AD-A123 239 CONCEPT STUDY FOR MILITARY PORT DESIGN USING NATURAL PROCESSES(U) NATURAL PROCESS DESIGN NEWBURY PARK CA
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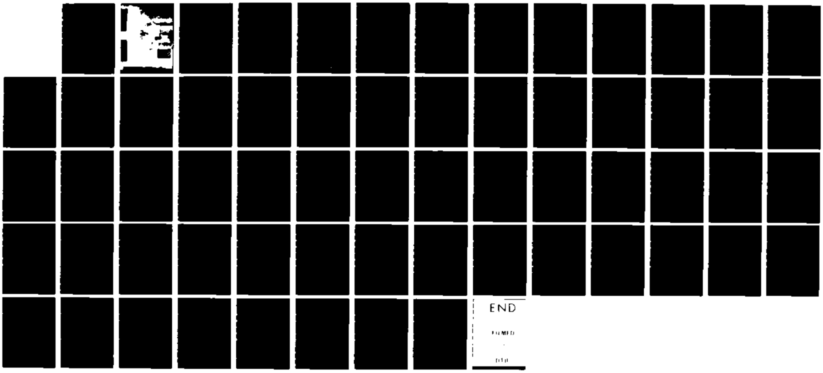
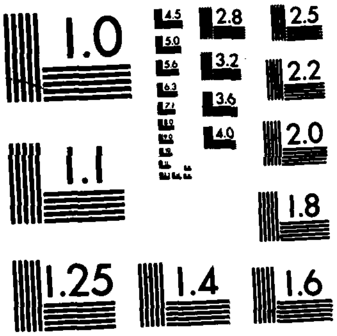
UNCLASSIFIED F/G 13/2 NL

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SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER

2. GOVT ACCESSION NO. AD-A123239

3. RECIPIENT'S CATALOG NUMBER

4. TITLE *(and Subtitle)* Concept Study for Military Port Design Using Natural Processes--Final Report

5. TYPE OF REPORT & PERIOD COVERED Final: Dec 1980-Jun 1982

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s) Carolyn Dry

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Natural Process Design
3196 Alice Drive
Newbury Park, CA

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
Department of the Navy
Arlington, VA 22217

12. REPORT DATE 15 June 1982

13. NUMBER OF PAGES 58

14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*

15. SECURITY CLASS. *(of this report)* UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Distribution Unlimited

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

mineral acretion
port design
structural repair and sensing
osmotic pump

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

This report considers various natural process approaches to port construction including accretion methods, self-repair, and pumping systems. A bibliography by subject is included.

CONCEPT STUDY FOR MILITARY PORT DESIGN USING NATURAL PROCESSES
FINAL REPORT

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Department of the Navy
Arlington, Virginia

June 15, 1982

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Special thanks to the following persons for their help:

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NATURAL PROCESS DESIGN

Natural process design draws from the experience of evolution, using materials and processes already available in the environment and chemically and physically well organized to accomplish certain ends, especially growth and cybernetic adaptation. It intergrates those principles into a new technology. We examine properties of entire systems and elements, their effect on each other and performance, based on interaction of the entire system. Ultimately the capacity to organize material in a complex way and reorganize it depends upon interrelationships among the elements and processes in the environment, not on a number of elements added up.

Building with natural processes is to build like a natural system does; that is (1) using only the most common and abundant resources, and (2) putting these into organization by means of technologies which are indigenous to the environment, (3) cybernetic regulation occurs through a process which is integral to the system's material and organizing system. The self-regulating process entails a way of sensing a need for change, re-organizing, re-collecting material and re-distributing it according to the new organization. Thus there is (1) material, (2) means of distributing the material and organizing principles, and (3) cybernetic ways of sensing and means of communicating, making decisions, and carrying out those decisions.

This phase of research into "Concept Study for Military Ports Using Natural Processes" focuses on chemistry and physical principles which can be applied to port design, while the first phase study used mainly larger scale biological analogies. This report covers specific proposals while the first was more broadly conceptual. All the proposals and ideas presented are original and newly presented herein with the exceptions of the nerve-like cable, the osmotic pump, and simple accretion.

BUILDING PORTS WITH NATURAL PROCESSES

Building with natural processes as applied to military ports is comprised of the following: (1) structural material which is distributed and organized by seawater processes, (2) which can self repair and has a sensing system. (3) It is a cybernetic computer system which can make decisions, carry them out and communicate that and (4) has a means to change or re-order itself.

STRUCTURAL MATERIALS

SIMPLE ELECTROLYTIC CALCIUM CARBONATE ACCRETION

Mineral accretion process uses the electrolytic properties of seawater to put seawater material into organization, to build with it. Calcium, magnesium, and sulfur are the most abundant elements in seawater after salt and water. Calcium and magnesium can be electrolytically accreted into a hard mineral coating.

Accretion is caused by any cathodic electrode put in seawater which discharges hydrogen making the water more alkaline. This imbalance causes materials like calcium carbonate to precipitate out, if there is enough calcium and carbonate in the water. So accretion is the result of a sudden shift in the PH factor due to electrodic action.

Cost/Benefits

The cost/benefit relationship is best shown by comparing present construction cost for a reinforced concrete structure to this method. In this method, electricity is the major cost. A deposition of 1 pound of accreted material costs $.12; standard reinforced concrete construction cost including material and labor costs $2.00 a pound. Labor is the largest cost saving in the accretion method followed by material cost.

Research

Professor Wolf Hilbertz has published the most experimental data on composition and strength of simply accreted mineral material. In a typical sample accretion on a half inch galvanized wire mesh with total surface area of 158 square feet, electricity was supplied for 170 hours at 30 amperes, 7 volts. The accreted thickness was 2.3 millimeters. The chemical composition of the accreted minerals was: brucite 61%, aragonite 5%, calcite 1%, halite 20%, other 13%. A phasing or curing technique was used to shift the percentages to: brucite 50%, aragonite 25%, calcite 1%, other 24%. The average psi strength was 4,265 (which is better than portland cement concrete).[1]

Often the ocean conditions are such that the amount of carbon in the seawater is too small to precipitate out adequate calcium carbonate repair material using electrolytic accretion alone. The problem is that attempts at mineral accretion of calcium carbonate with simple electrolysis produces mainly brucite, a relatively soft material. The ocean areas in which the electrolytic deposition of calcium carbonate are feasible, are those areas already laden with that compound, such as areas near coral reefs. We now recommend the following accretion technique with carbon added to the water.

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[1] IEEE Journal of Ocean Engineering, Volume 4, number 3, July 1979.

ELECTROLYTIC CALCIUM CARBONATE ACCRETION WITH CARBON ADDED TO THE WATER

Adding carbonated water in an ion permeable membrane helps to form the precipitate, calcium carbonate, a very strong material. A membrane keeps the carbonated gas from migrating. The design entails a double layer hardware mesh screen attached to electrodes just as in simple accretion but there is a cavity in the interior of the mesh screen. The membrane which holds the carbonated gas goes into this cavity. The calcium from the seawater goes through the membrane to join the carbonate. Due to a PH change, as the carbonate becomes carbonic acid, calcium carbonate is plated out on the metal mesh.

Research

Experimentation on this method of accretion entails testing the amount of carbon dissolving in the gas cavity from the carbon dioxide, the amount of calcium which penetrates through the membrane, and finally the amount of calcium carbonate produced by this method per energy and time unit.

Cost/Benefits

The cost/benefit ratio is dependent upon energy used and related to the amount of strong structural material produced. This method of accretion uses slightly more energy than simple accretion, because of the membrane process, but the structural product content is more controlled and much more valuable in terms of strength.

SILICATE ACCRETION WITH CARBON ADDED AND SILICATE PUMPING

Silicates can be precipitated out of solution by an anodic electrode put in seawater which discharges oxygen making the solution more acidic. This imbalance causes precipitation due to the change in PH. However, there is not a great deal of silicate material dissolved in seawater from which to make precipitate. So either fairly large quantities of water must be pumped past the electrodes to extract useful amounts of silicate or silicate can be dissolved into solution by electrolytically raising the alkalinity of the solution to a PH of 12, (then sand or some other natural silicate material is added or stirred up). Most of the shallow ocean bottom is made of such material, such as diatoms and sand. To precipitate these dissolved silicates, then a weak acid such as carbonic acid needs to be added, is added by bubbling carbon dioxide into seawater.

First the electrodes are turned on to drive the PH higher. Silaceous material from the bottom has to be stirred up and dissolved in solution. Like the procedure used for precipitating out calcium carbonate, carbonated water is added into an ion permeable membrane held in the metal mesh. This membrane keeps the gas from migrating. The acid produced causes the silicates to precipitate out.

The physical elements of the design are a double layer of hardware mesh screen attached to electrodes turned on. There is a cavity in the interior of the mesh screen in which a membrane is inserted to hold the carbonated gas. A pump (our magnetohydrodynamic pump) brings up bottom silicates to be dissolved in the area of high PH created by the electrodes. The silicates dissolved in seawater go through the membrane to join the carbonic acid produced by the added carbon dioxide. This chemical combination precipitates out on the wire mesh as a structural silicate material.

Research

The experimentation on this way of accreting structural material entails determining the amount of silaceous material which can be dissolved in the particular seawater conditions, the amount of carbon dissolving in the cavity from the carbon dioxide, the amount of silicate penetrating the membrane, and finally the amount of accreted material formed from the combination of carbonic acid and the silicates per amount of energy and time used.

Cost/Benefits

The efficiency of this method depends upon the energy used to the amount of strong material percipitated out. This method uses slightly more energy than simple accretion or the carbon added method of calcium carbonate accretion because the material is first pumped and then passed through a membrane. However, the silicate material is as strong as calcium carbonate. Moreover, the amount of silaceous material dissolved in seawater due to the pumping of bottom material is so abundant that quite a bit more accretion can be done and more quickly than with calcium carbonate accretion. This justifies the added energy costs for pumping.

Variations on the Accretion Method

There are other non-naturally occuring ways to precipitate calcium carbonate and silicates. (1) Soda ash or sodium hydroxide is added in place of carbon dioxide to produce the weak acid solution. (2) Sodium or potassium silicate is added to calcium chloride to produce calcium silicate in solution which has such low solubility that it precipitates out without an acid being added. (3) Another way of precipitating out calcium compounds is to pressurize the water making calcium very soluble and then reduce the pressure to precipitate out the calcium compounds.

ION EXCHANGE PROCESSES WHICH HARVEST CALCIUM AND MAGNESIUM AS STRUCTURAL MATERIALS

Ion exchange processes using resins is a very different way of getting structural materials from seawater. Seawater of normal composition is passed through an ion exchange resin. This plastic-like bead material chemically holds on to calcium and magnesium from seawater. Then an elution material takes the calcium and magnesium from the resin by chemical action. These minerals are then formed into a structure.

This ion exchange batching system is very much like developing and printing film in which material is diffused through a gelatin and takes the desired material out to be printed. The ion exchange method can be used to deposit the mineral material out in a preset form. This form can be a structural design or etched as a memory board for the saline computer. (Also a more favorable ratio of calcium to magnesium than occurs naturally in seawater can be obtained in the ion exchange process.)

This is a very efficient way of concentrating chemicals which are in dilute solution. The main issues of time and capital costs for the resin are successfully addressed by the resin bath design. This system can harvest a mass of material per day seven times the mass of the ion exchange resin. The energy efficient magnetohydrodynamic pump, which uses seawater as the electrolyte, can be used to move water in and out of the ion exchange baths.

Research

A simple experiment can be done on normal seawater using this ion exchange method. The operating cycle time and the amount of reagent used per amount of structural material obtained can be determined. Materials required are (1) the resin, made by Dow Chemical Company, (2) some elution material to get calcium and magnesium from the resin plus a small amount of heat and (3) the chemicals given off in the above step and an acid salt to recover the material in seawater.

Much of the analytic work required to design a speedy process and to design the batching forms required, has been done. A batch system in which the resin is shaped like a membrane with one small dimension for quick diffusion, is dipped quickly into several baths for a few seconds each. The first bath is a more concentrated solution, the last one has less calcium and magnesium in the bath. This continuous stripping off of the desired material takes 30 seconds to remove 80% or 90% of material from the resin.

Cost/Benefits

The batch system can transfer many times the weight of the resin in calcium or magnesium material, every day. If a one gram bead handles 5% material per cycle, 70 times the weight of the bead in calcium and magnesium material can be harvested per day.

Detailed Discussion of Ion Exchange Process for Harvesting Structural Materials

We are examining processing systems capable of recovering dissolved solids from seawater in combination with silica containing minerals to obtain output fractions of alkaline earth compounds-carbonates, silicates, etc. which may be formed into water resistant structures of useful strength for a variety of structural uses. This ion exchange process is a system in which reagents can be rapidly and efficiently cycled and regenerated with recovery of 90% or more or all reagents.

Process analysis

Cation exchange resins can function as acids or salts, while anion ex[illegible]nge resins can function as bases or salts. Resin bead attrition can be held [illegible]low 10^{-3} or 10^{-4} per operating cycle and regeneration can be accomplis[illegible] by "salt-splitting" (conversion of salts to acids and bases) of exter[illegible]or mobile reagents with low grade, perhaps waste heat sources. These [illegible]le acids and bases, which may contain locally deficient elements (LDE's) [illegible] are used to regenerate the ion exchange resins.

The overall power requirements will include the salt splitting energy which, in turn, will depend on the acid or basic strengths required, and power for pumping or moving water or other fluids, vapors and solids, and residual power for other reactors which do not involve ion exchange steps plus other unit operations.

For recovery of compounds without change in valence or oxidation - reduction state of the principal elements, the total energy requirement can be held to relatively low values. For example, the theoretical minimum energy to split salt into a strong acid/strong base pair is the heat of neutralization, 13.6 Kcal or 57 Kjoule/gram equivalent.

Performance parameters

There have evolved a series of performance parameters which are defined in Appendix I to characterize the principal engineering features of such systems or subsets. This permits one to quantify, compare and analyze processing rates, yields and purities, power and heat transfer requirements, and masses needed for capital equipment, chemical inventories and consumables such as fuel, and replacement chemicals and supplies due to reagent and equipment attrition, corrosion and wear. Also defined are specific attrition rates, reliability and lifetime parameters for process segments.

Detailed analysis of core process

We shall designate by core process those principal steps required to cyclicly extract magnesium and calcium compounds plus sulfate ion from dissolved solids in seawater and regenerate ion exchange resins and reagents used in the direct steps. The mean composition of seawater is listed in Appendix II along with the ratios of constituents of interest. The non-core process steps will include silicate mineral processing, optional generation of auxiliary materials such as oxygen, chlorine, caustic metals, concentrated acids, etc.

The primary or direct steps are based on the use of weak acid or weak base resins to recover the hard water alkaline earth ions (Mg^{++} and Ca^{++}) and major anions (Cl^- and $SO_4^=$) respectively from seawater. The ion exchange resins are regenerated by medium strength acids (primarily HSO_4^- of FHF^-) and the weak base (NH_3) respectively. The secondary steps involve asymmetric pyrolysis of ammonium salts to form NH_3 plus ammonium acid salts and added operations involving carbonation, and non-core process steps. The equations for the process steps are given in Table 1.

Process notes

(Step 1) The pronounced selectivity preference of weak acid cationic resins for divalent ions, Ca^{++} and Mg^{++}, over Na^+ permits the recovery of the former to the practical exclusion of the latter even in the presence of a nearly 4-fold excess of sodium equivalents. Since recovery of all the alkaline earth content from a given volume of seawater is immaterial, an excess of water can be used. The selectivity preference of Ca^{++} to Mg^{++} will raise the corresponding equivalents ratio to about 1:2 from its value of 1:5.21 in normal seawater. If one uses batch equilibration of seawater with a 5-fold excess of alkaline earth ions, unit volume of wet resin bed (for IRC-50) will require 137 volumes of seawater. Since the resin capacity is quoted as 9.5 meq/g dry resin, unit weight of dry resin can recover 0.22 times its weight of (2/3 MgO + 1/3 CaO) per operating cycle, or it will recover its own weight in less than 5 operating cycles.

(Step 2) The effluent from step 1 will be slightly acidified and alkaline earth depleted seawater. The acid release from step 1 will prevent absorption of alkaline earth ions in that step unless neutralized or very large excess volumes of sea water are employed. This problem can be solved by simultaneous absorption of anions on a weak base resin in free base form. Cross circulation of sea water between two vessels or incorporation of both resins in the same vessel may be used, although for convenience in regeneration, the former option may be preferable. Depending on needs for chloride ion, it may not be necessary to recover the same number of equivalents of anion as cation, but full neutralization may be necessary for proper operation of step 1.

Anion resin for step 2 has a nominal capacity of 5 meq/g dry resin. Selectivity preference of $SO_4^=$ over Cl- will probably raise the equivalents ratio of $SO_4^=:Cl^-$ from its seawater value of .0515 to about .3 for single stage or about .7 for two stage substitution. Unit mass of resin will then recover about 0.2 times its net weight of mixed anions ($.3(1/2SO_4^=) + .7\ Cl^-$) containing 0.072 times its mass of $SO_4^=$

(Step 3) Regeneration of the resin loaded in step 1 in acid form and recovery of the alkaline earth ions can be accomplished by any acid stronger than a carboxylic resin acid. IRC-50 has a $pK_a = 6.1$. Potential complications can arise based on solubility considerations. Limited solubility of $CaSO_4$ can effectively separate Ca from Mg, but can foul resin. Passage of bisulfate solution over strong anion column in chloride form can yield HCl of comparable acidity which can successfully elute the column. Use of bifluoride eluents can precipitate both CaF_2 and MgF_2. These can be removed with strong HF solution or alternatively anion exchange can be practiced.

(Step 4) Regeneration of the anion resin is performed with ammonia or ammonia/ammonium salt solutions. The latter option can improve separation and drying of ammonium salts for pyrolysis in step 5. A second stage absorption may be desirable to upgrade the sulfate content by depressurizing and stripping most of the ammonia from the first eluent and reabsorbing on a second smaller column. This column would be eluted with concentrated ammonia as for the first.

(Step 5) Following crystallization and removal of $(NH_4)_2SO_4$ from the effluent from step 4, the salt (or in an alternate option, NH_4F) is pyrolyzed at atmospheric or reduced pressures to yield ammonia and the corresponding acid salts which are used for steps 3 and 4. The process heats to dissociate per acid/base equivalent are 110 Kjoule and 78.5 Kjoule for $(NH_4)_2SO_4$ and NH_4F respectively. The reactions may be carried out at temperatures in the range 100 to 170°C depending on pressure.

(Step 6) Anion exchange can conveniently be done with a cation exchange resin of higher acid strength than used in step 1. The bisulfate or bifluoride ion is used to regenerate the resin in acid form, and the acid is eluted with ammonium or sodium chloride as HCl (or by substitution any other desired acid).

(Non-core process steps)

A complete self-contained processing system applicable to silicate minerals has been developed for processing lunar materials or alternatively earth resources such as coal ash. Silicates are of importance for conversion of calcium and especially magnesium compounds to acid resistant, water resistant structural materials. These can be formed from alkaline solutions (sodium silicates) or aqueous silica gels and soluble or suspended alkaline earth compounds by cold forming methods. If clay or aluminosilicates are accessible, this permits recovery of aluminum or its compounds.

Carbonic acid elution is a possible alternative method for recovery of Mg^{++} absorbed in step 1, although fairly large volumes of effluent are required. Calcium is effectively separated in the presence of higher levels of bicarbonate. Ammonium carbonate may be used as a secondary precipitant to recover $CaCO_3$ or $MgCO_3$. Although C is not plentiful in seawater, it can be obtained if fossil fuels are used.

Cost/Benefits and Engineering Requirements

Mass requirements can be conveniently divided into capital and operating requirements. With reasonably careful recycling operations, the major operating mass requirement will be for energy if obtained from fuel. One metric ton of petroleum has a heating value of about 44 X 10^9 joules and contains 84% carbon. This can be used to dissociate up to 0.4 X 10^6 equivalents of NH_3/HSO_4^- (or alternatively 0.56 X 10^6 equivalents of NH_3/FHF^-) while recovery of the CO_2 formed would provide an additional 0.07 X 10^6 equivalents. Heat pumping could perhaps double the available energy in the pyrolysis temperature region needed. One half million equivalents of mixed alkaline earth oxides of the ratio previously described has a mass of 11.5 million tons which would exceed 20 million tons as carbonate, sulfate or silicate compounds. Use of high grade power sources, on the other hand would lead to reagent replacement as the limiting mass expendable. For example, 99% ammonia recycling would lead to ammonia attrition at the rate of .74% of the rate of formation of mixed alkaline earth oxides. Even this would not require conventional resupply, since simple methods of nitrogen fixation at low pressure could be used to resynthesize ammonia.

The capital mass requirements in terms of ion exchange resins were already described. In proper geometries and using high strength materials, it appears that low pressure vessels weighing less than their contents would be needed. Estimates made for space processing plants of greater complexity yielded overall capital mass requirement equivalent to 63 hours of output stream accumulation. Even if a substantially higher value was representative, it would appear that for operation of 12 months or longer, the capital mass would be negligible in comparison with fuel mass for fossil fuel operation. For power supplied by other energy forms, a more detailed examination would be needed to determine mass-amortization.

The rate of output will be roughly linear with available power. If the overall power requirement is approximately 150 Kjoule/gram equivalent, the energy: mass or power: mass rate ratio equals 6,500 joule/gram for mixed alkaline earth oxides or 1.8 Kwh/kg. One kg/sec which accumulates to 30,000 metric tons/year would require 6.5 thermal megawatts.

No apparent difficulties appear to be present in regard to service life or corrosion of the equipment for the respective steps.

Environmental constraints

The processes chosen appear to be useful at a wide variety of locations including moving sources (ships or other vehicles), but some of the steps would operate more slowly under arctic conditions resulting in lower specific output rates.

Facility & operational constraints

As is true of nearly all recyle and regenerant processing systems, the elimination of requirements for predominant fractions of normally expendable reagents will increase the energy and capital equipment needs for producing unit masses of specific output products. The principal factors of importance in energy management include the temperatures or special characteristics of process heat and power required as well as power or energy fractions which could be operated successfully with interruptable (off-peak or waste) heat sources.

Table 1

Process equations

1. $\mathrm{RH + seawater \rightleftharpoons R(1/2Ca) + (1-\alpha)R(1/2Mg) + (seawater + HX - 1/2MX_2)}$

2. $\mathrm{(seawater + HX - 1/2MX_2 + R_b \rightleftharpoons \beta R_bH(1/2SO_4) + (1-\beta)R_bH(Cl) + (seawater - 1/2MX_2)}$

3. $\mathrm{R(1/2M) + HAc \rightleftharpoons RH + 1/2M\,(Ac)_2}$

4. $\mathrm{R_bH(X) + NH_3 \quad R_b + \frac{\beta}{2}(NH_4)_2SO_4 + (1-\beta)NH_4Cl}$

4b. $\mathrm{\frac{\beta}{2}(NH_4)_2SO_4 + (1-\beta)NH_4Cl + \gamma R_bH(X) \quad \beta R_bH(1/2SO_4) + (\gamma - \beta)R_bH(Cl) + (1-\gamma)NH_4X}$

5a. $\mathrm{(NH_4)_2SO_4 \xrightarrow{\Delta} NH_3 + NH_4HSO_4}$

5b. $\mathrm{2NH_4F \xrightarrow{\Delta} NH_3 + NH_4FHF}$

6a. $\mathrm{HSO_4^- + RNH_4 + NH_4^+ \rightleftharpoons RH + (NH_4)_2SO_4}$

6b. $\mathrm{RH + NH_4Cl \rightleftharpoons RNH_4 + HCl}$

R= cationic exchange resin, $\mathrm{R_b}$ + anionic exchange resin

M= divalent metal ion ($\mathrm{Ca^{++}}$or$\mathrm{Mg^{++}}$)

X= equivalent univalent anion ($\mathrm{Cl^-}$ or 1/2 $\mathrm{SO_4^=}$)

α, β, γ Numerical factor ($0<i<1$)
depending on resin selectivity

FORMING STRUCTURES FROM SILICATES AFTER ION EXCHANGING, USING HOT AND COLD FORMING CHEMISTRY

Detailed Discussion

In the above description we discussed a process for the recovery of calcium and magnesium compounds plus sulfates from seawater. Combinations of these constituents with silica from sand or silicate minerals and carbonate can lead to a wide variety of useful materials which can be shaped by cold or hot forming methods into useful structures.

Compositions

Final products may consist of one or more crystalline phases with nominally fixed compositions or amorphous (glassy) phases whose compositions may vary over substantial ranges. In addition, granular, fibrous or coarse extended reinforcing materials may be added to an adhesive matrix as in concrete and fiber-reinforced plastics. The materials may also possess variable water contents incorporated during processing or forming operations, not all of which may be lost before fabrication of the end products. Also, a number of useful chemical intermediates can be prepared which would be of value in various forming or preforming operations.

Table 2 lists compounds which are potentially recoverable from the above mentioned sources. The water soluble and insoluble salts (chlorides, sulfates, carbonates, and silicates) are generally derivable from low temperature process steps and the major energy input required consists of salt splitting pyrolysis of ammonium salts to produce acids and bases. Oxides or hydroxides will generally require higher temperatures such as for pyrolysis of carbonates or sulfates, and these compounds usually require more energy for their production per unit mass.

Properties

The hydrated minerals such as talc (M_3S_4H) are generally softer and possess lower strength than the anhydrous compounds, and for the latter class within the silicate group there is a general increase in hardness with increasing silica content. All of the above materials may be classified as brittle rather than ductile materials and as such must be used in designs avoiding appreciable tensile loads. When reinforced with fibrous or other extended materials, they may be used in place of metals for many applications requiring elevated tensile stresses.

(With respect to fundamental hardness, none of the accessible compounds represent an improvement over quartz sand, but they can be prepared in useful forms more easily or at lower temperatures than quartz following specified forms of processing.)

Cold forming

The selective hydration of various calcium silicates, particularly C_2S and C_3S provide the major long term hardening process operating during settling of portland cements. Hydration of $CYH_{1/2}$ to dihydrate CYH_2 is the principal reaction occuring during the hardening of plaster. Carbonation of free lime by CO_2 in air is involved in the hardening of mortar and occurs peripherally also in cement chemistry. These reactions plus in-situ precipitation of hydrated calcium and magnesium silicates or irreversible polymerization of silica gels can be used to cold form various simple or reinforced structures. For the most part, they will require one or more preforming operations usually requiring a hot processing step. This will often require operations to dry and/or dehydrate intermediates recovered from wet chemical processing.

Cold forming operations are customarily fairly slow in the rate of development of useful strengths. These curing or ageing steps can often be done with little or no attention and without tying up capital equipment. Energy requirements are usually minimal for cold forming operations.

Hot forming/processing

Dehydration of calcium silicate hydrates requires elevated temperatures and depends on both C:S ratio and ambient pressure. At atmospheric pressure for C:S ratios below 1, the hydrates can be dried at or below 500°C, but the decomposition temperature rises with increasing lime content. For the magnesium silicates, serpentine ($M_3S_2H_2$) may also be dehydrated in this range, but talc (M_3S_4H) requires higher temperatures (600-700°C).

Calcium carbonate will pyrolyze near 1,000°C while $CaSO_4$ requires temperatures in the range 1,200-1,300°C to yield the oxide. The corresponding magnesium compounds may be pyrolized at 200-300° lower temperatures.

By drying and heating the silicate compounds or mixtures in Table 2, it is possible to form a variety of glasses. Most of these have fairly high softening points, but by adding sodium compounds, it is possible to obtain glasses similar to commercial soda lime glasses. The glasses can be drawn into fibers which can be used as reinforcement for the cement-like crystalline matrices. It is also possible to form massive structures by melting and casting, or alternatively sintering crystalline silicate materials. In the latter case by incorporating certain low temperature melting phases, it is possible to reduce porosity and improve strengths of ceramic ware.

Cost/Benefits

Although it requires a substantial amount of energy to melt or fire these semi-refractory compounds, it should be noted that the energy requirement in terms of fuel mass needed to process unit mass of a typical glass is still much less than unity. For example, the total heat to fusion of even the highest melting silicates rarely exceeds 3×10^9 joule/metric ton as compared to ca 44×10^9 joule/ton combustion energy for a typical petroleum. Furthermore, it may be possible to process material in which only 10% to 20% of the final mass is subject to hot processing, and even in such cases, substantial recovery of the fuel energy from the cooling of hot fired products may be applied to the salt splitting operations of primary process recovery of the seawater components.

The capital requirements for hot and cold processing are perhaps more efficiently met by processing and forming aimed at production of many repetitive elements which could be assembled or formed into large structures when needed rather than processing very large batches of material at long intervals, especially for hot operations.

It is possible to reduce the capital mass requirements initially needed to reach any given output capacity by using a portion of the output to provide expansion of production facilities. Although the processes described will not provide steel or other high melting metal, the alkaline earth compounds recovered can provide such elements as thermal insulation, general refractories and foundation structures for equipment. Metal could also be incorporated into equipment as thin liners for a primarily ceramic structure. The widespread distribution of aluminum in the form of aluminosilicate minerals would also permit recovery of aluminum metal, and the utility of aluminum and/or magnesium could be greatly expanded by importation of small amounts of alloying metals, especially zinc to provide superior strength alloys.

Solution chemistry of silica

Silica, once brought into solution, can be precipitated in gel form and the colloidal "solution" (dispersion) may be adjusted to a wide range of viscosities. Such gels are subject to irreversible ageing effects, usually with an increase in viscosity. These liquids can also be used to prepare calcium and magnesium silicates by interacting with soluble (or sparingly soluble) alkaline earth compounds such as chlorides, bicarbonates or sulfates.

Soluble silicates may be obtained in either alkaline or acidic solutions. The former are prepared by dissolving silica in sodium hydroxide solutions or, alternatively, fusing sodium carbonate with silica. A variation is available for partially solubilizing a previously precipitated acidic gel with ammonia. The acid solution is prepared from hydrofluoric acid as fluorosilicic acid.

By neutralizing either of these soluble silicates one will obtain silica gels which may be washed free of the residual salts if desired and which may then be reacted with alkaline earth oxides, hydroxides or salts. Neutralization of acidic solutions may preferably be performed with NH_3 or NaOH, and basic solutions may be neutralized with carbon dioxide, bisulfates or other strong or weak acids. Recovery of the neutralizing agents is possible.

Operational scenarios

The general concepts covered in this and the above discussion can be adapted to a range of scales and process rates to meet a variety of potential mission requirements. In order for this approach to be economically justified in comparison with more conventional routes toward military and naval engineering, it is necessary that certain criteria be met--these having to do primarily with logistics of delivery of capital equipment and/or fuel vis-a-vis construction and assembly supplies. Consideration of these factors suggests several scenarios for which the indigenous material recovery method seems especially favorable.

A scenario might involve a plant scaled to a system operable for 6 months to a year on a single supply of fuel oil. For example, 30,000 metric tons of fuel will permit burning at the rate of one kg/sec for a year which could provide up to 10 or 20 times the fuel mass in useful product over a year's time.

Table 2

Chemical compounds recoverable from seawater, silicate minerals and a carbonated source

(Expressed in cement chemist's shorthand notation:
$CaO = C$, $MgO = M$, $SiO_2 = S$, $H_2O = H$, $CO_2 = B$, $SO_3 = Y$, $Cl = X$)

Basic Constituent(s)	Acidic Constituents				
	Oxides, Hydroxides	Sulfates	Carbonates	Silicates	Chlorides, other
CaO	(C, CH)	$\left\| CY, CYH_{1/2}, CYH_2 \right\|_{sp}$	CB, $(CB_2H)_{sp}$	CS, C_2S, C_3S, C_3S_2 +18 or more hydrates $C_mS_nH_p$	$\left\| CaX_2, CaX_2H_i \right.$ $\left. i = 1, 2, 6 \right\|$
MgO	(M, MH)	$\left\| MY, MYH, MYH_7 \right\|$	MB, (MB_2H)	MS, M_2S +3 or more hydrates $M_mS_nH_p$	$\left\| MgX_2 \quad MgX_2H_6 \right\|$
CaO+MgO			CMB_2	C_2MS_2, CMS, C_3MS_2, CMS_2	
Na_2O	$\left\| N, NH, NH_i \right\|$	NY, NY_2H, NYH_7, NYH_{10} NY_2H_3	NB, NB_2H, $N_3B_4H_5$, NBH NBH_{10}	NS, NS_2, NS_3, NS_3H_5, NS_3H_6, NS_3H_{11}, N_3S_8	$\left\| NaX \right\|$
other		$\left\| Y, YH, Y_2H, YH_i \right\|$	(B)	S, SH_i	(HX)

(Soluble or sparingly soluble compounds in parentheses or brackets)

STRUCTURAL REPAIR AND SENSING

A structural design made from seawater material which is able to be repaired, rebuilt and redesigned in place in response to the sensed actual dynamic loading and actual structural deterioration in the ocean because so many forces interact in a dynamic way, is the natural process design.

In response to the problem of structures which experience the extremes of marine environmental stress and deterioration, we have created methods in which the material is not allowed to deteriorate indefinitely but builds up in active response to wear and fatigue, and a sensing mechanism which determines where the added material is placed in response to stress or perhaps damage.

The need for extra material and design conservatism is reduced because the structure can repair itself and sense increased stress, and the construction problems and cost are eased because some of the repair construction is done in place by the ocean processes themselves.

MINERAL ACCRETION REPAIR AND RESISTIVITY SENSING

We recommend 1) electrolytically accreting a hard mineral coating from seawater on the area where it is needed to meet the loads and resist or repair deterioration, 2) sensing the actual corrosion rate, and 3) sensing the dynamic stress on the structure. Electrodes on the backside of metal piles cause deposition of mineral precipitate on a mesh on the front side. The electrodes are placed so that there is a small space between each accreting area. Thus you may thicken any discrete area which is thin and needs repair. A sensing grid measures electrical resistance through the deposition to determine what area is becoming thin. It can send an electrical signal back to the electrode to accrete more.

Cost/Benefits

The cost/benefit relationship is best shown by comparing present repair and construction cost for a reinforced concrete structure to this method. In this method, electricity is the major cost. A deposition of 1 pound of accreted material costs $.12; standard reinforced concrete construction repair cost including material and labor costs $2.00 a pound. Labor is the largest cost saving in the accretion method followed by material cost.

The efficiency of resistivity sensing and accretion repair systems is similar to that of structural accretion if the sensing is done on one side. However, if you pass a current through the accretion to measure resistivity then you have Ohmic or energy loss. One remedy is slow the current density through the accretion to reduce energy use. This slow rate also slows the accretion repair. So the penalty for passing a current through the accretion has to be paid in time or energy.

Research

The main objective of experimentation would be to examine the feasibility of this concept for a self-repair and sensing system for ocean structures using electrodes to accrete and sense.

Simply put, accretion is caused by any cathodic electrode put in seawater which discharges hydrogen making the water more alkaline. This imbalance causes materials like calcium carbonate to precipitate out, if there is enough calcium and carbonate in the water. So accretion is the result of a sudden shift in the PH factor due to electrodic action.

This chemistry has been proven in the lab setting many times. What is unique in our proposal is the accretion takes place in-situ. The amount of accretion obtained can be altered by varying the three factors: 1) the amount of voltage from the electrodes, hence the change in PH, 2) the amount of calcium in seawater, 3) the amount of carbonate in seawater. The fourth factor, the condition of the actual seawater is uncontrollable.

As a first approximation, to test the accretion process, we take a metal armature hooked to electrodes with a charge and submerge it in seawater. The electric current changes the PH, causing minerals to precipitate out onto the armature framework. The cathode gives off hydrogen; the anode gives off oxygen. A power supply from a battery charger of about 4.8 V at 200 Amp. connects to a carbon anode of about 10 cm by 2 cm on a piece of hardware cloth 1 ft by 1 ft in an aquarium 3 ft by 1 1/2 ft by 2 ft for a period of 500 hours. It produces an accretion of 10 mm. in a seawater mix of standard proportions. The main products are magnesium hydroxide followed by calcium carbonate. The accretion is thicker at the point where the cathode is connected to the hardware cloth.

As a first approximation, to test the sensing mechanism, we do another accretion experiment in which we block one area out. We use an electrode sensor to determine the resistivity, hence the thickness and select which area has the thinner accretion. It then sends an impulse to turn on the accreting electrode governing that one tile area. The accretion is thickened in that one area.

Next in the lab we would design a system which is close to the reality of repairing ocean structures. It consists of an electrode on the backside of the steel sheet with hardware cloth mesh on the front. The electrode causes deposition of a mineral precipitate from seawater (by changing the PH). This deposit is a mosaic looking tile cover, because the electrodes are placed so that there is a small space between each accreting surface. The accretion areas would be about one foot square of mesh with one to two inch spaces in between them. Thus you may send a signal to thicken any discrete tile area which is especially stressed or needs repair. After initial accretion, a small maintenance battery would be required - like a storage battery.

There is another electrode on the back of the steel which is a sensing grid which measures electrical resistance through the deposition and so can determine what mosaic area is becoming thin. This sensing grid can determine the thickness, for purposes of information only, or it can send an electrical signal back to build up the accretion thickness. The mosaic method can be used to deliberately build up areas of greater thickness by sensing the information on thickness and then directing the deposition process to build up an area. You can turn on the electricity for a particular grid area or you can simply measure the deterioration. This grid accretion process can accomplish sensing where damage occurs, measurement of corrosion rate, and the strengthening of specific areas as required.

In the lab design of this prototype we would focus on: I. impact of electrode impact on seawater PH by varying A. type of electrode B. electrode placement C. amount of voltage, II. amount of calcium in solution by varying A. chemical forms of calcium present B. the amount of calcium present, III. amount of carbonate by varying A. chemical forms of carbonate present B. amount of carbonate present, IV. interaction of calcium and carbonate to produce some amount of calcium carbonate precipitate by varying A. amount of chemically available calcium and carbonate relative to each other B. size and placement of electrodes, V. ability of sensor electrode to determine the amount of accretion by varying A. type of sensor electrode B. placement of sensor electrode C. amount of voltage.

We would, however, design an alternative prototype if 1) we determine that the ocean conditions are such that the amount of carbon in the seawater is too small to precipitate out adequate calcium carbonate repair material, 2) or if the repair is such that large amounts of pure calcium carbonate is required. In that case the design may entail adding carbonated water in an ion permeable membrane to help the precipitation of calcium carbonate. The prototype design then entails a double layer hardware mesh screen attached to electrodes on the front of the metal surface with a cavity in the interior of the mesh screen. The membrane which keeps the carbonated gas from migrating, goes into this cavity. Calcium from the seawater goes through the membrane to join the carbonate. Due to the PH change, calcium carbonate is plated out on the metal mesh. A third electrode for sensing measures the electrical resistance of the accretion deposited. It then directs accretion to those areas needing more thickness. In the actual ocean situation, after the initial deposition of calcium carbonate on the structure, the sensing electrode measures the thickness to determine repair needs and sends a signal directing accretion to thin areas or as desired.

Next we would test the basic repair and sensing concept in the ocean on an actual structure and then make modifications based on the data from those tests. As an example of this, we would choose to use a semi-rigid port structure such as steel sheet piles which yield somewhat to wave energies, etc. Since environmental loading on a semi-rigid wall is so highly variable, usual design information has to be derived from empirical data. The corrosion rate for steel sheet pile structures is affected by location, tide range, exposure, earth cover, and can be a highly localized phenomena. Traditionally, permanent steel structures have been designed with extra metal thickness to account for the unexpected material loss over the life of the structure. But even then, local pit growth can be many times the expected rate, and 1/6 inch additional metal thickness for this is often required.

Our design solution applied to this semi-rigid structure of steel sheet piles in an actual ocean setting entails: (1) sensing the actual dynamic environmental loading on the wall due to waves, etc. (2) sensing the actual corrosion rate and (3) accreting a concrete-like mineral coating from seawater on the area where it is needed to meet the loads and resist or repair deterioration. Such an adaptable design for a particular structure under unique conditions reduces the need for the extra steel normally designed to meet corrosion loss or a catastrophic event. Structures which can put the material where it is actually needed will be stronger, more efficient, and cost effective.

(This calcium carbonate repair system and resistance sensing works using silicate accretion also.)

OTHER WAYS OF SENSING AND REPAIR

Repairing with an electrostatic discharge field

A way of repairing the accretion, without requiring sensing is an electrostatic discharge field. This electric field leaps out into a certain volume of seawater, rather like a halo effect. Electrolytically activated accretion would then grow just so far and then stop, where the field stops. If an area of accretion were thin, more current would flow there, automatically filling it up. This system does not need to be smart, nor have a sensor to direct repairs.

Sensing with ultrasonic pulse echoes

Another sensing mechanism is an ultrasonic pulse echo. This method looks like piezoelectricity, in that if we change pressure with a pulse we develop an electrical field. When the pulse hits the piezoelectric mineral and pressurizes it, you can measure the amount of electricity given off divided by time elapsed to get the thickness measure. The echo bounces back when it hits the discontinuity, for instance when it has penetrated the accretion and reached seawater on the other side. It pulses back to activate a piezoelectric effect and sense the thickness.

Sensing PH variance with voltage

Another sensing/repair system utilizes the fact that voltage depends upon PH. In this oxidation/reduction system you want to sense any variation in PH. In the accretion layer any especially porous or weak area should be sensed. If you pressurize one side of the accreted wall by squeezing in a fluid with a PH different than the outside seawater, you can easily locate the voltage difference, hence the PH difference, where the fluid fills a porous and weak area. This system can repair also. The added PH fluid can be such that it attracts more voltage. This added power will be used to repair the accretion electrolytically. In silicates, if the PH is high, the voltage could help the precipitation process. This sensory system works if you have an organic base with an oxydized and reduced form in equal amounts which will remain that way. Voltage then depends upon PH. However, in the repair system paired with the sensory system, you need to (1) keep the oxydized and reduced forms in equal amount (2) you cannot use up either form in the repair process (3) you cannot allow the PH material to diffuse away. One design solution would then be to suspend large molecules in a fluid beneath the membrane.

Sensing with induced magnetic fields

One method of sensing is tied to the silicate accretion repair system in which water has to be pumped to raise silicates from the bottom. The moving water, which is electrolytic, produces an induced magnetic field. Then the ripple effect can be measured. The physical act of moving water in the earth's magnetic field pushes the field out of the way and that can be measured. This method of sensing with an electromagnetic field can also report if objects are nearby interrupting the field. It can also determine the orientation of the structure vis a vis the earth's electromagnetic field. This is very useful for building in the ocean, it takes the place of a plumb line.

For moving ports or piers an electromagnetic compass will give orientation. As the port or pier moves in salt water (which is an electrical conductor) water is moved out of the way by this solid body. The seawater moves through the earth's magnetic field and disturbs it. Sensing coils oriented with the port's motion determine how the port is moving in relation to the earth's field.

It is known that the progression of time-harmonic plane water waves (such as tidal waves) through a density stratified, rotating, electrically conducting sea, over a stratified conducting earth and under a nonconducting atmosphere, produces an electromagnetic field within, above, and below the sea. Thus it is possible to measure east and west deep ocean fluid motions by electromagnetic means by remote antennas in airplanes. The Navy does this. Sharks use this horizontal component of the earth's magnetic field to produce direct current low-frequency voltage gradients in water which mainly stem from potential differences at their skin-water interfaces. By swimming to the east for instance, the shark generates - according to Faraday's law - an internal induced electromagnetic force which gives rise to electrical current that flows through the moving fish and loops back through the stationary environment. When the fish turns north or south, the potentials vanish. When the fish turns west, potentials of opposite polarity are induced. Interaction with the vertical component of the earth's magnetic field allows the fish to induce motional electric fields parallel to their transverse body ones. Thus they may determine the magnetic latitude of their position on the globe.

For an ocean structure which will not be moving, but has the seawater surrounding it in motion, the stationary building acts as an interruption in the water's normal flow. The plumb line orientation to the earth's fields can be determined from this information.

CYBERNETIC SYSTEM

COMMUNICATION, DECISION MAKING, AND IMPLEMENTATION

THE SALINE COMPUTER

This saltwater electrochemical computer can be used for such in-place ocean processes as 1) sensing changes in temperature, pressure, salinity 2) directing an action such as accretion of minerals to repair a structure 3) recording what action has been taken such as repair and recording changes in the environment (4) combining with a communication system to transmit data or interpret input from other sources.

This computer is the director of a cybernetic process. Like the processes it directs, it is made out of the elements and processes available in the chemistry of seawater. It performs logic, computation, and memory using seawater chemistry. In sum, the saline computer is a low power electrochemical computer, the operating elements and memory system of which uses seawater as the electrolyte and source of most chemicals.

These electrochemical system components in various combinations can be assembled to provide stable - very low-power circuits to perform logic, computation, and memory functions in submerged locations with potential reliabilities far exceeding that of semiconductor systems. The electrochemical elements when operating as switches perform much more slowly then conventional circuits, but are relatively immune to radiation, water pressure, sealing technology problems and various forms of insulation failure.

In this idea we extend the solion concept of a chemical switch to include 1) open electrochemical systems using natural seawater as an electrolyte and some seawater compatible chemicals many of which are generated from the seawater itself, 2) self-powered batteries or power supplies not dependent upon expendable energy but which use the properties of seawater, and 3) erasable or reversible as well as permanent or non-reversible modules which can function as memory elements, many of which are made from seawater such as accreted minerals. This is the basis of a very elegant and flexible language of computer function.

Solions

A series of devices, termed "solions" have been developed to provide various sensing and switching functions to measure pressure, flow rate, integrated charge, temperature, etc. Some of these operate as electrochemical equivalents of fluidic devices. Although stable operation has been achieved, these systems generally employ sealed electrolyte systems such as iodide-triodide redox cell whose current-voltage behavior could be controlled by an external potential or signal derived from the desired sensor or transducer. They act like transistor circuits, but operate at not very high switching speeds. Their interest is that they use a low power supply and a current to use as an amplifier or integrator. They are very simple, but can convert pressure to a signal through a flow meter to electrical signals and vice versa. It is a logarithmic correspondence to pressure. Also it can be a multiplier, so you can multiply the current times flow and get velocity or it equals voltage output. So it is an analog, not a digital system. It is an electrochemical cell which can respond to pressure, flow, fields, etc.

The System

In this project we intend to extend and broaden the above solion concepts to include "open" electrochemical systems using natural seawater as an electrolyte, self-powered batteries or power supplies not dependent on expendable energy sources, and the development of "erasable" or reversible as well as "permanent" or non-reversible modules which may function as memory elements.

The elements

The elements of the computer are a chemical system which can 1) perform sensing and switching functions without the need for enclosure from the seawater surround 2) provide power to a) amplify those functions or b) change the chemistry to create those elements which can accomplish the functions desired or c) to accrete material for use as memory storage and 3) store memory in a system of reversible and non-reversible memory cells.

The batteries

The battery which is expendable and renewable, one you set and forget, in a submerged location is activated by seawater. It is needed for amplification because the electrochemical half cells give a weak signal not much above the noise level. Amplitude clarifies the true signal. The battery can supply a circuit to change the ion signals given off by the electrochemical half cells and it can generate power for the accretion memory.

One design is to have a few insulator planes into which seawater leaks along a long path to produce a current. One interesting possibility for near surface oceanic applications is analogous to wave energy recovery and involves a series of standing pipes or labyrinths with one-way or "diode" valves to trap a reservoir with pressure greater than average sea level value. Using reverse osmosis or other recovery system, this can be used to recharge a conventional electrochemical cell or reversible battery.

Another battery system uses osmosis. Night time cooling allows one to collect condensing evaporated water like dew (or rain water for fresh water). This fresh water acts as one electrode, seawater being the other saline electrode. As the fresh water passes a membrane, attempting to dilute the saltwater, it gives off a charge. Enough power can be obtained in this way to operate a low power system. This uses the dialytic battery concept and can be called an electroosmotic cell.

Open electrochemical half cells

The elements of this system which can perform sensing or switching are open electrochemical half cells which are reversible - i.e. the ions can take on an exterior ion or give one up. You need two half cells, an anode, and a cathode to make up one complete cell. The half cells need to have the following characteristics 1) be reversible so they can sense and switch in a variety of ways 2) have low solubility in the presence of chloride ions (i.e. the salt in saltwater) so that they do not dissolve and float off into the seawater and 3) be active in a range where the dissolved oxygen is not too much of an interruption. Oxygen is a powerful oxydizing agent and the anode chosen is already the oxydizing agent. You need one reducing half cell (i.e. the anode) and one oxydizing half cell (i.e. the cathode). If they operate at different natural potentials, then you get an equilibrium voltage across the whole cell. Of course, an outside circuit from the battery may be used to change the state of the cell so this cell can be used to control another cell.

The chemistry of electrochemical half cells which are compatible with seawater as the electrolyte and are open systems which have reversibility are of three main categories: 1) Metal- metal ion systems with very low metal ion solubility controlled by natural constituents of seawater (Examples: Ag, Ag^+, Cl^- control, Hg, Hg^+ , Cl^- control, Pb, Pb^{+2} , $So_4^=$ control, Ba-Amalgam, Ba^{++} -- $So_4^=$ control, Fe^{++}, Fe^{+++}, OH^- control, Cr^{+3}- G^{+6} , Ca^{++}control), (2) Nonmetallic redox systems with very low saturation solubilities controlled by natural constituents of seawater (Examples: As^{+3} - Ag^{+5}, Ca^{++} control), (3) Self generated oxidants from seawater such as a chlorine system (Examples: Cl_2, Cl^-, O_2, OH^- peroxide, OH^-, O_3 - OH^-, etc.). Various techniques can be used to minimize diffusion of the active constituents in solution including gellation, counter ion permeable membranes, etc.

The oxygen-peroxide cycle, hydrogen-hydrogen ion cycle, and the chlorine-chloride cycles all can get their chemical constituents from seawater. The self-generating oxidants are present in seawater if you pass a charge at the anode where the oxidized material will develop. Chlorine is the most easily discharged oxidant followed by sulfate. If the sulfate electrochemical half cell can then be made into an oxygen/hydrogen peroxide cycle by passing a current from the battery through it, then this allows the cell to accomplish even other things.

The metal-metal ion ones such as silver chloride are insoluble in seawater and because they will not migrate, you need only a small amount. (For instance, you can make a calcium carbonate accreted structure with silver in it. This silver would tell how much chlorine is in the seawater, i.e. the salinity because the potential of silver and therefore the voltage will change when the amount of chlorine changes. It is an analog system. As an example, you can monitor discharges from sewage plants this way. The amount of discharge will change the salinity of seawater by diluting it. This silver system can measure such a salinity change.)

The choice of chloride electrochemical half cells as opposed to metal - metal ones depends upon what you need to accomplish in terms of sensing, switching, etc. One very interesting application of chlorine-chloride cycle is in deep cold water situations. The higher pressure and colder temperatures allow chlorides to dissolve. This then creates an efficient device for monitoring a deep water sensor or cable which can be retrieved at a later time.

Another design issue is the gases given off at the electrode. These reduce the degree of control possible. The remedies are: to raise the pressure which keeps the gas dissolved or have two electrolytes with a membrane in between, one electrolyte is seawater, the other one, not being seawater, does not give off a gas.

Memory cells

Reversible or nonreversible storage of information is possible for selected electrochemical half cells. A reversible deposit of material from seawater (such as calcium carbonate) can be deposited and then dissolved by reversing the current.

The irreversible deposit system forms a layer which does not dissolve. The non-erasable, corrosion electrode can deposit a layer of platable metal such as copper which is non corrosive, over which a reversible material is laid. This reversible material can be deposited or erased to form a pattern which can be read as a shiny pattern reflected off the metal layer by a light system, or a single layer of reversible material allows light to pass through a thin or erased area. Like an electronic computer memory, these memories can be erased and used over many times.

The memories can be used in several ways. 1) These memory cells can be combined with underwater sensors which detect pressure, salinity, or temperature to record their findings. The electrical signal converted from the pressure or salinity effect can be used to activate the deposition process (like the accretion process). 2) A sensor can measure some variable and trigger an electrochemical switch when it gets to a certain value. For instance, after a number of hours in which the temperature is too high, voltage could reach a critical level and a constant current device, is activated, passing the current which accretes material. By measuring the depth of the accretion and therefore the charge, you get the number of hours the current was on. This translates into the number of hours of critically high temperature. 3) Cells with an anode and cathode memory could be used to pass a current and record two different sides of a chemical situation. Parts of either side could then be erased, to some purpose.

The chemical composition of memory cells can be as follows:
(1) Reversible or erasable cells made from:
  a) platable metals such as silver, copper, zinc, chromium, lead, tin, etc.
  b) acid base precipitation systems, aluminum hydroxide, tin oxide
  c) polarizable electrode systems

(2) Non reversible cells made from: corrosion of non-platable metal films, such as aluminum, magnesium, beryllium, titanium. Corrosion of selected patterns on fiber optic structures can lead to leakage of transmitted light and create visual patterns for information readout.

(3) Anodization of aluminum, titanium, magnesium or tantalum. With restricted electrolyte volume, electrolysis of seawater could lead to chlorine evolution and diffusion of free chlorine out of cell and depletion of chloride concentration. This would be followed by formation of stable anodic oxide coatings.

(4) Alkaline accumulatin cells made from: accretion of calcium carbonate. Cathodic evolution of hydrogen leads to build up in alkalinity (PH). This in the presence of air or carbonation causes fixation of CO_2 and accretion of calcium carbonate.

Research

We need to develop the three elements of the system, one at a time. In the open electrochemical cell with a seawater electrolyte using chemicals from seawater, we have a device which acts like an open solion. We propose testing it using sodium, potassium, calcium, magnesium, and chlorine as the chemicals. We need to test and verify the interrelationships between current flow and applied voltage, and between current flow and local concentration changes, and how these are affected by the electrode material and design, by the solution chemistry and concentration and the mass transfer of solution.

In the memory storage system we will test reversible and irreversible types of memory cells, verify their operation (what voltage does it take to perform certain tasks - how does the memory decay) and in several sets of trials vary the amounts of acid (dilution), voltage, etc.

In the battery system we will test the labyrinth diode valve system in which water under pressure is trapped and then released using reverse osmosis. The areas to be explored are the amount of energy to be produced as related to the membrane cost for recovery and recharge. Also we will test the dialytic battery using seawater and using dew or rain as the fresh water. Much of the research on this battery type has been done by Dr. Sidney Loeb as discussed in the following section. The energy production for this battery is well known; the areas to be explored are membrane cost and reliability, and use in this context, i.e. as a computer power source.

Cost/Benefits

The cost/benefit or feasibility for the accretion type of memory cell is partially covered in the discussion on structural accretion methods. The dialytic battery feasibility is discussed in the next section on electroosmotic cells and in the section on nerve-like cables. The feasibility of electrochemical cells is discussed in the detailed discussion section in the following pages.

Summary

The advantages of an open chemical computer in the ocean using seawater chemistry are 1) The computer can create a whole language of connected chemical reactions in order to switch, do logic, and remember. 2) It can sense information, switch and make decisions, direct action such as repairs, construction, and other sensing modes, and can communicate or receive data. 3) It uses reversible reactions and steps which restore the original chemistry and energy with a low outside energy input to give us flexibility to do many things in a controlled way in a discrete area of the ocean's waters. 4) Combined with electrochemical elements already in place, such as for accretion, sensing, repair - it can use their voltage and electric current to make an extremely economical system. 5) One can carefully measure what is taking place or can cause a precise event or series of events to occur. 6) As an underwater computer it is reliable and not prone to insulation failure. 7) It uses the same chemical order explicit in biological nervous systems. It therefore exploits well the available order in saltwater chemistry. The similarity of the chemical processes in our nervous systems, in our bodies' bones, nerves, etc., and the saline computer and undersea structures made from calcium carbonate are striking. This hints at further interfaces and connections between the human nervous system and computers, and building structures in the ocean. Like the human nervous system the saline computer's elements can transmit many kinds of information. It can bring information from sensors. It can carry instructions to the structure or to the reorganizing system to accomplish something - move, build faster, etc. It can produce memory. It can select certain types of messages to transmit while ignoring others. In short, it can give a port using natural processes a cybernetic order. 8) This saline computer can be used not only to process information in one location but, can communicate information by broadcasting long distance signals. Long, low frequency signals is an appropriate mode for the saline computer, even though these have a low rate of information.

Detailed Discussion of Saline Computer, Especially Electrochemical Cells

The electrochemical devices have some functional similarity to vacuum tubes and transistors, in that the internal flow of charged particles is controlled through various factors of design to yield a desired behavior in an external electrical circuit. In the vacuum tube, the internal particles are electrons, the working medium is a vacuum, and the control is obtained through imposition of selective fields. In the transistor, the internal particles are both electrons and "holes," the working medium a crystal lattice, and the control is again obtained through electric fields. In our devices, the internal particles are ions, the working medium an electrolyte solution, but control in this case can be exercised through both electric fields and mass transport.

Because the velocities of ion movement in solution are low in comparison to the electron velocities in vacuum tubes and transistors, our electrochemical control devices are inherently lower frequency devices (<1000 cps). Although this limitation to low frequencies places them at a disadvantage insofar as incorporation into present electronic circuitry is concerned, they possess distinct advantages in applications which require measurement or control of phenomena at low frequencies.

Components

All our electrochemical devices employ an electrochemical system of a reductant and an oxidant dissolved in seawater. As in vacuum tubes, the size, dimension, and form of the electrodes and the spatial arrangement of several electrodes throughout the system are used to obtain performance variations from different units.

Our electrochemical devices can be divided into two major categories 1) those in which one can carefully measure what is taking place by using current and voltage to control the situation or 2) using a small amount of material and power, one can cause a precise event, one which can be stopped, started or reversed precisely.

Electrochemical phenomena involved in operation of the electrochemical device

Passage of current through the oxidant-redundant electrolyte solutions used in most half cells is accompanied by the following generalized electrode reactions:

At the cathode, where X is the chemical

$$X_3^- + 2e \longrightarrow 3X^-$$

and at the anode,

$$3X^- - 2e \longrightarrow X_3^-$$

There is thus no net change in any component in the solution, so that in the absence of undesired side reactions, current can flow through the solution indefinitely with no change in the total system, although there will be local changes in the concentration of the oxidant and reductant. In general, our electrochemical device revolves around the inter-relationships between current flow and applied voltage, and between current flow and local concentration changes, and how these are affected by electrode design, solution concentration, mass transfer of the solution, and many other such factors.

Polarization characteristics

Considering only two electrodes in an oxidant-reductant solution, the functional relationship between current and applied voltage will depend on the electrolytic resistance through the solution and the flux density (ions/sq cm/sec) of reductant ions to the cathode. In the usual device operation, the electrolytic resistance is made negligible by using a large excess of another reductant.

In a typical plot of the current-voltage relationship for solutions of different concentrations, the current increases rapidly with voltage, following Ohm's law for the electrolytic resistance of the solution, until the supply of oxidant to the cathodes becomes limited, at which point the current levels out and becomes voltage independent or "concentration polarized." The second increase in current at about 1.0 v is due to reduction of hydrogen ions from the solvent; this undesired side reaction is avoided by limiting the bias to <0.9 v.

The plateau regions are called "limiting diffusion currents;" for quiet isothermal conditions, their values are given by

$$X = nFAD(dc/dx)$$

where n is the number of electrons involved in the electrochemical reaction, F the value of the Faraday, A the cathode area, D the diffusion coefficient of the tri-reductant species, and dc/dx the concentration gradient of tri-reductant at the cathode. The value of dc/dx in the equation is a function of:

(1) The bulk concentration of oxidant. This makes it possible to read electrically the concentration of oxidant at any point in the electrochemical device.

(2) The degree of stirring or bulk fluid movement in the vicinity of the cathode. Thus, curves could be obtained from the device by using different flow rates through the orifice cathodes, even though the bulk concentration of oxidant is constant.

(3) The spacing between the anode and cathodes, provided they are close enough together that the concentration gradient extends all the way from one electrode to the other. Thus, curves could be obtained from the device by using different spacings between the electrodes.

Faraday equivalence

The exact equivalence between the total quantity of electricity passed through an electrochemical system and the changes in chemical content which occur at the electrodes (Faraday's law) is used as the basic phenomenon in several types of our devices.

In operation, a current (usually in the order of microamperes) is passed through the solution, and the change in concentration around one of the electrodes is determined. Since the number of coulombs passed is given by

$$\int idt$$

then by Faraday's law

$$\int idt \quad \frac{\text{(g oxidant transferred) (value of the Faraday)}}{\text{(equivalent weight of oxidant)}}$$

and the value of the integral is obtained by any method which determines the amount of oxidant transferred. This is usually done by confining the oxidant to a fixed volume and reading concentration.

Concentration voltage

Two electrodes immersed in different concentration of oxidant at room temperature will exhibit a potential difference of

$$E_{conc} = 0.030 \log \frac{C_1}{C_2}$$

provided only that there is a continuous electrolytic path between the two electrodes. The potential developed can be used for either reading a concentration or as a supply voltage to drive another element (such as another integrator, a relay, or a transistor).

Electroosmotic pumping

The electroosmotic cell serves as a complementary unit to a variety of other electrochemical devices in that it is used exclusively as a micropump to feed fluid flows into other coupled units. The electrochemical phenomena involved in these units are quite different from those of the oxidant reductant system used in the electrochemical control devices. Electroosmosis is the movement of a liquid through a porous medium, such as fritted glass or a membrane, under the influence of a potential gradient.

In these electroosmotic cells, unlike the units using the oxidant reductant system, it is desired that the liquid exhibit a very low conductivity, so that electrode polarization will be minimized, and most of the applied voltage will appear as IR drop. It should be noted that as current flows through the cell, there is a transfer of electrode material from anode to cathode, so that current flowing constantly in one direction would eventually consume the anode, and the cell would cease to function. Currents are only a few microamperes on the average, however, so a few grams of silver for instance would suffice for several years of operation.

Typical values of pumping rates are 10^{-3} to 10^{-5} cc/sec, or, if the flow is impeded by pumping into a diaphragm, pressures of a few thousand dynes/sq cm may be developed.

Operating characteristics of typical electrochemical units

Our devices may be classified according to the function performed, such as: (1) detectors, flow meters, transducers, (2) integrators, and (3) differentiators, multipliers, and amplifiers. Units in the third category are generally combinations of single devices, i.e., an electroosmotic cell plus a detector, integrators plus electronic components, integrators in series, etc.

Detectors, flow meters, and transducers

These units operate on the increase in current which results from the disturbance of the solution near a cathode which is concentration polarized. In the detector the cathode is in the form of an orifice through which the solution may be pumped by means of an external pressure across the detector diaphragms. With no flow through the orifice, and with the electrodes biased at 0.9 v, a background current of a few microamperes will flow in the external circuit. Forcing fluid through the orifice disturbs the diffusion layer there and causes the current to increase. The fluid motion through the orifice can be either direct or pulsating; in either case, a d-c current is produced which is a function of the amplitude of the flow. By suitable design of the detecting cathode, the functional nature of the response to flow may be varied. The simple orifice, when properly designed, gives an output which is logarithmic; a porous cathode gives a linear output; and a small box containing offset pinhole orifices gives a square root response.

Integrators

The integrator is essentially a coulometer of unique design; the design factors which make the integrator a practical device are the method of readout and the method of retaining the integral. At the present time, the integrators are clearly the most important units, and the only ones to have reached commercial production, (under the name of solions).

Readout of the integral is accomplished by any method which determines concentration. The three methods used most extensively are (1) the diffusion-limited current at a cathodic element in the integral compartment; (2) the concentration cell voltage between an electrode in the integral compartment and another electrode in a constant reference concentration; and (3) the color density of the solution in the integral compartment. The diffusion-limited current readout is preferred in most cases, since enough power is available through the readout current to operate subsequent electrical circuits for control purposes. However, the other two readout methods are uniquely suited to certain integrating applications.

Techniques to increase or decrease diffusion

A technique can be used to increase or decrease diffusion in order to produce a more accurate integration system which will last over a long time period. Using an iodine - iodide solion system as an example, this technique is as follows: All solion integrators contain an integral compartment and an iodine reservoir, connected by a solution bridge. During integration, iodine is transferred by electrolysis from the reservoir into the integral compartment, after first removing all the iodine from this compartment. For high accuracy, it is essential to retain all of the transferred iodine in the integral compartment and at the same time prevent any iodine reaching this compartment by any process other than the desired electrochemical transfer. However, since there must be a solution bridge between the two compartments, iodine will diffuse from one to the other at a rate dependent on the concentration gradient and the geometry of the diffusion path. The two methods used to "retain the integral" (i.e., to minimize diffusion transfer) are electrical shielding with a negatively biased electrode, and the use of a two-phase solvent system with a high distribution coefficient for iodine between the two solvents.

Electrical shielding can be illustrated by the following description. Before operation, the "readout" electrode is shorted to the "shield" electrode; the negative bias on these two electrodes will quickly transfer all the iodine from the volume below the shield into the reservoir. The readout electrode is then returned to its original connection, but since there is now no iodine in the lower region, no current flows between the readout and the "common" electrode. Some iodine will diffuse through the capillary, but it will be "picked up" (reduced) by the shield electrode and transferred electrochemically back into the reservoir. The current to be integrated is passed through the integrator between the "input" electrode and the "common" electrode so that iodine is transferred from the reservoir into the integral compartment. The iodine thus transferred is formed on the surface of the common electrode and diffuses across to the readout electrode where it is picked up and redeposited at the common electrode. The transferred iodine is thus retained inside the integral compartment.

Where the integral must be retained over very long periods (months), the two-phase solvent system is used. Imagine the separator containing the capillary to be replaced by a fritted-glass disc or a membrane. If the fritted structure or membrane contains a water phase saturated with an iodine salt, and the volumes on either side contain butyl alcohol in which the iodine-iodide system is dissolved, the concentration of iodine in the aqueous phase at equilibrium will be very small due to the high distribution coefficient for iodine between butyl alcohol and water. The concentration gradient of iodine across the water phase is therefore very small, and diffusion transfer is essentially negligible.

Differentiators, multipliers, and amplifiers.

These are "compound" units, in which two or more electrochemical devices are hydraulically or electrically coupled to perform a desired mathematical function, or in which transistor circuits are combined with electrochemical device circuits. Most of these involve coupling the electroosmotic cell to electrochemical device detectors of various designs. Because of the very low frequency response of the electroosmotic cell, all of these devices operate from very low frequencies down to very near d-c.

In the amplifier the electrochemical device detector operates linearly, and since the pressure developed by the electroosmotic cell is linear with applied voltage, the output of the detector follows the input to the micropump, but with large current gains. Typical inputs to the micropump are a few microamperes at less than a volt (i.e., microwatts), while outputs from the coupled detector are milliamperes at about a volt (i.e., milliwatts).

The electrochemical device differentiator consists of the same two units as does the amplifier, but with a hydraulic capacitance, such as a stiff diaphragm or bellows, inserted in the fluid flow circuit. An understanding of how the differentiator works is best gained by drawing an analogy to the corresponding electrical network. In general, the important parameters of hydraulic circuits have exact analogies in electrical circuits, and the most common of these are

Electrical	Hydraulic
voltage	pressure
current	fluid flow rate
resistance	hydraulic resistance (fritted disc)
capacity	hydraulic compliance (diaphragm or bellows)
inductance	hydraulic inertance (capillary tube)

One of the simplest electrical networks is a resistor, R, and a capacitor, C, in series (RC differentiator). A voltage, E, applied to the terminals of this network results in a current which follows the equation

$$I_t = C\, dE/dt\, (1 - \exp - t/RC).$$

The analogous equation for the RC series hydraulic unit is

$$dv/dt = C\, dP/dt\, (1 - \exp - t/RC).$$

The flow rate, dv/dt, can be converted into a current, I_{out}, by an electrochemical device detector, while dP/dt can be generated by a voltage dE/dt fed into an electroosmotic cell. Under these conditions, the equation becomes

$$I_{out} = 10^{-3} FNkC\, dE/dt\, (1 - \exp - t/RC),$$

where F is the value of the Faraday, N the normality of the oxidant, and k is the pressure output of the electroosmotic cell (in dynes/sq cm) at 1.0 v applied.

Comparison of the last equation with the first equation shows that the differentiator works essentially like the simple RC electrical differentiator, but with some rather important practical differences. First, the value of the RC product, which determines the frequency range over which differentiation occurs, can be made quite large in the hydraulic case, and good derivatives are obtainable down to frequencies as low as cycles per kilosecond. The electrochemical device, however, cannot compete at frequencies above about 10 cycles/sec. Second, amplification is inherent in the differentiator, the power being obtained from the battery in the linear detector circuit. The third difference of some importance is the absence of electrical coupling between the output and input of the electrochemical device, which greatly simplifies the design of circuits containing these units.

The electrochemical multiplier is somewhat more complex than the differentiator and amplifier, but illustrates nicely the wide variety of functions which can be obtained by combining the various electrochemical phenomena in different ways. The detector for the multiplier is essentially a linear detector in which the fluid flowing to the detecting cathode contains no oxidant unless it is formed in place by a second external current. This is accomplished by the electrode arrangement. Here the "generator" electrode and the "scavenger" electrode form the opposite faces of a very narrow corridor through which the electrolyte flows before it reaches the detector electrode. These electrodes are insulated so that their inner faces only are exposed to the solution. If the electrolyte initially contains no oxidant, and if there is no input current to the generator electrode, no oxidant reaches the detector gauze regardless of the magnitude of flow. Conversely, if there is no flow, any oxidant formed at the generator electrode by making it an anode will simply diffuse across the scavenger where it is reduced to reductant, and again no oxidant reaches the detector gauze. If, however, both flow and generating current are present, the amount of oxidant reaching the detector gauze, and hence the output of current, is proportional to the product of flow and generating current. By remembering that with other electrochemical device units flows may be produced from electrical currents or electrical currents from flows, it may be seen that a product of any combination may be taken. Further, by incorporating suitable values of hydraulic capacitance in the circuits, products of derivatives in various forms may be obtained in the same unit.

Conclusion

Such electrochemical devices could occupy an important position in the future of such things as control circuits and automation for ports, where low-frequency hydraulic measurements are common; in instrumentation, where long-period differentation, integration, etc., are often desired; and as components in almost any situation where low-frequency hydraulic or electrical signals are available. They use low power and can be an inexpensive form of sensor.

The main economic advantage in using electrochemical half cells is in situations where we already have electrochemical elements. For instance in the sensing and repair of port facilities using accretion, we already have voltage, a circuit and saltwater electrolyte. The addition of the little material to that system in order to do logic and have control makes it very economical.

The main interest in the electrochemical half cell system for ports is that we will be able to 1) sense changes in temperature, pressure, and salinity 2) direct an action such as accretion 3) record what action has been taken and 4) communicate and transmit data and interpret input.[2]

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[2] The above discussion is based on "Solions", by Ray M. Hurd, Reinhold Encyclopedia of Electrochemistry, 1964

NERVE-LIKE CABLES

The Communication System

Membrane cables in seawater are like our nerves in their saline lymph. The inside of a nerve cell has more negative ions (less sodium) than the outside of the cell. This means there is a potential difference across the cell membrane. If the neuron is excited by a chemical signal, the permeability of its membrane changes. Sodium ions from outside rush in to equalize the concentration. This wave of permeability sweeps through the nerve, creating a measureable electrical impulse.

In the saltwater membrane-cable in the ocean, ions moving across a charged osmotic membrane create such an electrical impulse. The cable is a membrane tube containing saline solution of less concentration, across which ions enter from the ocean, to equalize the concentration gradient, thus losing their charge and giving off an impulse. In the case of a membrane cable the general conclusion is that electrical signals can be generated by the membrane without the direct intervention of metabolism, by selectively changing the ionic permeabilities and allowing ions to flow downhill along their electrochemical gradients.

Detailed Discussion of the Dialytic Battery

Doctor Sidney Loeb has actually built these nerve-like cables in series in order to produce a net energy gain instead of signals. He calls it a dialytic battery. "In it voltage and current are produced directly by diffusion of ions across perm-selective membranes separating the concentrated and diluted solutions.

Research

Assume that a membrane permeable to ions of one sign, say to cations, (cation exchange membrane) separates river water and sea water, and that Ag/AgCl electrodes, i.e. reversible, are at each end of the container. If these electrodes are connected through an external resistance, current will flow and useful energy will be obtained. However, the voltage due to the concentration difference will be very low even at the maximum value, i.e. at zero current. The voltage can be multiplied merely by increasing the number of membranes using alternate cation and anion exchange membranes to separate the river water and the seawater in the membrane stack.

In large scale application it would not be appropriate to use Ag/AgCl electrodes. Irreversible permanent electrodes would be used, thus causing electrochemical reactions at each electrode. These reactions consume energy but this loss would be minimized by using a large number of membranes. A more serious source of energy loss is the electrical resistance of the stack given as the sum of the resistance of the membranes and the solution-pair compartments.

Test equipment and procedure

Weinstein and Leitz (1976) conducted dialytic battery tests on a membrane stack containing 31 cation and 30 anion-exchange membranes each 0.6 mm thick and with a total membrane area of 1.4 m^2. They used 0.57 molar NaCl solution to simulate sea water and measured power delivery as a function of the salt concentration of the "river" water, consisting of dilute NaCl solutions. The tests confirmed their theoretical analysis, and enabled calculation of minimum energy costs, as given below.

Cost/Benefits

Membrane replacement cost, which accounts for half the total energy cost, has been estimated as a function of solution-pair type and the membrane process employed. The data are based on the use of presently available membranes tested for possible salinity power service, but developed for other applications. The estimated minimum replacement costs range from \$0.10/kwh for osmotic membranes to \$1.5/kwh for dialytic membranes. Clearly the costs are too high.

Energy costs with the dialytic battery

Present costs

The membrane replacement cost with presently available membranes, used primarily for electrodialysis, is 1.8 \$/kwh for river water - seawater and, surprisingly enough, 1.5 \$/kwh for seawater with either Dead Sea brine or concentrated NaCl brine made from solid salt. The high value of 1. 5 \$/kwh with concentrated brines can be explained . The maximum power output is a direct function of the ratio of the salt activities and not of the difference in the activities. This ratio is actually less for the solution-pair seawater - concentrated brine than for river water - seawater (although compensated for by the lower resistance of the stack when the former solution-pair is used).

Prospects of lower membrane replacement costs with the dialytic battery

Dr. Loeb used an original membrane cost of 10 \$/m^2, an areal resistance of 11 ohm/cm^2 for the membranes, and 40 ohm/cm^2 for the river water compartment in determining membrane replacement costs with present membranes. Furthermore he assumed a 4 year membrane life. Weinstein and Leitz consider it within the realm of possibility to reduce original membrane cost and overall resistance each by a factor of ten by using very thin membranes and river water compartments. They also believe that membrane life can be doubled (compared to electrodialysis, a more stringent application. In electrodialysis, both polarization and membrane failure are more serious than in reverse electrodialysis). If all these improvements are attained the membrane replacement cost will be in the order of $1.80/200 \simeq 0.01$ \$/kwh, a very respectable figure".[3]

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[3] Loeb, Sidney, M. Rudolph Bloch, John D. Isaacs, "Salinity Power, Potential, and Processes, Especially Membrane Processes", Advances in Oceanography, ed. Henry Charnock, Plenum Press, N.Y. 1978

MEANS OF CHANGING AND REORDERING STRUCTURE

A MAGNETOHYDRODYNAMIC PUMP USING SEAWATER AS THE CONDUCTING MEDIUM

Our methods in which portions of the port can be changed and reordered by movement, that is can be raised and lowered, cargo lifted, and silt material pumped, use the nature of seawater, its electrolytic and osmotic properties. In the magnetohydrodynamic pump or water jet, the electrolytic nature of seawater is utilized as the conductor for the current generated by the electrodes which interact with a magnetic field creating a force to drive the water as a jet. Electrodes put a voltage into seawater in the presence of a magnetic field. These two fields interact causing a resultant force which moves the water at right angles to the magnetic and electrical lines of interaction. The result is a directed jet of water. The idea is to create a cost efficient and accurate way of pumping water using seawater as the conducting medium.

Cost/Benefits

The magnetohydrodynamic pump is nearly as efficient as a normal pump. The materials and technology needed to build it are off the shelf. Extra underwater insulation is required. If a permanent magnet is used then the only electric current is that supplying the electrodes. A low current sent down a long pipe to a transformer gives a high current, low voltage situation.

The efficiency of electric power in relation to pressure and water volume flow is nearly as efficient as an electric motor centrifugal pump. The efficiency of a normal pump is 65%-80 %, while the efficiency of the magnetohydrodynamic pump would be about 50% - 60%. Normal pumps, however, may be short lived due to abrasion and fouling. This new kind of underwater pump which uses seawater as the electrolyte would not be subject to these problems.

Research

The main objective of research would be to examine the feasibility of the concept for a magnetohydrodynamic pump. It could lead to the development of a powerful pump which is cheaper and more energy efficient to operate because it uses seawater as the conducting medium and causes two force fields to interact, thus achieving a powerful resultant force.

Faraday's equation says that you can move a conductor through a magnetic field to generate a voltage or (as we chose to do) if you apply voltage across a conductor to give a current, and that current interacts with a magnetic field, a force is created. That has been proven numerous times. What is unique in our idea is the use of seawater as the conductor and the employment of the resultant force to push seawater.

The amount and direction of the force produced can be altered in several ways: 1) vary the voltage amount and/or the quality of the seawater conductor and thus the size of the electric field 2) vary the magnet size and so the size of the field 3) vary the interaction of the two fields in power and direction and thus the resultant force in power and direction can be varied.

Design

As a first approximation, we take a pipe with magnets at the end which gives a DC field. Looking at the end of the pipe, the magnetic field goes for instance from 6 o'clock to 12 o'clock. We insulate the tip of the pipe around this magnetic portion. The electrodes are placed on the pipe to produce a current from 3 o'clock to 9 o'clock. The pipe is submerged in seawater which is the conducting medium. The voltage is turned on and these two force fields interact in a crossed pattern to produce a resultant force moving in or out. The force is at right angles to the fields and so moves water out of the pipe.

In the design of the prototype we would focus on: I. size and direction of the electric field by varying: A. types of electrodes B. electrode placement C. amount of voltage to use D. some figure for seawater conductance, II. size and direction of magnetic fields by varying: A. size and types of magnets B. magnet placement C. insulation of magnet area, III. interaction of two fields in size and direction by varying: A. size of fields relative to each other B. placement of fields relative to each other C. size and shape of pipe, IV. resultant force required, size and direction by using: A. an average weight of water and material in it B. an average movement of water and material in it.

The main factors in the Faraday equation would be researched under different conditions. Controlled factors and a prototype using this information and making informed estimates of the uncontrollable factors are tested in the lab. Then the prototype is tested in the actual ocean to assess the influence of the uncontrollable factors - seawater conductance and actual conditions of the water to be moved.

A Cartesian Diver Pump

If we lift cargo, port elements, and whole ships up and out of the water with a column of water, a pump, we may also submerge them with an air column projected down into the body of water, which column has a variable buoyancy. This is a Cartesian diver. It would complete the range of vertical movements.

OSMOTIC PUMP

Another way of adapting the structure in a changing environment is done by an osmotic pump. A brine acquires potential energy as hydraulic pressure by virtue of water permeation from a dilute to a concentrated solution against the hydraulic pressure gradient. This energy can be used to lift against gravity, to pump.

If we have a saltwater pond in a closed chamber, especially in a hot climate, evaporation causes the water to become saltier. This brine acquires potential energy as water enters the chamber with a concentrated solution from the more dilute surrounding seawater, across an osmotic membrane. Several engineering refinements such as using a countercurrent multiplier for increased salinity to make larger concentration differences and a countercurrent exchanger for increased flow from less to more concentrated solution, increase the pump's speed and power.

Dr. Sidney Loeb worked out this concept, which he called pressure retarded osmosis. In his system "the volume-enhanced brine would be subsequently depressurized through a hydroturbine generator to produce energy. Again the replacement cost, which accounts for half the total energy cost, has been estimated as a function of solution-pair type and the membrane process employed.

Detailed Discussion of Osmotic Pump, the Principle of Pressure-Retarded Osmosis

If brine is separated from water by a semi-permeable membrane, i.e. a membrane permeable to water only, the water naturally permeates from the water side to the brine side in the process of osmosis. The process can be stopped if a sufficiently high hydraulic pressure is applied to the brine side. The hydraulic pressure required to maintain this osmotic equilibrium is called the osmotic pressure, .

If the volumetric permeation rate of the water through the membrane ΔV , is divided by membrane area, we have the water permeation flux, J_1. The relation between water permeation flux and applied forces, in the ideal case, is given by:

$$J_1 = A (\pi - P)$$

where P is the hydraulic pressure applied and A is the water flux constant, primarily a characteristic of the membrane used.

Salinity power

It is clear from the equation that if $P = 0$ we have osmosis, for which $J_1 = A\pi$, and that if $P = \pi$ we have osmotic equilibrium, i.e. $J_1 = 0$. However, if P is between zero and π we have pressure-retarded osmosis (PRO), so defined because the direction of permeation flux is still the same as in osmosis but the flux is decreased as the hydraulic pressure increases. It is important to understand that in PRO water permeates against the hydraulic pressure gradient, i.e. the flux is "uphill". The subsequent depressurization of the permeate through a hydroturbine-generator set would produce power by what may be described as an "osmotic waterfall", and the magnitude of the power produced at any instant would be the product of the hydraulic pressure head and the volumetric permeation rate, i.e. would be:

$$\text{Power (Ideal)} = P\Delta V$$

The PRO principle would still apply for the case that the liquid is a pressurized solution, i.e. also possesses both hydraulic and osmotic pressure, as long as:

$$J_1 = A(\Delta\pi - \Delta P)$$

We are always be considering this more general situation in which water permeates from a permeate-donor solution into a permeate-receiver brine (the solution-pair).

Research

Test equipment and procedure

In PRO, liquid streams must flow freely on both sides of and in close interfacial contact with a membrane across which a large hydraulic pressure drop exists. These dual requirements can be met by very fine hollow fibers fabricated to be essentially thick-walled tubes in terms of the ratio of outside to inside diameter.

The hollow fiber used by Loeb et al. (1976) was the du Pont B-10 Permasep hollow fiber. This fiber, made for seawater desalination by reverse osmosis is fabricated from an aromatic polyamide fiber to have outer and inner diameters of 98 and 42 microns respectively. Furthermore the fiber possesses a thin but dense skin on the outside surface,the remainder of the fiber wall having a relatively porous substructure, i.e. the membrane is asymmetric. Such asymmetry can be of value in minimizing resistance to permeation flux.

Testing consisted of passing permeate-receiver brine (partially diluted Dead Sea brine or a sodium chloride brine) at a hydraulic pressure of 53 atmospheres on the outside of the bundle of hollow fibers, while the permeate-donor, filtered seawater, was pumped into the inside of the fibers at an inlet pressure sufficient to supply the permeate rate ΔV and the desired flushing solution rate FS. Because of the small inner diameter of the fiber bores, the required inlet pressure was appreciable, in the order of 5-15 atmospheres. The relation measured was water permeation flux as a function of driving force, $(\Delta\pi - \Delta P)$ and subsequent calculation of the water flux constant, A.

Membrane replacement costs $/kwh, which represent about half the total cost of the energy are 0.22, 0.13, 0.10, and 0.13 for the solution-pairs river water-seawater, seawater-Dean Sea brine, seawater-NaCl brine, from surface salt and seawater-NaCl brine from a salt dome.

Cost/Benefits

Prospects of lower membrane replacement costs with PRO

It does seem possible ultimately to cut membrane original cost in half and to double the permeability,i.e. the A value. The total effect would be to reduce membrane replacement costs by a factor of four, giving about 0.05 \$/kwh for river water-seawater and about 0.03 \$/kwh for the other two solution-pairs. Assuming that membrane replacement costs are half of the total energy costs, the total energy costs would be 0.10 \$/kwh for river water-seawater and 0.06 for seawater-Dead Sea brine and seawater-NaCl brine.

Consumption rates of feed streams with 100 megawatt plant

It is important to realize that, because for the relatively low value of the free energy of mixing, the consumption rates of feed streams entering a PRO complex would be quite large. For a 100 megawatt plant the river water rate is about 5 times the water consumption rate of New York City. Also the sodium chloride consumption rate would be in the same order of magnitude as the world production rate of sodium chloride".[4]

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[4] Loeb, Sidney, M. Rudolph Bloch, John D. Isaacs, "Salinity Power, Potential, and Processes, Especially Membrane Processes", Advances in Oceanography, ed Henry Charnock, Plenum Press, N.Y. 1978

SUMMARY

SEAWATER CHEMISTRY AND LIFE PROCESSES

Water molecules, one oxygen and two hydrogen atoms, give a cluster with a slight plus charge on one side and a slight negative charge on the other which give it its chemical reversability. It can attach to positive or negative molecules.

Saltwater is an electrical conductor and the salts in it are combinations of chemical acids and bases. Thus seawater is the ideal electrochemical medium, because it can go easily from salt to acid or base and back again and conduct electrical charges.

Seawater is the basis of electrochemical reactions, acidic and basic because ions in it have an electrical charge and a chemical nature. Ion movement in a saline solution along an electrical and concentration gradient forms the basis of much of life's systems and energy release systems.

Life's systems - those of bone formation, nerves and brain, muscle movement, are those processes which do what we set out to do for ports in seawater - that is, they can make reversible structures, can repair themselves, can do sensing, communication, and carry out actions and decisions. All these life processes and port processes use electrochemical reactions in seawater in which ions are exchanged by membranes or exchangers going across a concentration and electrical gradient with an outside input of small amounts of energy in a whole sequence of reversible steps which have great chemical control of ions.

Like nature, we wish to do an entire series of steps, a whole language of sequentially connected chemical reactions. We need reversible reactions in a series of steps with a way of restoring the original chemistry and energy while giving us flexibility, low energy input, and ion control in a discrete area. Unlike chemistry alone, we do not want to utilize separate steps with by-products.

As an example of the type of chemistry described above, in nature, our nerves can do this. Neurons have a chemical as well as an electrical nature. A synapse between them is a small, fluid-filled gap. We now know that a signal crosses the gap not as a spark jumping between two slightly separated wires but rather as the diffusion of a chemical transmitter substance. When an electrical impulse arrives at the end of an axon, it stimulates the release of a few molecules of chemical stored there in tiny sacs. Released into the fluid of the synaptic gap the molecules quickly diffuse across the gap to the surface of the next cell. If the cell is stimulated enough, it converts the chemical signal back into an electrical impulse, which it relays down its own axon. Electrical components operate in a very predictable manner, but the interaction among chemicals allows many more possibilities.

Nerve cells may be differentially sensitive to certain types of messages. Our axons transmit many kinds of information. Some bring it from our sense organs. Others carry instructions to muscles and glands or bring them information about the position of the body in space. Some are intimately linked with our physiological processes, and others, of course, help produce thought and memory. The neuron seems to be able to select certain types of messages to transmit while ignoring others.

Some of our port processes, ion exchange resins and electrochemical half cells, for example, have those desired abilities, i.e. these sequential language-like electrochemistries of relationship are capable of great control of ions with little energy expenditure and ease of chemical restoration to the original state in which many different things can be accomplished. Ion exchange resins can get and hold onto an ion and pass it along to another chemical while restoring the original state. These resins and an electrical field can control the flow of ions to the place they are wanted with little energy expenditure. The electrochemical half cells allow one to change the chemistry on one portion of a current loop in a forward or reverse manner by oxidation or reduction with a current and voltage. This chemical reaction can be very carefully controlled, stopped, started, or reversed. Indeed the electrochemical half cell computer can, like the nerves described above, sense changes in the environment, transmit information and direct action, record actions taken, and select messages to transmit or interpret while ignoring others. This flexible and articulate language of electrochemistry is, like life processes themselves, based on the elegant order inherent in seawater chemistry.

ADVANTAGES AND CHARACTERISTICS OF THE VARIOUS ELECTROCHEMICAL PROCESSES DESCRIBED

The questions are: What are the attributes of these processes and when are they best employed.

In ion exchangers it is a simple matter to cause the proper ions to migrate through a membrane or to an exchange resin, when a voltage is applied, instead of adjusting the PH of solutions by the addition of acids or bases. The power is cheaper in this process than the cost of the chemical agents which would otherwise be required. At the same time, the solution being treated does not suffer from the introduction of a salt which often complicates subsequent operations. Often a useful by-product, such as an acid or base is recovered to be used, perhaps to restore the original chemical situation. The advantages with ion exchangers are 1) no additional chemical agent is required 2) the desired product is not contaminated by added salts and 3) the chemical by-products may be reused 4) using ion exchange resins you can control the ions or extract them. Using an ion exchange membrane you can also have separate cells in which to do different chemical reactions or pass along only certain ions through the membrane. (Ion exchange membranes from a chemical and physical-chemical viewpoint are quite similar to ion exchange resins.)

The electrolysis or electrode processes change the chemistry, change the state of oxidation and so the acidic or basic nature without adding any acid or base chemicals. They do this by the use of electricity. In electrolysis, the electrodes can plate out material and so change it from a solution to a solid state (or gas state). It is a way of separating things without the use of consumable chemicals. The main accomplishment is to plate out material and change the phase.

In electrochemical half cells the useful particles are ions, the working medium an electrolyte solution, but control in this case can be exercised through both electric fields and mass transport. The exact equivalence between the total quantity of electricity passed through an electrochemical system and the changes in chemical content which occurs at the electrodes allow great control to be exercised. The advantages are that one can carefully measure what takes place by using current and voltage to control the situation or by using a small amount of material and power one can cause a precise event to start, stop, or reverse.

In summary this general category of electrochemical oxidation, which includes ion exchangers, electrolysis, and electrochemical half cells, takes place on an interface using an electrode, a membrane, or a resin, etc. in a small area with a small amount of energy so that a great deal of control is maintained. Moreover the reactions are reversible, giving flexibility. There are very few added consumable chemicals and yet separations are accomplished.

Comparison of Separation Processes in Terms of Energy, Efficiency, and Speed

When dealing with large quantities of liquid material with very dilute amounts of chemicals in it - such as we have in the oceans - the dilute nature of the desired chemicals and the capacity for water to ingest huge amounts of external heat become very significant. Thermal means of separation, such as freezing and thawing, are impractical because the energy requirements in this heat sink, the ocean, become too high.

The simple electrochemical separation processes which have no thermal component such as membrane processes (excluding ion exchangers) and electrolysis are more advantageous in terms of efficiency and speed. These, however, are slower and require more energy than pyrochemical processes (that is, normal controlled chemistry separations using heat). Because in electrolytically plating out material, for instance, the atoms obtained from the ocean are so small in relation to the energy required that it is not very efficient. To plate out one gram equivalent of silver takes twenty-seven ampere/hours (about half a car battery's energy).

The most efficient, energy conserving, and fastest separation processes in a very dilute solution in large quantities, like the ocean, are ion exchange chemical reactions because they can control the movement of ions in the water volume. It is a more energy efficient means to get that one gram of silver. (Electrolysis takes twice as long and ten to twenty times more power than a chemical ion exchanger.)

In the ocean, where you have very small amounts of a chemical, like calcium or magnesium, ion exchangers gather the desired ions in the membrane or resin and then the ions are removed from there. The ratio of magnesium to calcium can be reversed in the ion exchange process so that much more calcium is obtained in relation to magnesium than normally occurs in seawater.

Until recently these ion exchange processes, especially the resins, were too slow and costly in terms of the amount of resin required per amount of material produced. However, both problems were solved by a new operating method. The resins are normally in a column with liquid percolating through. In the new process resins in sheet form are rapidly dunked into a solution so that the material is quickly transferred from the resin. The same ratio of resin to material holds, that is, one pound of resin to get one-sixth pound of material, but the resin is used more quickly and over and over again. The new method takes thirty seconds to remove eighty to ninety percent of the material from the resin. This batch system can transfer seventy times the weight of the beads or membrane every day.

In sum, ion exchange methods are so good in this ocean heat sink with its diffused materials because it uses its chemicals to attach the ions and then to make acids and bases which release these ions from the resin and you can harvest the materials desired from seawater in the ratios required. It uses little heat for the chemistry or electrical attraction.

The electrochemical half cells, do not fall into the category of separation processes, but are used mainly for the control of processes or information processing. Even so very small amounts of material are required, (in the order of one millionth of a gram) if they are used for amplification or sensing.

Recommended Lines of Future Research on Port Design Using Natural Processes

The next project recommended would be to design an integrated port building project using the ion exchange method of separation and the saline computer (electrochemical half cells) for control and information processing, working through the chemistry completely.

Appendix I

Performance parameters

A. Total yield, Y_t = refined output mass + input mass

B. Element yield, Y_i = combined mass of element i in refined output streams (as elements or compounds) + mass of element i in input

C. Specific mass or mass per unit output rate, $(SM)_{an}$ or $(SM)_{ag}$ are the net and gross mass of item a; $m_a + \dot{m}_{ot}$ where $\dot{m}_{ot}$ is the time rate of generation of total refined output mass. SM has the dimensions of time. a can be c, capital equipment (n = net process equipment, g = process equipment plus power supplies, heat rejection equipment + spare parts); r, reagents (n = net remote suplied element fraction, g = gross reagent, solvent and lubricant mass (less H_2O)) s, support services including labor, maintenance, life support,etc.

D. Attrition ratio $(AR)_a$ = actual or equivalent rate of mass loss of item a; $AR = \dot{m}_a + \dot{m}_{ot}$ where a and m are as defined in C.

E. Equivalent lifetime, $t_a = m_a + \dot{m}_a = (SM)_a + (AR)_a$

F. Output stream purity, P_{ij} = output mass of element or compound of i + total output of stream j where i is major constituent of j (P_{ij} 1)

G. Specific energy E = energy consumed per unit output mass or power consumed per unit mass rate of output (units joule/kg or Kwh/kg, etc.)

H. Reliability per unit time, R_{kb} of process step k = probability of continued successful operation per unit time after b hours;
R_{kb} $1 - t_k^{-1}$ where t_k is equivalent lifetime of the k th equipment module.

These parameters may be quantified in terms of provisional goals and/or least acceptable values.

Appendix II

Properties of Seawater

Mean salinity 35 parts per thousand

Elemental Analysis

	parts per million	moles/liter
Cl	18,980	.549
Na	10,561	.471
Mg	1,272	.0537
S	884	.0283
Ca	400	.0103
K	380	.01
remainder	115	

Ratios	Equivalents	Moles
$Na^+ : M^{++}$	3.68	7.36
$Mg^{++} : Ca^{++}$	5.21	5.21
$Cl^- : SO_4^=$	9.70	19.40

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