, yielding power $(F_0)P_0/2$. The actual system, with concentration αC_0 in the pressure chamber, will operate at a pressure of $\alpha P_0/2$ and a membrane flux of αF_0. The pump rate, r, necessary to maintain the concentration αC_0 is $r = \alpha^2 F_0/(1 - \alpha)$. The net output power is the total flow times the pressure, minus the power dissipated in the pump. Dividing by ideal power, the overall efficiency is $\alpha^2[1 + \alpha(1 - 1/E)/(1 - \alpha)]$, where E is the pump efficiency. Given E, the efficiency can be maximized with respect to α, which determines the pump rate.
10. F. E. Littman, H. K. Bishop, G. Belfort, *Desalination* **11**, 17 (1972).
11. D. Stevens and S. Loeb, *ibid.* **2**, 56 (1967); K. D. B. Johnson, J. R. Grover, D. Pepper, *ibid.*, p. 40.
12. J. W. O'Meara, *ibid.* **14**, 239 (1974).
13. H. P. Gregor, *Science* **185**, 101 (1974).
14. O. Levenspiel and N. de Nevers, *ibid.*, p. 102.

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Asteroids: Surface Composition from Reflection Spectroscopy

Abstract. *Minerals partly composing the surfaces of 14 asteroids are determined by using asteroid reflectance spectra and optical properties of meteorites and other materials. Individual electronic absorption features are identified in the asteroids' spectra. The energies, relative strengths, and shapes of these features are interpreted by using laboratory and theoretical studies. Analysis of the initial 14 asteroid reflectance spectra indicates the presence of the following types of surface materials: six carbonaceous chondrite–like; two stony-iron–like (metal/silicate ~ 1); one iron meteorite–like; one basaltic achondrite–like; and four silicate-metal assemblages (metal/silicate ~ 0.25). These results support the conclusion that the asteroid belt is a source of at least some meteoritic material, and they show a relation between certain asteroids and certain classes of meteorites.*

McCord *et al.* (*1*) reported first spectral reflectance measurement of an asteroid, Vesta, with sufficient spectral resolution, range, and photometric precision to define absorption features. Between 0.3 and 1.1 μm several electronic absorption bands appeared. These features were interpreted as indicating that a magnesian pyroxene is present as the major mafic mineral and that the surface of Vesta has a composition similar to that of certain basaltic achondrite meteorites.

The first analysis of the composition of an asteroid and the direct relation uncovered between the asteroids and meteorites led to a comprehensive program of asteroid study. To date, the spectral reflectances (0.3 to 1.1 μm) of about 100 asteroids have been measured at the telescope (*2*). A comprehensive study has also been made of the optical properties of the mineral assemblages found in meteorites (*3*).

Considerable experience has been gained in using reflection spectroscopy for remote mineralogical analysis by working both with lunar sample material (*4, 5*) and with telescopic spectra for the surfaces of the moon (*6*), Mars (*7*), Mercury (*8*), and the satellites (*9*). Also, detailed laboratory studies of the optical properties of minerals and mineral assemblages have become available (*5, 10*). We have now begun to analyze the telescopic spectra for asteroids. This is a first report on the early results; a more detailed discussion will appear elsewhere (*11*).

After the success of the Vesta study (*1*), several attempts were made to determine asteroid compositions by using optical properties of meteorites. Chapman and Salisbury (*12*) compared the spectral reflectances for 36 asteroids with those for 41 meteorites. Johnson and Fanale (*13*) studied nine carbonaceous chondrite samples and one iron meteorite for comparison with asteroid spectra. These early studies utilized an empirical curve-matching technique which is less sophisticated and less generally applicable than that used in our interpretation. However, where definite interpretations were made we find good agreement between our results and those of the previous investigators.

The study reported in part here is the most extensive in terms of the variety of terrestrial, lunar, and meteoritic material used for interpretation, and great care was taken to relate optical properties to analyzed mineral constituents in the sample material. Our philosophy has been to interpret absorption features in the asteroid curves in terms of the minerals producing or modifying each feature. A set of features reveals a suite of minerals. This approach does not rely on the exact match of asteroid spectra with meteorite spectra. The meteorite sample material, which is used to study the optical properties of solids, is used as a source of mineral assemblages, the occurrence of which is cosmochemically reasonable in the asteroid belt.

The reflectance spectrum for the asteroid Ceres is shown in Fig. 1 superimposed on the reflectance spectra of 156 meteorites. The meteorite spectra are grouped according to class and therefore according to mineralogy. Note that the variation of the spectra within a class is usually less than the differences between classes. Changes in mineralogy and metamorphic grade through the classes are easily seen in the spectra.

The reflectance characteristics of the meteorite curves are understandable in terms of the type, composition, abundance, and distribution of the component mineral phases. Four spectral classes of minerals can be defined on the basis of their contribution to spectra of mixtures of phases: metals, opaques, and silicates with and without transition metal ions such as Fe^{2+} (*3*). The effect a mineral has on the spectrum is approximately proportional to its abun-