12. T. Ishikawa *et al.*, *Nature* **391**, 773 (1997).
13. H. M. Yun and J. A. DiCarlo, *Proceedings of the 23rd Annual Cocoa Beach Conference and Exposition*, Cocoa Beach, FL, 25 to 29 January 1999, in press.
14. K. Kumagawa *et al.*, *Ceram. Eng. Sci. Proc.* **18**, 113 (1997).
15. M. Takeda *et al.*, *ibid.*, p. 779.
16. H.-P. Baldus, G. Pasing, D. Sporn, M. Jansen, J. Göring, *Proceedings of the First International Conference on Ceramic and Metal Matrix Composites*, M. Fuentes *et al.*, Eds. (Trans Tech Publications, Uetikon-Zürich, Switzerland, 1997), vol. 127–131, p. 177.
17. We thank H. Jüngermann and K. Rigby (Bayer AG, Germany) and B. Weide (Max-Planck-Institute of Solid State Research, Stuttgart) for assistance in preparing this manuscript. We also thank the German Ministry for Education and Science for financial support (BMBF-contract no. 03-N-3038-A1).

REVIEW

Thermoelectric Cooling and Power Generation

Francis J. DiSalvo

In a typical thermoelectric device, a junction is formed from two different conducting materials, one containing positive charge carriers (holes) and the other negative charge carriers (electrons). When an electric current is passed in the appropriate direction through the junction, both types of charge carriers move away from the junction and convey heat away, thus cooling the junction. Similarly, a heat source at the junction causes carriers to flow away from the junction, making an electrical generator. Such devices have the advantage of containing no moving parts, but low efficiencies have limited their use to specialty applications, such as cooling laser diodes. The principles of thermoelectric devices are reviewed and strategies for increasing the efficiency of novel materials are explored. Improved materials would not only help to cool advanced electronics but could also provide energy benefits in refrigeration and when using waste heat to generate electrical power.

Imagine having generators that directly convert heat to electricity, or refrigeration devices that use electricity to pump heat from cold to hot, both without any moving parts or bulk fluids [liquids or gases like chloroflurocarbons (CFCs) or hydrochloroflurocarbons (HCFCs)]. Such thermoelectric (TE) devices already exist. They are lightweight, small, and inexpensive, and they completely eliminate the need for CFCs or HCFCs and heavy compressors in small-scale refrigeration. Most refrigeration failures are due to gas leaks or to the failure of moving parts in the compressor. The former, of course, may also pose environmental problems. TE devices are potentially much less prone to failure because no moving parts are involved. Currently, the world market for TE cooling devices is still small (about $80 million to $160 million per year). Major uses for these TE devices include cooling laser diodes and electronic coolers for picnic baskets. These same devices can also be used as electrical generators when a source of heat is present. Yet, if these TE devices are so useful, why are they not more widely used?

Presently, the use of TE devices is limited by their low efficiencies. The efficiency of a refrigerator is expressed by the coefficient of performance (COP), which is the amount of cooling divided by the electrical energy input needed to obtain that cooling. The laws of thermodynamics tell us that a maximum efficiency, called the Carnot efficiency, cannot be exceeded. The COP at Carnot efficiency is just $T_{\text{cold}}/(T_{\text{hot}} - T_{\text{cold}})$, where T_{hot} and T_{cold} are the temperatures of the ambient environment and of the coldest part of the refrigerator, respectively. The real efficiency of any device is often given as a percentage of the Carnot efficiency. Present TE devices operate at about 10% of Carnot efficiency, whereas the efficiency of a compressor-based refrigerator increases with size: a kitchen refrigerator operates at about 30% of Carnot efficiency and the largest air conditioners for big buildings operate near 90%. Today's TE devices are particularly useful when rapid on-off cycling is required at low temperature differences. Moreover, TE devices are used, for example, when the efficiency is a less important issue than small size, low weight, or high reliability. However, there is no known limit to the potential efficiency of a TE device, except for the Carnot limit.

The efficiency of a TE device is determined by the materials used in making the device, and thus the current focus of research is on finding better materials. If the low efficiencies can be overcome and if new materials can be made at reasonable cost, it would revolutionize the cooling industry. Other industries, such as microelectronics, could also benefit from the development of active cooling technologies. The national semiconductor roadmap (*1*) indicates that higher operating frequencies, higher capacitances, and larger chip sizes will result in doubling of the heat dissipation requirements from 1997 to 2005. In addition, the potential to operate devices below room temperature holds the promise of improved reliability and speed of CMOS-based microprocessors. Likewise, when used as electrical generators, TE devices could tap the waste heat generated in engine combustion to make automobiles more efficient, for example. Thus, the economic benefits of finding higher efficiency TE materials would be large. A conservative estimate is that the world market for efficient TE materials alone (at current TE materials prices) is billions of dollars per year. If one includes the value added to systems including the TE devices, such as home refrigerators or computers and many new applications, the economic impact could be huge. Here I discuss the current status of research to improve the materials used to fabricate TE devices.

Improved Devices

A schematic of a TE cooler is shown in Fig. 1A. Currently available devices are made by joining two doped semiconducting materials together, one *n*-type and the other *p*-type. If a current flows from the *n*-type material to the *p*-type, the dominant carriers in both materials move away from the junction and carry away heat. The junction thus becomes cold because the electrical current pumps heat away from the junction. This effect was discovered in 1834 by Jean Peltier, a French scientist. The heat flow (dQ/dt, measured as energy per second) away from the junction is equal to the magnitude of the current (I) times the Peltier coefficient (Π), so that $dQ/dt = \Pi I$. If there are no heat inputs to the junction, the junction temperature must decrease. If the materials are chosen carefully, Π will be large enough to produce significant cooling (temperature drop of ~50°C). Such a device can also be used to generate electricity when the junction is intentionally heated. In this case, the heat is partly transported by the flow of the electrical carriers from the junction to the base, which generates a voltage between the two ends of the device (Fig. 1B).

In addition to the heat flow away from the junction in a TE cooler, there are heat generation effects to consider. Driving electrical current through the device causes the familiar

---

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA. E-mail: fjd3@cornell.edu

Joule heating, which is proportional to the device resistance (R) times the square of the current (I^2): RI^2. Also, if the junction temperature is less than the temperature at the base, heat will flow back toward the junction driven by the temperature difference ($dQ/dt = K\Delta T$, where K is the thermal conductance of the device). Both of these heat loads limit the temperature drop at the junction. Because the Peltier cooling is proportional to current and Joule heating is proportional to the current squared, the maximum decrease in the junction temperature is obtained at an optimal current. At the optimal current, the coldest attainable junction temperature is proportional to $\Pi^2/(RK)$. Thus, as the above discussion indicates, the cooling is increased if Π is large and if R and K are small, minimizing the heat load terms.

In 1822, Thomas Seebeck discovered that a material placed in a temperature gradient develops an electrical voltage between the hot and cold ends. The thermopower is the voltage divided by the gradient ($S = V/\Delta T$) and is the basis of the TE power generator discussed above. Based on experimental observations, Lord Kelvin posited in 1854 (and only in 1931 did Lars Onsager prove) that $\Pi = (S_p - S_n)T$, where S is the thermopower of each material (n- or p-type) and T is the temperature of the junction. Although Π is difficult to measure, S is very easy to measure. If the geometric factors that determine the resistance and thermal conductance are taken into account, a materials figure of merit can be defined: $Z = S^2/\rho\kappa$, where ρ is the electrical resistivity and κ is the thermal conductivity. In most circumstances, a dimensionless figure, Z times T, or just "ZT," is quoted.

The best materials available today for devices that operate near room temperature have a ZT of about 1, a value that has increased by only a few tens of a percent since the late 1950s. These materials are alloys of antimony and bismuth tellurides with traces of other elements to dope the semiconductors. TE coolers with ZT of 1 operate at only 10% of Carnot efficiency. At infinite ZT, 100% of Carnot efficiency would be achieved, but that limit need not be reached to allow many new technological uses. Some 30% of Carnot efficiency (comparable to home refrigeration) could be reached by a device with a ZT of only 4. Increasing ZT by a factor of 4 has remained a formidable challenge.

Why has the goal of ZT $>$ 4 been so elusive? Understanding electrical carriers in crystalline solids is one of the triumphs of modern quantum mechanics, and a theory of TE semiconductors has been available for about 40 years (*2*). This transport theory needs one input: the electronic band structure. More recent advances in determining the band structure, based on density functional theory and modern computers, give acceptable results (*3*). The main input to band theory is the crystal structure of the material. Known compounds can be sorted into a much smaller group of crystal structure types. A given structure type may be adopted by many compounds, and by comparison, we can often predict which elemental compositions will have this same structure because of similar atom sizes and average valence, for example (*4*). However, many new ternary and quaternary compounds adopt new structure types which cannot be predicted beforehand, and without the crystal structure, electronic band structure cannot be calculated. Not only is the inability to predict crystal structure (and thus composition or properties) the main impediment to predicting which new materials will make better TE devices, this inability is most often the limiting factor in obtaining improvements in most other materials applications. However, the current theory can at least be used as a guide to suggest general characteristics of materials that might be better suited for TE devices.

Given the slow advance in TE efficiencies since the late 1950s, why is this a good time to look for better TE materials? Progress in synthetic methods and especially in structure determination by x-ray diffraction has been rapid and allows much more complicated materials to be studied than those used in present TE devices. In some cases, atom-by-atom control of the growth of artificially structured or compositionally graded materials can be obtained. Modern computers make it possible to rapidly calculate a realistic electronic description of the carriers (band structure). The combination of all these advances has increased the chances of developing improved TE materials. The remainder of this article focuses on current TE research. An excellent review of the theoretical and experimental situation has recently been published (*5*), but other reviews in professional society magazines may be more accessible to the nonexpert (*6, 7*).

Current Research

One way to categorize the research efforts is by materials type: uniform bulk materials and compositionally modulated films. Bulk materials can often be prepared in large quantities by traditional synthetic methods such as direct solidification from a melt. Modulated materials may have periodic variations in structure or composition on the scale of nanometers. These can be obtained by evaporation or chemical deposition to make films or by chemical infusion into nano- or microporous materials prepared by a variety of techniques.

The most promising approach in vogue for bulk materials preparation is to create highly doped, small band-gap semiconductors. The problem is that the three parameters in ZT (S, ρ, and κ) are not independent. In general, as S increases, so does ρ. The best compromise seems to be to use heavily doped semiconductors to produce a carrier density of about $10^{19}/\text{cm}^3$. Furthermore, κ has two contributions, one from the electrical carriers, κ_e, and one from the lattice vibrations (phonons), κ_{ph}. Although κ_e is proportional to $1/\rho$, in many semiconductors κ_{ph} is much greater than κ_e, so that one challenge is to minimize κ_{ph}. One way to do this has been known for some time: use compounds made from heavy elements. High atomic masses reduce the atomic vibration frequencies and the thermal conductivity (at room temperature and greater). However, low vibration frequencies also raise the electrical resistivity somewhat. Nonetheless, the commercial TE materials fit this description because they contain elements such as antimony, bismuth, tellurium, or lead. Other approaches include having a large number of atoms (N) in the unit cell or using alloys to prepare structurally complex materials. The large N lowers the fraction of vibrational modes (phonons) that carry heat efficiently (the acoustic modes) to 1/N. The disorder of random atomic substitution in an alloy scatters the phonons, which reduces the thermal conductivity, again at the partial ex-

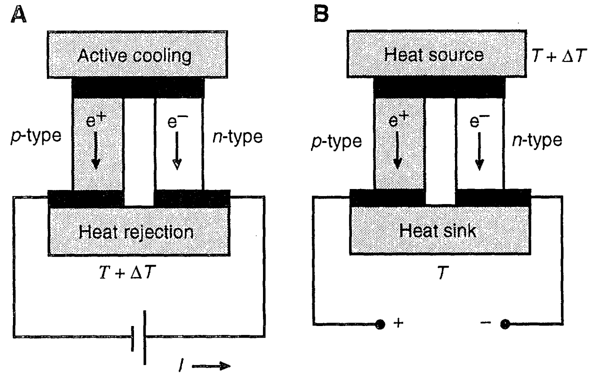

Fig. 1. (**A**) A schematic of a TE couple. It is composed of two electrically conducting materials: one n-type and the other p-type. They are joined at the top by a metal (black bar) to make a junction. When the current flows as shown, the negatively charged electrons in the n-type material flow from the junction toward the base, while the positively charged holes in the p-type material also flow from the junction to the base. Both carriers conduct heat away from the junction and the junction becomes cold. Commercially available devices contain from 18 to 128 couples. (**B**) When the junction is instead heated, both types of carriers conduct heat to the cold base and a voltage difference is generated at the two base electrodes. This type of thermoelectric generator is used in some space missions for system power, with a radioactive plutonium mass as the heat source. In terrestrial uses, any source of heat above ambient temperature could be used.

pense of possibly raising the electrical conductivity. In the last approach, preparing materials with a particular kind of structural complexity, so that one or more component elements "rattle" in a cage made from a framework of other elements. The rattling vibrations lower the lattice thermal conductivity, hopefully without increasing the resistivity, because the carriers travel only in the framework. Slack has called such materials "phonon glass and electron crystal" (*8*), since glasses have the lowest of all lattice thermal conductivities. It is now possible to efficiently synthesize such materials and to rapidly determine their structure.

Once the lattice thermal conductivity has been lowered, the electronic factors must be addressed. In the standard model of semiconductor transport, one can show (*2*) that ZT is a monotonically increasing function of two parameters: E_G and B, where E_G is the band gap and B is determined by a number of materials parameters (see below). In this analysis, it is assumed that the semiconductor carrier density (*n*- or *p*-type) has been adjusted by doping to the optimal level. Then, the band gap E_G must be greater than kT (the thermal energy) by a factor of about 10 to maximize ZT for a given B. B is a product of several factors: $B \propto N_v \mu m^{3/2}/\kappa_{ph}$. The need to minimize κ_{ph} was discussed above. N_v is the degeneracy of the band extrema near the Fermi level, μ is the electronic mobility, and m is the band mass determined by the density of states. Each parameter can be considered in turn. N_v in present TE materials is typically 6 or even 8. The crystalline symmetry limits the maximum value of N_v. In cubic space groups, it might be as high as 48, followed by values of 24 in hexagonal groups, 16 in tetragonal, 8 in orthorhombic, and 4 or less in the remaining groups. If the compound has a large number of atoms in the unit cell, there is an increased chance of attaining the maximum value of N_v. In general, it is not known how to design materials with high N_v, and approaches to attaining high values of N_v have not yet been well explored. The electronic mobility μ should be high, but generally, the mobility and the band mass m are not independent. The mobility is inversely proportional to the band mass in the direction of the current flow, m_i:$\mu = e\tau/m_i$, where τ is the carrier scattering time. Thus, B is proportional to $N_v \tau (m)^{3/2}/m_i \kappa_{ph}$. In noncubic materials, m_i can be different from m. In that case, when $m > m_i$, B is increased. However, exploiting an anisotropic mass may run counter to increasing N_v, so a compromise must be struck. Interestingly, the current TE materials all have cubic or hexagonal symmetry. Finally, long scattering times τ are possible if the electronegativity differences between the elements in the material are small and optical vibrations have small coupling to the carriers. The latter condition is difficult to control or design, but small coupling is favored if the each atom has a large number of near neighbors, say six or greater.

To summarize, the features of a new semiconductor material with high ZT will likely be (i) a high symmetry crystal structure (high N_v) with a large number of heavy elements per unit cell (low κ_{ph}), (ii) small electronegativity differences between the elements in the compound (high mobility or long scattering time), (iii) alloying or "rattling" to further reduce the lattice thermal conductivity, (iv) at least one high effective mass, and (v) the ability to dope the material to a high carrier density of about 10^{19} carriers/cm^3 (this generally gives optimal $S^2/\rho\kappa$ ratios). This list of needs remains daunting, because the structure of most new materials cannot be predicted. There are grounds for optimism that a ZT of 4 can be attained, but little basis for predicting when this will occur.

Recent society meetings (American Physical Society, American Chemical Society, and Materials Research Society) have included sessions on TE material research and development. A recent article summarizes many contributions from individuals at the December 1998 Materials Research Society meeting (*9*). Whereas many new materials have been synthesized and examined, and whereas much has been learned about "designing" materials properties such as low thermal conductivity, the goal of considerably enhancing ZT has not yet been reached in bulk materials. However, some new approaches to speed up the discovery rate of new TE materials offer hope that the higher ZT goal may be achievable in the near future.

The current research method involves making materials one at a time and examining their properties in some detail. At Symyx Technologies, a combinatorial approach to materials problems (including TE materials) is being developed. The key to using combinatorial methods for material discovery is to develop an appropriate screening method that identifies the important property or properties of interest. The tools to prepare hundreds of samples at once and to evaluate them in parallel are in hand, and an accelerated search has begun. John Badding at Pennsylvania State University has developed a second approach that exploits pressure tuning of materials parameters. Most phenomena of interest in solids depend on interaction parameters that are determined by the electronic structure of the solid, which in turn is dependent on interatomic spacing. So, by applying pressure, one explores a piece of "interaction space" in a continuous (but not completely predictable) manner. This pressure-tuning method contrasts to making many samples, each of which is characterized by a point in this interaction space. Several very recent pressure experiments indeed suggest that ZT > 1 is possible. Perhaps such observations can be translated into practical materials that operate at atmospheric pressure.

Most of the focus of research on bulk materials has been on small band-gap semiconductors, but some research has concentrated on metals with unusually high thermopowers. The most interesting of these latter materials are the rare earth intermetallics that display an unusual electronic state, called the intermediate valence state (*10*). No material with a ZT greater than ~0.2 has been reported, but recent experiments by Badding's group on alloys of one of these materials ($Ce_{3-x}Nd_xPt_3Sb_4$) have suggested that ZT values somewhat above 1 can be attained under pressure (*11, 12*). If these results and those on several other materials are confirmed by further study, a "proof of principle" that higher ZT can be attained would be achieved.

Finally, I briefly address the compositionally modulated film approach. The synthetic methods used to make such materials are related to those used in fabricating modulated semiconductor optoelectronic devices such as $Ga_{1-x}Al_xAs$ multi–quantum well (MQW) lasers. In MQW materials, nanometer-thick layers of an active material and an "inert" spacer material are sequentially deposited by techniques such as MBE (molecular beam epitaxy) (*13*). The challenge in making modulated films is to make very thin, atomically perfect layers, not to invent new materials, as is the case with bulk materials. The materials used to build the active layers are usually just those materials that are already known to be good bulk TE materials.

There are two types of film devices: in the first, the current and heat flow parallel to the layers; in the second, both flow perpendicular to the layers. In the first approach (*14*), an increase in Z has been calculated to arise from a number of factors, including an increase in the electronic density of states per unit volume and a consequent increase in thermopower that would occur for small well widths (several nanometers), as well as an increase in carrier mobility if modulation doping is exploited. Experiments using PbTe as the active-layer material suggest modest increases in ZT to perhaps 1.2 are possible at room temperature (*14*). A potential difficulty in obtaining higher ZT from such devices is that the inert spacer does not contribute to the Peltier heat flow, but does have a thermal conductivity that increases the heat load and lowers the effective ZT. In the second approach, materials and layer structures are designed so that the impact of the barrier layer is minimized. Recent work has suggested these structures may have a much more profound effect on phonon transport, resulting in significant reductions of thermal conductivity either through phonon confinement (*15*) or phonon scattering mechanisms (*16*). Scientists at the Research Triangle Institute (*17*) have reported a significant enhancement of ZT to about 3 at 300 K using a Bi_2Te_3/Sb_2Te_3 superlattice structure in which the current flows perpendicular to the layers. A reduced thermal conductivity compared to the commercial bulk alloys without lowering the electronic mobility is claimed. These results are obtained from difficult, but state-of-the-art, measurements perpendicular to a very thin film. If these observations can be repeated on much thicker multilayer films, the result would be very exciting. If such film devices with high ZT values can be built, they may prove useful as "on-chip" coolers for electronic systems, where perhaps even a ZT of 2 would be useful. It seems unlikely, however, that the films will be used in systems with large heat loads, such as a home refrigerator, because very thick films, or stacks of films, of more than a millimeter thickness would be needed. High MQW manufacturing costs would likely prohibit the production of very thick or very large area films. For these applications, better bulk materials are a likely necessity.

More recently, attention has turned to the development of thermoelectric structures based on one-dimensional confinement, quantum wires. Theoretical predictions suggest such materials will have more favorable thermoelectric properties than the two-dimensional MQW systems, due to further increases in the density of states. In addition, a number of templating and vapor-phase methods that have been developed for the synthesis of nanowires in general are being exploited in the synthesis of these new TE structures. It is too early to know if such approaches hold promise.

Summary

The search for better TE materials has recently accelerated due to advances in materials synthesis techniques, in x-ray diffraction technology, and in computational capabilities. There are theoretical grounds for some optimism that materials with ZT > 4 will be found. However, the current inability to predict new structures and compositions of new solid-state compounds makes the search for more-efficient materials nonsystematic, which has led to a specification of generic materials characteristics and Edisonian synthetic searches for those characteristics. Nonetheless, the recent growth of research activities has resulted in many discoveries of novel, complex, and structurally beautiful compounds, and some of these classes of materials may indeed be the answer to our quest. Many groups are now participating in that search, and methods to speed up the search are being explored. Hopefully, the advances will come soon.

References and Notes

1. Sematech, *The National Semiconductor Roadmap* (Sematech and Semiconductor Industry Association, Austin, TX, 1994).
2. R. P. Chasmar and R. Stratton, *J. Electron. Control* **7**, 52 (1959).
3. R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer-Verlag, Berlin, 1990).
4. For example, see the entire issue on Trends in Materials Data: Regularities and Predictions, J. P. Rodgers and P. Villars, Eds., *Mater. Res. Soc. Bull.* **18** (no. 2), (1993).
5. G. D. Mahan, *Solid State Phys.* **51**, 82 (1998).
6. B. Sales, *Mater. Res. Soc. Bull.* **23**, 15 (1998).
7. G. Mahan, B. Sales, J. Sharp, *Phys. Today* **50** (no. 1), 42 (1997).
8. G. A. Slack, in *CRC Handbook of Thermoelectrics*, D. M. Rowe, Ed. (CRC Press, Boca Raton, FL, 1995), p. 407.
9. T. M. Tritt, *Science* **283**, 804 (1999).
10. See K. A. Gschneider and L. Eyring, Eds., *Handb. Phys. Chem. Rare Earths* **2**, 797 (1985); *ibid.* **16**, 105 (1993); *ibid.* **19**, 177 (1994).
11. C. D. W. Jones, K. A. Regan, F. J. DiSalvo, *Phys. Rev. B* **58**, 16057 (1998).
12. J. F. Meng *et al.*, unpublished results.
13. L. D. Hicks *et al.*, *Phys. Rev. B* **53**, 10493 (1996).
14. M. S. Dresselhaus *et al.*, *Mater. Res. Soc. Symp. Proc.* **478**, 55 (1997).
15. A. Balandin and K. L. Wang, *J. Appl. Phys.* **84**, 6149 (1998).
16. G. Chen, *Phys. Rev. B* **57**, 14958 (1998).
17. R. Venkatasubramanian, private communication.

18. I chose a subset of topics in TE research that interests me; omission of some topics does not imply that they have no promise. I am grateful to many people for input and constructive criticism. These include students and colleagues at Cornell: T. Braun, B. Carpenter, S. Lee, K. Poduska, K. Proctor, and Y. Wang. Others include J. Badding (Pennsylvania State University), G. Mahan (Oak Ridge National Laboratories), J. Pazik (U.S. Office of Naval Research), and J. Sharp (Marlow Industries).

REVIEW

Environmental Engineering: Energy Value of Replacing Waste Disposal with Resource Recovery

R. Iranpour,[1]* M. Stenstrom,[2] G. Tchobanoglous,[3] D. Miller,[4]
J. Wright,[5] M. Vossoughi[6]

Although in the past, environmental engineering has been primarily concerned with waste disposal, the focus of the field is now shifting toward viewing wastes as potential resources. Because reclamation usually consumes less energy than producing new materials, increasing reclamation not only reduces pollution but saves energy. Technological innovations contributing to this shift are summarized here, and are variously classified as emerging technologies or research topics, as either new departures or incremental improvements, and as opportunistic innovations, or examples of a unifying strategy. Both liquid and solid waste examples are given, such as a recent discovery of effects in disinfecting microfiltered reclaimed wastewater with ultraviolet light. In addition to its value in reducing pollution and conserving energy, this reorientation of environmental engineering could contribute to a more general shift toward greater cooperation among organizations dealing with the environment.

All human endeavor interacts with the environment, yet environmental engineering has been carried out in relative isolation from the rest of society. It has been understood as the field that develops technologies for waste disposal and builds and operates facilities implementing these technologies. The principal concern has been to dispose of wastes in the most convenient and least expensive way, without attempts to convert them into useful substances, and with little interaction between disposal agencies and the organizations, and populations that produce the wastes.

There is now a growing recognition that neither wastes nor resources are rigidly defined concepts, but rather depend on customs or values (real or perceived) and on available knowledge and technology to determine whether a substance is considered potentially useful, hence a resource, or useless at best, and therefore a waste. With greater understanding or ingenuity, it may be possible to process useful components from what had previously been considered entirely useless waste streams.

---

[1] Applied Research Group, Hyperion Treatment Plant, Los Angeles Sanitation, 229 21st Street, Santa Monica, CA 90402, USA. [2] Department of Civil and Environmental Engineering, Post Office Box 951593, University of California-Los Angeles, Los Angeles, CA 90095–1593, USA. [3] Department of Civil and Environmental Engineering, University of California-Davis, Davis, CA 95616–5294, USA. [4] Tech Research, Post Office Box 34543, Los Angeles, CA 90034, USA. [5] Department of Civil Engineering, Purdue University, West Lafayette, IN 47907–1295, USA. [6] Biochemical and Bioengineering Research Center, Sharif University, Tehran, Iran.

*To whom correspondence should be addressed. E-mail: rezairanpo@aol.com