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LAWRENCE LIVERMORE LABORATORY ENERGY AND TECHNOLOGY REVIEW

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October 1975

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Briefs

The short items on this page announce recent developments of importance. Some of these items may be amplified in future issues; none of this material is reported elsewhere in this issue. Summaries of this month's articles appear on the opposite page.

CDC-7600 GOES ONLINE AT CTR COMPUTER CENTER

On October 7, a fully dedicated CDC 7600 computer at the National CTR Computer Center at LLL went online to five major CTR laboratories, offering large-scale computational support and advanced computer technology for solving the problems of fusion research. Features of the new computer include 64 000 words of small-core memory, 500 000 words of large-core memory, and disc storage. The center's computing power will accelerate development of the theoretical models and associated computer codes needed to predict the behavior of plasma confinement systems and the operating characteristics of fusion power reactors.

Service is presently being provided via telephone lines. Eventually these will be replaced by a wide-band communications network (leased 50 000-bit/s transmission lines) on which we are now testing protocols.

The CTR Computer Center is connected to smaller computer systems (PDP-10's) at the five laboratories. These timeshared PDP-10's are user service centers; that is, both local computers and remote job entry terminals to the 7600. Small jobs and experimental data processing are handled by these service centers; large numerical calculations are routed to the 7600 in batch mode and the results sent back to the PDP-10's.

Future plans call for extending the service to 16 other laboratories and universities across the nation that are involved in ERDA-supported CTR research projects. These, too, will require user service centers or remote job entry terminals. The anticipated computational load is such that we expect to add a second central computer in FY 1977.

The CTR Computer Center is funded by ERDA's Division of Controlled Thermonuclear Research (DCTR). Computer time is available to all research groups funded by DCTR. The allocation of time and priorities is decided by the DCTR upon advice of the Computer Users' Advisory Committee, which consists of one delegate from each of the laboratories plus selected university and DCTR representatives.

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Our recent studies of typical half-mask cartridge respirators have shown these devices to be unsuitable for certain organic vapors because the effective service life is too short. The experimentally determined service life for many vapors is shorter – sometimes significantly shorter – than predicted by adsorption theory.

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Flow microfluorometry has become a key tool in biomedical research because it allows cell analysis at extremely high rates (100 000 cells per minute) with statistical precision and sensitivity. One application of the LLL bicolor flow microfluorometer is to detect variability in the DNA content among individual mollusk and mammalian sperm. DNA variability should be a sensitive indicator of mutagenic events in these cells. Ultimately, we hope to identify and assess the effects on man and his environment of the chemical byproducts from various energy-production processes.

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To meet projected domestic demand for copper, deeper ore deposits will have to be exploited and a technology developed to process these ores. Over the past five years, we have worked extensively on one promising recovery process: nuclear rubblization and in situ leaching of copper ores. More recently, a joint study with Kennecott Copper Corporation and ERDA has affirmed that our nuclear chemical mining concept is technically feasible and identified the process uncertainties that must be resolved before its commercial viability can be assured.

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LLL is extending its studies of four methods (above) for producing heavy water on a large scale. National needs for heavy water are expected to increase during the next decade, especially if heavy water reactor technology penetrates the U.S. utility market. The four methods and our progress to date are described in the article beginning on the opposite page.

ADVANCED ENERGY SYSTEMS

HEAVY WATER PRODUCTION: NEW LLL STUDIES

This Laboratory is extending its studies of methods for producing heavy water (deuterium oxide) on a large scale. The basic goal is a threefold reduction in U.S. production costs (currently \$125-135 per kilogram). The heavy water inventory in heavy water reactors now accounts for 20 to 30% of their total cost. The cost reduction, plus recent and anticipated improvements in heavy water reactor technology, could make these reactors a cheap and highly reliable source of electrical power as compared with any technology — nuclear, fossil-fueled, or unconventional — yet proposed.

Heavy water (D_2O) is nearly an ideal moderator and coolant for nuclear reactors that operate with basically thermal neutron spectra. It is comparatively dense and has excellent thermodynamic properties, very low neutron-absorption cross sections (for both deuterium and oxygen) and, because of the deuterium's nearly neutronic mass, high specific neutron scattering power.

Partly because of historical development (see next page), the U.S. has preferred reactors using graphite (carbon) or ordinary water as the moderator and other substances, chiefly ordinary water, as the coolant. These light water reactors are in widespread domestic use. They require enriched uranium as the nuclear fuel, compelling a sizeable investment in uranium isotopic enrichment processing facilities (which the U.S. has already commenced). This difference is due to the thousandfold-higher neutron absorption cross section of ordinary light hydrogen (protium) relative to deuterium, leading in turn to the need for a neutronically richer uranium fuel to make up the losses from moderator absorption. Today's light water reactors are considered interim technology en route to breeder reactors, which produce at least as much nuclear fuel as they consume for power generation. The U.S. is committed to breeders as one long-term solution to the energy problem, and has achieved world leadership in both uranium enrichment and light water reactor technology.

Other nations, especially Canada in recent years, have pushed the development of heavy water reactors. One such reactor has established a record of service

reliability for central-station power generation that is, as Hans Bethe recently noted, unrivaled by any other central-station technology, either fossil-fueled or nuclear. These reactors use natural uranium rather than enriched uranium as the nuclear fuel and thus are not tied to enriched-uranium production facilities. Their "special material" requirement — heavy (or deuterium-enriched) water — is a much more readily available commodity, in which a large and multisource international market exists. This is viewed as a significant advantage by many foreign buyers unwilling to commit themselves to any major enriched-uranium supplier (such as the U.S. or the Soviet Union) over the 20- to 30-year lifetime of a light water reactor.

The two chief drawbacks to heavy water reactors, until recently, have been the sizeable startup costs associated with their large heavy water inventory (about 2 kg per kW_e of plant capacity in first-generation systems) and their seeming inappropriateness as breeders. At the current U.S. price of \$125-135/kg for heavy water, the capital costs for the initial inventory are indeed huge, being comparable to those of the associated steam turbogenerator system. But Canada, whose annual heavy water production is now some eight times greater than ours, estimates its present production costs in the range \$75-100/kg. This reduction, coupled with continuing reactor design improvements to reduce the heavy water inventory, may give Canadian heavy water reactors a substantial economic edge over U.S.-developed light water reactors.

Also, it is possible for heavy water reactors to function as true "thermal breeders," producing more fuel than they burn. Their breeding ratios will be somewhat less than those of fast breeders (which use suprathermal neutrons), but they can achieve 0.9-1.1 running on the thorium-²³³U cycle, compared with an estimated 1.05-1.25 for fast breeders. Such thermal-breeder heavy water reactors might be introduced without any essentially new technological developments.

It is now considered probable that world heavy water requirements by 1985 will approach 9000 tonnes annually, due to Canadian-derived heavy water reactor technology alone. U.S. requirements, for nonreactor uses, are projected at some 1000 tonnes annually for the period 1980-85.

Contact Lowell Wood (Ext. 3444) for further information on this article.

HEAVY WATER PRODUCTION: HISTORICAL OVERVIEW

Deuterium, the rare component of heavy water, was discovered by Harold Urey and associates in 1930. Urey's group used very careful, low-pressure distillation of liquid hydrogen to achieve a tenfold concentration of deuterium in the tiny fraction of liquid remaining in the distillation vessel at the end of their experiment. The enrichment was due to deuterium's slightly lower vapor pressure compared with protium, the much more abundant form of hydrogen. Deuterium's discovery, and the concurrent observation that there is 1 atom of deuterium for every 6000 atoms of ordinary hydrogen in water, preceded by two years the discovery of the neutron, the particle that distinguishes deuterons from protons.

Early in their wartime efforts, the U.S. and Nazi Germany both recognized heavy water as the ideal moderator for nuclear reactors in which the material for nuclear explosives would have to be produced. Germany tried to capitalize on conquered Norway's virtual monopoly on heavy water production, but this attempt was thwarted by repeated bombings and, finally, by a famous commando raid that sank a ship carrying most of Norway's heavy water production. The U.S. meanwhile turned to high-purity graphite as a substitute moderator. Germany's prolonged dependence on heavy water (which never arrived) and our early switch to graphite are generally considered decisive factors in the U.S. victory in the race for military nuclear explosives.

After the war, the U.S. emphasis was on developing the then-current technology for producing heavy water, which involved electrolysis of water to concentrate the deuterium remaining in the electrolytic cell. This process, both slow and energy-intensive, met the whole world's heavy water needs until the 1950's. Hundreds of tonnes of heavy water were produced by electrolysis.

However, expanding needs for deuterium in the 1950's, associated mainly with our thermonuclear explosives program, stimulated better technologies. The gaseous separation (GS) process, developed and implemented during these years, reduced energy requirements and cut the total production costs nearly tenfold. In this process, advantage is taken of the different affinities of protium and deuterium for water and its analog compound, hydrogen sulfide (H_2S). A feedstream of water containing deuterium in natural abundance passes through huge, multipass, isotopic stripping towers. As the water is alternately heated and cooled in the presence of hydrogen sulfide, a relatively small portion (about 20%) is enriched in deuterium, the remainder becoming slightly depleted. This process is practical from natural deuterium concentration (about 0.015% deuterium) to an enrichment of about 1%. Thereafter other methods, such as electrolysis or vacuum distillation, are economically superior for attaining the 99+% purity required for nuclear reactors.

Rapidly expanding U.S. heavy water production capacity peaked in the early 1960's at more than

Advanced Heavy Water Production Technologies

We are extending our studies of four advanced technologies for producing heavy water:

- *Isotopically selective single-step photodissociation*, which capitalizes on differences in the optical absorptivity of normal and deuterated species to effect large isotopic selectivities in photochemical decomposition reactions.
- *Isotopically selective two-step photolysis*, which couples isotopically selective vibrational excitation of the desired species with radiative raising of the energy of the excited molecules to near their dissociation edge, from where isotopically selective chemical decomposition occurs.
- *Isotopically selective photodesorption*, which uses low-energy photons to induce isotopically selective desorption of molecules from transparent surfaces.
- *Metallic chromatographic separation*, by which deuterium is separated from protium by displacement

chromatography in a column packed with an intermetallic compound of, for example, a rare earth and a transition metal.

Theoretically, each of these processes -- described below -- offers the potential for a considerable savings in heavy water production costs. Our plan is to continue investigating each until a clear choice can be made of which process to pursue through pilot-plant construction.

Unless otherwise stated, all percentages in the following discussion, such as deuterium's natural concentration in hydrogen (0.015%), are expressed as mole or atomic percentages.

Isotopically Selective Single-Step Photodissociation. Isotopically selective photodissociation of simple hydrogen-bearing compounds such as formaldehyde ($HCHO$) offers the prospect of single-step deuterium enrichment from natural concentration up to about 10%. Initial low-level enrichment is the costliest step in the present gaseous separation (GS) process, due to

450 tonnes per year, which soon exceeded our domestic needs. One reason was our impending national decision to emphasize light water over heavy water reactors for civilian power production. This emphasis grew out of our relatively advanced naval reactor technology and what was then a superabundance of U.S. uranium-enrichment capability. As capacity continued to outstrip national needs and the production plants aged, they were phased out in stages. Current production – about 270 tonnes annually – is roughly in balance with our present domestic demand for heavy water.

Meanwhile, another line of civilian nuclear reactor development was being pursued north of the border. Canada, denied access after the war to U.S. uranium-enrichment technology, determined to develop natural-uranium power plants using heavy water as the moderator and coolant. Also, there may have been reluctance to commit the huge sums needed for building and operating gaseous-diffusion uranium-enrichment plants. The Canadian program received substantial impetus from the advent of the GS process and, in the 1960's, they launched an ambitious program of heavy water production to support their power-reactor technology, the CANDU (Canadian deuterium-uranium) system. Indeed, the U.S.' chief customer for surplus and stockpiled heavy water during the late 1960's and early 1970's was the Canadian nuclear-power-reactor complex, which bought extensively for the purpose of commissioning CANDU reactors for their internal use and foreign sales.

That 20 to 30% of the cost of electrical power from CANDU power plants is due to capital charges for their large heavy water inventory has stimulated the Canadians to seek improvements in heavy water production technology. The bulk of this effort has gone into the GS process, but Canada is also supporting the world's largest program to explore other processes. Intensive efforts to commission large heavy water production plants have now culminated in a production capability of about 1550 tonnes annually. Accelerating demand is so great that Canada plans to produce some 35 000 tonnes by 1990 and over 90 000 tonnes by the end of the century.

Their heavy water plants initially were located in the more northerly parts of the nation, where the Canadians cleverly exploited a little-appreciated feature of isotopic geochemistry. Air masses containing water evaporated from oceans in the tropics and advected to the northerly latitudes by planetary circulation become successively drier due to precipitation. At the same time, the fraction remaining in the atmosphere becomes enriched in deuterium to as much as 0.023% at high latitudes. The corollary, of course, is relatively "depleted" rain over most of the U.S. Thus the early Canadian plants could operate with feedstocks as much as 40% richer in deuterium than those, for example, in the southern U.S. This difference is significant because most of the costs for heavy water production by the GS process are associated with the multiple passes of large volumes of feedstock needed to achieve an enrichment approaching 1% deuterium.

the several steps of reprocessing large volumes of water feedstock associated with this technology (see the historical overview). The chief problem in the GS process is relatively poor single-step isotopic selectivity.

By contrast, the isotopically selective photodissociation process (Fig. 1) allows the relatively large differences in optical absorption between normal and deuterated species to effect large isotopic selectivities by adsorbing single photons at specific wavelengths in the range (for HCHO) of 300 to 355 nm. The photoactivated molecule then dissociates into CO and H₂ gas. Such optical selection of deuterium-bearing species can be made to occur with an isotopic selectivity ratio approaching 10 000 (ten-thousandfold better than the normal occurrence of 1 part in 6000). Separation of the selected species takes place at near unit quantum efficiency by the automatic dissociation process into readily removable HD gas.

Isotopically selective photodecomposition of formaldehyde was first experimentally demonstrated

by Yeung and Moore,¹ who separated HCHO from an equimolar mixture of HCHO and DCDO. The scientific feasibility of deuterium separation by selective photodecomposition of HCDO, the naturally occurring deuterium-bearing form of formaldehyde, was recently demonstrated at this Laboratory.² We used light from a helium-cadmium laser at 325.03 nm to irradiate HCHO-DCDO mixtures at room temperature and 530-Pa total pressure. Analysis of the resulting hydrogen gas showed a net fifteenfold deuterium enrichment. Irradiation of formaldehyde with natural deuterium concentration resulted in hydrogen gas containing 0.5% HD, a suitable level for subsequent enrichment by other inexpensive, proved technologies such as vacuum distillation.

The maximum expected isotopic selectivity ratio in these experiments, based on the relative optical absorptions of the two isotopic species at 325.03 nm, was about 30. Using this laser at 325.03 nm gave us a convenient and stable light source for verifying the basic feasibility of the formaldehyde process, but this

wavelength is not optimal. The use of frequency-tunable lasers in this spectral region should permit the selection of formaldehyde-photodecomposition frequencies for which the optical isotopic selectivity ratio exceeds 1000, based on absorption spectral measurements by previous workers.

Three areas of this process remain to be investigated. First, selectivity ratios of 1000 or more from tunable laser sources must be demonstrated, to

avoid wasting relatively expensive uv photons on absorption in nondeuterated formaldehyde. One possible approach here is to select a suitable frequency and tune a suitable laser to it, using frequency selection with etalons and other laser-tuning elements. A second approach is to put nondeuterated formaldehyde (HCHO) into the laser optical cavity so that lasing can occur only at frequencies at which the HCHO is transparent. The transparency bands in HCHO can then

Fig. 1. Isotopically selective single-step photodissociation process for deuterium enrichment from natural concentration (0.015 mole%) to about 10 mole%. This is a continuous flow process using deuterium-depleted formaldehyde to strip deuterium from a feedstream of natural methane. Laser light of the proper wavelength excites the deuterium-bearing formaldehyde molecules, which dissociate into CO and HD gas. The HD is readily removable. A small amount (about 0.1%) of makeup formaldehyde is required. Feedstream costs are practically nil because methane depleted of its natural deuterium is suitable for any usual purpose.

be selected at which HCDO is highly absorbing. Both schemes have advantages and drawbacks, but the latter superior with respect to frequency stability - presently seems preferable.

The second area requiring investigation is demonstration (1) that formaldehyde can rapidly exchange deuterium with a homogeneous feedstream such as water, methane, or hydrogen gas, and (2) that, afterwards, the formaldehyde can be readily and cheaply stripped from the feedstream. Deuterium-depleted formaldehyde gas will have to be isotopically regenerated; otherwise, U.S. heavy water production will be tied to formaldehyde-synthesis plants and thus limited to only several hundred tonnes per year. Exploitation of the statistical thermodynamics of the formaldehyde-feedstream deuterium exchange may enable a factor-of-2 chemical isotopic selection, thereby permitting formaldehyde feedstock with a 0.03% deuterium content to be supplied to the photolytic process. This exchange, and the subsequent efficient stripping of formaldehyde from the feedstream, must be demonstrated and quantitatively evaluated.

The third area is development of tunable uv light sources with overall electricity-to-light energy efficiencies of at least 1%. The present efficiency of tunable dye lasers is about 0.3%, so substantial progress is needed. From a large-scale industrial perspective, the most attractive scheme is an efficient visible or uv gas laser used directly or to pump a tunable uv dye laser. Substantial research and development need to be directed to these possibilities. Recent progress by other workers in the rare-gas/fluoride laser field, demonstrating 3% or better pumping efficiency in the near-uv region, is especially encouraging with respect to pumping the required lasers.

Isotopically Selective Two-Step Photolysis. The photodissociation edges of vibrationally excited molecules are shifted considerably toward the red relative to those of vibrational ground-state molecules. Indeed, the redward shift in dissociation energy may be a substantial multiple of the total vibrational excitation. This characteristic, plus the large isotopic shifts for vibrational transitions in homogeneous molecules corresponding to M-H bond excitation (M being the remainder of the molecule), naturally suggest a two-step photolytic separation process (see Fig. 2). The first step is isotopically selective vibrational excitation of the desired species, by lasers or incoherent sources. The second step is radiative raising of the excited molecule to near its dissociation edge: that is, to a predissociation level if the subsequent

excitation transfer is minimal, or well beyond the edge if the excitation transfer poses problems.

Lasers are not mandatory for either step inasmuch as relatively broadband radiation (such as filtered blackbody radiation) may be used to effect both levels of excitation. However, to minimize the complexity of the reaction kinetics, lasers may be preferred because of their uniquely high spectral brightness. The most obvious application would be to the infrared-excitation step, due to the low quantum energy involved plus the relatively high pumping efficiency (greater than 10%) of lasers in this spectral region. Filtered flashlamp or metal-arc sources may be the most appropriate for the near-uv photodissociation step.

We have obtained isotopic selectivity ratios greater than 1000 in model system calculations for two molecules: hydrogen bromide and formaldehyde. Using lasers and filtered incoherent sources, we now intend to reduce these model systems to practice and to determine the actual isotopic-separation performance parameters for design and pilot-plant construction.

Isotopically Selective Photodesorption. Physical adsorption of gases with low boiling points occurs at temperatures around 100 K with binding energies of, at most, 8 kJ/mole. This suggests using low-energy photons to induce isotopically selective desorption of molecules from some transparent surface (see Fig. 3). Even 10 000-nm photons, corresponding to low-energy vibrations, carry energies aggregating to a kJ/mole of photons, more than adequate to induce photodesorption. The absorption of a molecule on a surface induces changes in its electric dipole moment, activating previously radiatively nonabsorptive vibrational modes. Thus, by irradiating the system at an adsorption-induced infrared absorption frequency, only the adsorbed molecules containing the hydrogen isotope of interest will absorb the radiation and be desorbed. This ensures a very "clean" isotopic separation, as very little energy transfers between the isotopic species. Also, vibrational modes of different isotopic species have rather large differences in their frequencies: for example, H_2 absorbs at 2400 nm while HD absorbs at 2750 nm; methane's "breathing mode" for CH_4 is 3430 nm, while for CH_3D it is 4535 nm. Thus one may use filtered, efficiently generated, blackbody light sources for inducing isotopically selective desorption.

Our experiments on isotopically selective photodesorption thus far look favorable. A Dewar flask, constructed with two sets of double sapphire

windows sealed into it 180° apart, held a piece of specially conditioned, porous Vycor glass in a copper block cooled from a liquid-nitrogen reservoir. The irradiation source was a quartz-iodide movie-camera spotlight shining through a narrow-bandpass infrared filter, with a transmission half-height width from 2733 to 2884 nm and better than 75% transmission at 2778 nm. This source was calibrated with a thermopile power meter. Deuterium analyses were accomplished

in a glow-discharge sample cell. We observed relative intensities of the Balmer β -emission spectra of H and D at 486.13 and 486.00 nm, respectively, with a high-resolution spectrophotometer. This means of analysis yields only ratios of total deuterium to total hydrogen atoms and does not directly provide the ratios of H_2 to HD or HD to D_2 .

For a gas sample adsorbed onto cold Vycor with an initial D/(H+D) ratio of 21% — that is, 63% H_2 ,

Fig. 2. Isotopically selective two-step photolysis is also a continuous flow process using, in this case, deuterium-depleted hydrogen bromide to strip deuterium from a feedstream of ordinary water. Long-wavelength (infrared) laser radiation excites the deuterium-bearing hydrogen bromide molecules, which are then dissociated by short-wavelength (ultraviolet) radiation. Ordinary hydrogen bromide molecules, not being excited by the infrared radiation, are not dissociated. Once again, only a small amount of makeup hydrogen bromide is required, and the feedstream costs are almost nil.

Fig. 3. Isotopically selective photodesorption is a batch process that effects a very "clean" separation of deuterium from light hydrogen (protium). The chamber is cooled to liquid-nitrogen temperature, and natural hydrogen is pumped across porous transparent panels (e.g., pretreated Vycor glass) irradiated by infrared radiation of the proper wavelength. Both deuterium and protium are adsorbed on the panels, but the deuterium is promptly and selectively desorbed (evaporated). The process may be continued until one monolayer of H_2 gas is adsorbed everywhere on the panels. Then the chamber must be warmed and flushed in preparation for a new cycle.

33% HD, and 4% D_2 — initial data indicate about an eightfold deuterium enrichment in the irradiation-desorbed gas with a quantum efficiency of roughly 80%. This high efficiency, meaning that 80 molecules of HD are desorbed from the Vycor and released into the surrounding gas envelope for every 100 photons absorbed, is not well understood mechanistically but is extremely encouraging. It is much higher than needed to stimulate commercial interest in this process.

Present experiments are directed toward demonstrating comparable isotopic enrichments and quantum efficiencies in samples with much lower initial deuterium contents. These experiments necessarily use mass spectroscopic analysis, which yields $H_2/HD/D_2$ ratios. Some decrease in efficiency is expected, due to the greater likelihood of collisional deexcitation in samples with lower initial enrichments. However, the separation process itself, in principle, is independent of the relative isotopic ratios, because there is no overlap of the infrared absorption bands of H_2 and HD. Thus, higher concentrations of H_2 cannot interfere with radiation absorption by HD and will not cause substantial collisional deactivation of radiatively excited HD at moderate pressures.

The apparatus for this process consists of a temperature-insulated column containing thin sheets of

porous Vycor glass whose adsorption surface is $250 \text{ m}^2/\text{g}$. Over this column flows hydrogen gas previously cooled to liquid-nitrogen temperature (78 K). Through infrared-transparent windows, the Vycor sheets are irradiated with 2778-nm light, the frequency of the HD stretch. By using helium, for instance, as a continuous carrier gas with a pulsed flow of hydrogen, one effects a photon-mediated separation in which the HD is selectively desorbed faster than the H_2 , thus exiting the system before the hydrogen.

Present cost estimates for such a system are necessarily crude but strongly suggests modest capital investment and low operating costs (hydrogen, cooling, and irradiation). Hydrogen costs can be considered negligible because hydrogen depleted of its deuterium can be readily used for other purposes such as ammonia production. Cooling costs likewise are low. Thus the total operating costs seem likely to be small. The modest investment and low operating costs, plus ready availability of prepurified hydrogen on a large scale (about 1800 tonnes of heavy water equivalent annually from U.S. ammonia plants alone), all indicate commercial feasibility.

Problems of considerable technical import need to be solved. For example, the nature and magnitude of energy transfer from photoexcitation to vibrational and translational motion of the hydrogen molecule

(e.g., V→T transfer) are not well characterized. Indeed, it has been speculated that a major fraction of the 43 kJ/mole of the photodesorbed molecules may end up as either vibrational or translational energy of the molecules leaving the absorption surface.

We need to optimize infrared-light sources for photodesorption. The choice is between filtered blackbody radiation and various laser sources. By using a reflective filter for a blackbody source, which would pass only the desired frequency and reflect the rest back onto the source, one might dramatically increase the efficiency of a blackbody radiation generator as a narrow-band frequency source. However, as noted above, this might not be necessary.

Metallic Chromatographic Separation of Deuterium.

It was experimentally demonstrated some 15 years ago that deuterium can be separated from protium by displacement chromatography in a chromatographic column packed with palladium at room temperature.³ Palladium adsorbs hydrogen to form palladium hydride, protium forming a stronger hydride bond than deuterium. Separation is effected when a hydrogen-deuterium mixture is passed through the column. Initial deuterium concentrations of less than 2% have been quantitatively separated from protium by this technique. Palladium's $\text{H}_{100}^{\text{D}}$ cost has made this process economically impractical for large-scale heavy water production.

Fig. 4. Metallic chromatographic separation is also a batch process but can be made almost continuous in large-scale applications. It depends for its selectivity on the stronger affinity of protium than deuterium for certain intermetallic compounds such as LaNi_5 . As shown here: (a) a column packed with the intermetallic compound is filled with an inert gas (e.g., nitrogen); the gas mixture to be separated – natural hydrogen – is forced in from the bottom until the column is 25 to 50% filled with hydrogen. (b) Then a pusher gas such as deuterium-depleted protium is introduced, pushing the slug of hydrogen up the column. Deuterium, with its weaker affinity for the intermetallic compound, travels faster than protium and gathers on the leading edge. (c) Finally the hydrogen slug is forced out of the column, with the deuterium-rich leading edge (the leading 1%) emerging first. The remaining hydrogen is then pushed out the column top, and a new cycle begins.

However, workers at Phillips Laboratories recently discovered a group of compounds of the general formula AB_5 — A being a rare earth and B a transition metal — that absorb and desorb up to six hydrogen atoms per molecule of intermetallic compound at room temperature and hydrogen pressures of about 10 to 100 kPa.⁴ The absorption and desorption reactions are rapid and quantitative. If one of these relatively inexpensive compounds can be substituted for palladium, the chromatographic method of hydrogen isotope separation becomes practical.

The method of choice (Fig. 4) is displacement chromatography rather than the more familiar elution chromatography used in analytical work. In displacement chromatography, the column is filled with an inert gas — one not strongly absorbed by the column — and the gas mixture to be separated is forced in from the bottom until the column is about one-quarter to one-half filled with the mixture. Then the mixture is pushed on through the column by a different gas of equal or greater absorptivity (one that moves no more rapidly through the column than the mixture it is pushing or displacing). In hydrogen isotope separation, deuterium-depleted protium can serve as the pusher gas, and the inert gas might then be nitrogen, which would be readily available if the deuterium production unit were operated in conjunction with an ammonia plant.

In a large-scale separation plant, multiple columns would be operated together so that, while some columns were being filled with the hydrogen-deuterium mixture, others would be undergoing column purge. In this manner, batch-process disadvantages could be minimized. Because deuterium comes off the column first, there is no need to carefully flow the mixture completely through the column. After the first 1% or so of the mixture emerges, that remaining in the column can be purged rapidly and the column set up for the next cycle.

Calculations based on $LaNi_5$, one of the better hydrogen-binding intermetallic compounds, suggest substantial economies for chromatographic separation procedures using materials of its general properties. U.S. rare earth mining and purifying facilities, now running well below capacity, are capable without expansion of producing the amounts of rare earths needed for large-scale intermetallic-hydride chromatographic deuterium separation plants. Very large quantities of prepurified hydrogen feedstock are available at virtually no cost from ammonia plants, as noted above.

The chromatographic method is expected to have substantial cost advantages over the water-hydrogen sulfide method now used for heavy water production because it is a single-temperature, single-step process requiring only the comparatively minuscule amounts of energy needed for compressing the hydrogen gas to column-flow conditions.

We have done preliminary experiments to measure the hydrogen and deuterium pressures in equilibrium with various AB_5 hydrides at different temperatures. In addition to $LaNi_5$, these tests to date have included many other rare earth-transition metal combinations in varying proportions. Most show deuterium pressures about 20% higher than hydrogen; some exhibit deuterium pressures as much as twice as high. Even 10% pressure ratios are adequate for purposes of chromatographic separation. A 100% ratio implies very small, highly efficient columns. Separation factors are now being measured for the most promising intermetallic compounds.

Experimental separation of deuterium from hydrogen feedstocks of varying isotopic enrichments is currently being demonstrated with early versions of such columns. These efforts will soon culminate in attempts to demonstrate hundredfold single-step enrichment using natural hydrogen as the feedstock. Single-step quantitative separation of deuterium from enriched hydrogen feedstock (5% deuterium) has already been demonstrated using large column loadings and a fast feed rate.

Much work remains to develop a practical deuterium production process. There are other intermetallic compounds of the same general type as $LaNi_5$ that may have similar hydride-formation properties but considerably cheaper constituents. A systematic study of these compounds is underway to determine isotopic separation factors, speed of equilibrium attainment, equilibrium pressure ranges, compound stability and useful lifetimes, and costs of compound preparation.

Summary and Conclusions

We believe the above to be promising approaches to substantially reducing the production costs for heavy water. When one couples these cost reductions with existing and anticipated improvements in heavy water reactor technology, it appears that the present large fraction of power-production costs due to the heavy water inventory — some 20 to 30% — can be reduced to less than 10%. If this happens, heavy water reactors will apparently become

both a cheap and reliable source of electrical power as compared with any technology — nuclear, fossil-fueled, or unconventional — yet proposed.

This potential strongly suggests the need to reevaluate heavy water reactor technology. It also provides impetus for the present LLL studies. The U.S. and all mankind may benefit substantially from an

accelerated introduction of this economical, reliable, and safe technology for nuclear power generation.

Key Words: heavy water-production; isotope separation — deuterium; nuclear reactors; breeder reactors; CANDU; uranium enrichment; deuterium enrichment; GS process; isotopic selectivity; single-step photodissociation; two-step photolysis; photodesorption; metallic chromatographic separation.

ENVIRONMENT AND SAFETY

SAFETY LIMITS OF HALF-MASK CARTRIDGE RESPIRATORS FOR ORGANIC SOLVENT VAPORS

Our recent studies of the effective service life (safety limits) for typical half-mask cartridge respirators have shown these devices to be unsuitable for certain organic vapors — methanol, methylamine, vinyl chloride, and dichloromethane — because the effective service life is too short. For these vapors we recommend other forms of protection, such as air-supplied respirators. The experimentally determined service life for many vapors is shorter — sometimes significantly shorter — than predicted by adsorption theory.

Respiratory protective devices have been used for decades to protect workers from toxic gases, vapors, and particulate matter in their working environments. A common device is the half-mask respirator worn over the nose, mouth, and chin, whose major components are a removable cartridge (filter), through which air is inhaled, and a valve, through which exhaled air is expelled. The usual filter material is activated carbon. Such masks are regularly used for potentially hazardous operations associated with normal laboratory routines at LLL and elsewhere.

Recently we began studies of the effective canister service life of these devices for several common organic vapors under a variety of working conditions (ambient vapor concentration, humidity, work rate, etc.). Our tests addressed adsorption characteristics of the cartridges, not possible leakage through mask components. Airstreams containing known vapor concentrations were continuously forced through standard canisters. A flame-ionization detector measured the vapor concentration downstream of the canister. We considered the canister's safety limit to be exceeded when the downstream concentration reached 10%. Thereafter, the concentration climbs rapidly to about 50% before leveling off to a slower rate of increase.

Experimental results were compared in all cases with values calculated from adsorption theory. With four common vapors — methanol, methylamine, dichloromethane, and vinyl chloride — we found the service life to be less than 30 minutes, too short for

TESTING EQUIPMENT

Concurrent with the studies described in this article, LLL has designed and built much of the cartridge and canister testing equipment for the Testing and Certification Laboratory (TCL) of the National Institute of Occupational Safety and Health. TCL is charged with testing and approving all respiratory protective devices before they are issued to the general public. Testing involves preparation, control, and analysis of contaminant gas mixtures in air. Typical test gases are carbon monoxide, sulfur dioxide, nitrogen dioxide, ammonia, methylamine, hydrogen chloride, chlorine, and carbon tetrachloride.

safe use of a half-mask respirator. For ten of the vapors studied, the actual service lives are shorter than those calculated from theory.

Adsorption Characteristics

The activated carbon in all commercial organic-vapor cartridges is a granular solid usually manufactured by heating coconut shells or petroleum. Subsequent heating with steam produces a highly porous surface that collects the vapors of interest.

Figure 5 shows a schematic cross section of a carbon granule during adsorption. Gas or vapor passing across the solid surface diffuses into the microporous structure. The gases, experiencing loose Van der Waals' attraction, begin to condense, and the pores continue to fill until equilibrium is reached.

The carbon's adsorptive capacity (total amount of pore filling) is not affected by the breathing rate through the cartridge. The pores fill faster at faster breathing rates, of course, but only to levels determined by other factors: ambient concentration, relative humidity, and gas or vapor properties. Figure 6 shows that the service life is inversely proportional to the inhalation rate — the pores filling faster at heavier work rates — and that the time to equilibrium is a function of the vapor type. Relative humidity and the ambient concentration are held constant in this figure.

Figures 7 and 8 show the effects of these latter variables. Service life is a function of not only the relative humidity at use time but also the relative humidity at

Fig. 5. Vapor undergoing adsorption in the micropores of an activated carbon granule.

Fig. 6. Cartridge service life as a function of breathing rate for three organic vapors.

which the cartridge is stored: the lower the humidity, the longer the life. Likewise, the service life is lengthened by lower ambient concentrations of the vapors.

Fig. 7. Cartridge service life as a function of relative humidity (storage and use) for a carbon tetrachloride concentration of 1000 ppm.

Fig. 8. Cartridge service life as a function of ambient concentration for three organic vapors at a heavy work rate.

Pore filling varies widely for different gases or vapors. The more volatile solvents with lower boiling points are more difficult to adsorb than those of higher molecular weights. The degree of adsorption is a complicated function of the nature of the carbon and the vapor and cannot be assigned to a single physical property. Table 1 gives examples: the adsorbed saturation capacities of six different vapors under identical experimental conditions.

Calculation of Service Life

Adsorption theory has advanced significantly from the traditional treatment in elementary physical-chemistry textbooks. Today, the most generally accepted theory is Dubinin's adsorption isotherm equation,⁵ which explains adsorption in terms of pore filling. Using this complex equation, one can calculate the volume of vapor adsorbed at maximum filling for any given temperature, concentration, and vapor. Once this is known, the cartridge service life can be calculated from the Mecklenburg⁶ or modified Wheeler⁷ equation. The former is based on a diffusion model (molecular migration) and the latter on a kinetic model (molecular motion).

Typical examples of actual and calculated service life times are given in Table 2. Note that the more volatile materials show the widest deviation from theoretical values. This is caused in part by competition with water for the available adsorption sites. Adsorption theory does not now adequately correct for the presence of moisture in the air.

The practical consequences are obvious. For example, the safety limit for methanol, widely used as an industrial antifreeze and fuel for stoves and soldering torches, is about three minutes compared with the theoretical eight or nine minutes. Other

Table 2. Actual and calculated cartridge service lives for various organic vapors^a

Vapor	Service life (min)		
	Actual	Calculated	
		Mecklenburg equation	Modified Wheeler equation
Acetone	54	94	91
Benzene	101	114	110
Dichloromethane	23	26	24
Hexane	77	83	81
Isopropyl alcohol	91	199	103
Methanol	3.2	8.6	7.9
Methyl acetate	46	74	82
Methylamine	18	49	47
Methyl chloroform	73	89	86
Vinyl chloride	23	32	31

^aExperimental conditions: 1000 ppm, 22°C, heavy work rate.

vapors showing significant deviations from theory include methylamine, the precursor for almost all compounds containing amines (18 minutes vs 47-49 minutes predicted); methyl acetate, a solvent for resins or oils (46 minutes vs 74-82 minutes predicted); and acetone, a paint remover, industrial solvent, and ingredient in explosives, film, and rayon (54 minutes vs 91-94 minutes predicted). All the vapors listed in Table 2 deviate from the theoretical values to some extent.

From this table, also, one can identify which vapors penetrate the cartridge rapidly. Methanol is the chief culprit. Our studies, at 1000 ppm, represent a concentration that could easily result from a methanol spill in a closed area on a warm day. (The complete volatilization of just one cup - 1/5 litre - of methanol in a garage or storage shed could produce this concentration.) Other vapors whose safety limits are less than 30 minutes are methylamine, dichloromethane, and vinyl chloride. Along with its derivatives, vinyl chloride is used in refrigeration, plastics (such as PVC pipe), and hair sprays. It is also a suspected carcinogen. For such quickly penetrating vapors, we recommend other forms of protection, such as air-supplied respirators.

Summary

Respirator cartridge service life is a complex function of the breathing rate, ambient concentration,

Table 1. Volume of condensed vapor adsorbed per gram of carbon for various solvents at 1000 ppm

Vapor	Liquid volume adsorbed, cm ³ /g
Acetone	0.18
Benzene	0.34
Carbon tetrachloride	0.40
Dichloromethane	0.09
Hexane	0.44
Isopropyl alcohol	0.38

and relative humidity as well as the nature of the adsorbed vapor and characteristics of the activated carbon. Theoretical calculations using the adsorption isotherm, Mecklenburg, and modified Wheeler equations can deviate sharply from observed values, especially for volatile materials at elevated relative humidity. Our testing program has established practical safety limits for half-mask respirators for several organic vapors and proved conclusively that activated carbon does not perform acceptably for certain vapors, either in theory or in practice.

We have devised our own equation for the service life of activated carbon respirators, which is based on the normal boiling point of the vapor of interest. This will be published shortly, along with the full results of our studies.

Key Words: respirators; masks; respirators - testing; respirators - service life.

FLOW MICROFLUOROMETRY: ANALYZING SPERM DNA CONTENT

Flow microfluorometry has become a key tool in biomedical research because it allows cell analysis at extremely high rates (100 000 cells per minute) with statistical precision and sensitivity. One application of the LLL bicolor flow microfluorometer is to detect variability in the DNA content among individual mollusk and mammalian sperm. DNA variability should be a sensitive indicator of mutagenic events in these cells. Ultimately, we hope to identify and assess the effects on man and his environment of the chemical byproducts from various energy-production streams.

Fundamental to many biomedical problems is an understanding of the molecular processes that underlie critical functions of the living cell. Of special concern is the danger of chemical damage to important biological molecules - to DNA, the chemical basis of heredity, or to the large proteins that carry out the cellular life processes. Cancer production or mutation are dramatic possible outcomes of changes in DNA. We know little about the consequences of subtle changes in cellular function and control processes, but some obvious possibilities are embryonic or fetal disturbances and reduced life expectancy.

Bicolor Flow Microfluorometer

A key tool in our cell studies is the flow microfluorometer.⁸ Analysis of cell populations by high-speed flow methods has become widespread in recent years. In the bicolor flow microfluorometer at LLL, cell suspensions, previously stained with an appropriate fluorescent dye, are introduced into a laminar-sheath flow of distilled water or saline solution

in a vacuum system (see Fig. 9). The cells move at constant velocity (about 10 m/s) in a narrow stream (10- μ m diam) through an elliptical beam of exciting light. The light source is an argon-ion laser operated at 488 nm with a light-stabilized beam power of 1 W. The laser's elliptical shape is produced by a pair of crossed cylindrical lenses with 25- and 1.6-cm focal lengths. The beam is oriented with its major axis horizontal; cells flow vertically through its center.

When excited by the laser beam, each cell emits fluorescent light whose duration is determined by cell velocity and beam dimension. Typical pulse widths are a few microseconds; typical pulse rates are 1000/s. These light pulses are collected by a 20X microscope objective whose optical axis is perpendicular to both the laser beam and sample stream. After passing through an optical filter that suppresses the 488-nm light scattered from the laser, the fluorescent light pulses illuminate the photocathode of a photomultiplier, which converts them into electrical pulses. (A second photomultiplier is available for simultaneously measuring fluorescence in a different spectral region.) Each electrical pulse is integrated and amplified; the magnitude of the resulting pulse is digitized and stored in the memory of a multichannel pulse-height analyzer. The memory then contains a frequency distribution of the number of cells as a function of fluorescence; this data can be displayed, recorded on magnetic tape, and transmitted to a computer for processing. In one minute, the flow microfluorometer can measure and record the fluorescence of 100 000 cells.

Because of an interface between the microfluorometer's pulse-height analyzer and storage computer, cell distributions can be accumulated and analyzed in a matter of minutes. After collecting data

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Fig. 9. Schematic diagram of the LLL bicolor flow microfluorometer. Cells flow one at a time through an intense beam of laser light at rates of about 100 000/min. Each resulting fluorescent light pulse is detected photoelectrically and processed to yield a value proportional to the total fluorescence intensity. The value is stored in the memory of a multichannel pulse-height analyzer, which accumulates the fluorescence distribution histogram of the population.

in the analyzer for a cell population (10^5 to 10^7 cells), the experimenter can request a data transfer to the computer. The computer reads the data, stores the data on disc, and transmits it back to a display at the experiment station for verification. The experimenter then uses a separate remote graphics terminal to request a distribution analysis program. The frequency distribution, or histogram, is analyzed by fitting a linear combination of Gaussian functions, a polynomial function, and an exponential function to the experimental data by a least-squares best-fit code. The computer requests peak locations through the terminal. In less than a minute, data with the fitted curve and the extracted parameters is redisplayed, allowing the experimenter to evaluate the outcome of his work (see Fig. 10). He can have the computer analyze the data of each experiment after any number of data transmissions up to 1000 spectra.

A histogram gives the distribution of the fluorescent stain over the cell population. If cell preparation has been successful, the cellular stain content is proportional to the content of a specific cell

component — say DNA — and thus the DNA distribution of the population has been measured. Relative DNA content is derived from the means of the Gaussian function, cell frequency from the areas, and measurement variability from the dispersions.

A companion instrument, the electronic cell sorter, operates analogously to the flow microfluorometer but has the additional feature of droplet generation and deflection. If the fluorescence signal from a cell falls within a preset range, the fluid column is electrically charged at the moment the measured cell drops away from the column in droplets. A group of three droplets, one of which contains the cell, is thus electrically charged and deflected into a collection vial. If the fluorescence signal is outside the preset range, the droplets are not charged and pass into a different vial.

At present, there are four major applications of microfluorometry to biomedical research at LLL: (1) analysis of sperm DNA content, (2) detection of cervical cancer cells, (3) sorting and isolation of chromosomes, and (4) cell-cycle analysis. In the latter

Fig. 10. A sample initial data display is shown in the larger graph. The experimenter indicates the portion of the spectrum to be analyzed by marking the left- and right-most channels *not* to be fitted (dashed vertical lines). When the data are redisplayed (upper right), the abscissa is an expanded version of the channel numbers of interest; the ordinate changes to frequency of occurrence. On this new spectrum, the experimenter marks seven peak locations (crosses). After the seventh value has been keyed in, a least-squares-fit program is executed, resulting in the best fit (red curve) and a printout of the areas, means, and coefficients of variation. The experimenter then has the option of keeping the fit or requesting another try with the same data.

two studies, we are working with cells or cellular parts that we want to isolate for further analysis (e.g., chemical). In the sperm and cancer studies, we are looking for unknowns — i.e., for parameters of abnormal cells that will enable the flow system to identify and sort out these aberrants. Our study of sperm DNA content illustrates the potential and difficulties of flow microfluorometry.

Analysis of Sperm DNA Content

Flow microfluorometric analysis of sperm is central to our goal of measuring the variability of DNA content among mammalian testicular (spermatogenic) cells and sperm, so that from these measurements we can identify and assess the effects of energy-related agents on man. We want to learn if any chemicals from the various new energy-production processes (such as

in situ coal gasification or geothermal resource recovery) change the DNA content of sperm and thus are mutagenic. For example, is H_2S , a foul-smelling byproduct of geothermal wells, or ethylene dibromide (CH_2BrCH_2Br) mutagenic? The latter chemical compound is used as a lead substitute in gasoline, as a soil sterilizer, and as a grain fumigant, particularly for wheat. In this last application, it adheres to the stored grain and so is present in many processed foods. We know that high concentrations of the compound cause sperm abnormalities in cattle and sheep, reducing their fertility. The question is whether ethylene dibromide is mutagenic in the low concentrations likely to be ingested by man.

Variability in DNA content should be a sensitive indicator of mutagenic events in spermatogenic cells. We are now running tests with known mutagens to

see how they affect the DNA content of mollusk and mammalian sperm. Our objective is to define the parameters of an abnormal sperm so that we can program the microfluorometer's computer to recognize and sort out these aberrant cells. The differences in DNA content between normal and abnormal sperm, however, are likely to be very small, requiring very high resolution in microfluorometric analysis for detection.

Effects of Sperm Geometry. We compared the fluorescence frequency distributions of acriflavine-stained sperm from three untreated mollusk and six untreated mammalian species.⁹ Because sperm are usually homogeneous in appearance, haploid in DNA content, and lacking in DNA synthesis, they should generate narrow, unimodal DNA distributions with flow-system analysis. As shown in Fig. 11, spherical or cylindrical sperm from the three mollusk species — oyster, octopus, and abalone — produced the expected narrow, symmetric distributions. However, the stained populations of flat sperm from the six mammalian species — hamster, mouse, rabbit, stallion, boar, and bull — produced skewed distributions, with a peak representing lower fluorescence values and a lateral extension to higher values (Fig. 12).

Sperm of the mammalian species thus far examined have a common basic morphology. The sperm's profile view varies little from one to another. The head is

considerably flattened; in the bull, for example, it is only 0.5 μm thick. The most striking differences involve the plane view of the head; in the bull, boar, rabbit, and stallion, the head is roughly oval and more or less bilaterally symmetric (see Fig. 13). In the hamster and mouse, the head is hooked and asymmetric.

In contrast, the sperm of the three mollusk species are radially symmetric. Sperm heads of the oyster are small spheres with diameters of approximately 2 μm . Abalone sperm heads are cylinders about 2 μm in diameter and 7 μm long. Octopus sperm heads are slim and oblong, measuring 12.5 μm in length and 1 μm in diameter.

To account for the skewed histograms obtained with flat sperm, we altered the operating characteristics of the flow microfluorometer, looking for their effect, if any, on the distributions. Variation in cell analysis rate (300 to 2000 per second), change in barrier filter cutoff (512 to 610 nm), 90° rotation of the laser's polarization plane, and reduction of the detector light-collection angle from 30° to 4° all had no appreciable effect on the shapes of the histograms. Nor were the histograms of flat sperm affected by alternative fixatives, stains, and staining conditions. However, when flat sperm heads were positioned on microscope slides and their fluorescence analyzed, we noted that their orientation affected the resulting distributions. Hamster sperm heads with their plane

Fig. 11. Frequency distributions from flow microfluorometry of acriflavine-stained mollusk sperm. Each coefficient of variation (CV) is computed assuming a normal distribution for the indicated (---) peak. Channel number is directly proportional to the intensity of cellular fluorescence within each spectrum, and thus to DNA content. The spectra were measured at different times; modal channel numbers are not an indication of relative brightness of sperm of the different species.

Fig. 12. Frequency distributions from flow microfluorometry of acridavine-stained mammalian sperm. Same conditions apply as given in Fig. 11.

surface parallel to the optical axis (i.e., on edge) gave 25 to 30% larger fluorescence values than those lying flat, and each distribution was symmetrical. Cells selected randomly gave a skewed distribution.

Fig. 13. Live stallion sperm. Their heads are about 4 μm wide and 9 μm long; center thickness is approximately 0.3 μm . Tails vary from 40 to 60 μm in length. By comparison, the diameter of a human hair is some 90 μm .

These data suggested that a homogeneous sperm population can yield a broad range of fluorescence values depending on the spatial relationship of each cell to the excitation source and detector. To test this explanation, we devised a simple, two-dimensional mathematical model. We assumed a flat sperm with a rectangular cross section and a width-to-thickness ratio of 10:1. We used the same geometry as in the microfluorometer, i.e., the axes of flow, exciting light, and detector were orthogonal. Cell orientation about the flow axis was random. We also assumed cells immersed in water, uniform distribution and excitation of stain, no self-absorption of fluorescent light, and a detector light-collection angle of 30°. For light emitted at angles greater than the critical angle, we accounted for multiple internal reflection (light piping). Light emitted at angles less than the critical angle is transmitted through the interface between the cell and the medium and is refracted away from the normal — i.e., toward the plane of the head. We ignored internal reflection of the reflected component of this light. Based on geometrical optics, our model also ignored possible physical optical effects due to

the sperm head's thickness approximating the wavelength of the excitin* light.

Computation of the distribution of fluorescent light emission as a function of angle showed more light bent toward the plane of the head than normal to its flat surface, resulting in more light collection by the detector when it views the sperm head edgewise. Combining the effects of this angular light distribution with those of the random cell orientation about the flow axis and the detector light-collection geometry, we obtained a theoretical fluorescence distribution qualitatively similar to our experimental skewed distribution. That is, the theoretical distribution had a peak due to heads oriented with their flat surfaces toward the detector and a lateral extension toward higher fluorescence values due to heads oriented with their edges toward the detector. On the whole, therefore, the model appeared to be a reasonable approximation of reality and supported our explanation of the skewed distribution.

Further confirmation of this interpretation comes from two other experiments. First, we found that the degree of asymmetry of the DNA distributions was reduced by raising the refractive index of the suspending fluid closer to that of the sperm. And second, we have sorted sperm from various parts of the asymmetric distribution and found that each of these subpopulations regenerates the complete distribution when put back through the flow microfluorometer.

If the flow microfluorometer is to be a useful tool in mutagen testing with sperm, the resulting DNA spectra must be well characterized to clearly mark deviations from normalcy. The coefficient of variation for abnormal sperm is likely very small — perhaps

only a few percent — and could be masked if the coefficient of variation of the DNA spectra in general is 5% or more. As was shown in Fig. 11, the abalone sperm heads yielded a narrow, symmetric fluorescence distribution with a 2% coefficient of variation, suggesting their potential use in mutagen testing. Our recent studies with abalone sperm has reduced this coefficient to an even more promising 1.25%. The asymmetry of the flow-sperm distributions, on the other hand, currently restricts the utility of flow-system analysis of mammalian sperm for studying mutagenesis. It appears, however, that this asymmetry can be eliminated by either controlling sperm orientation with planar flow conditions or sensing and then accounting for sperm orientation. A cost analysis of six potential corrective schemes is now under way.

Further Studies. Once we are able to identify and isolate abnormal sperm, we will be looking to answer a number of questions about the effects of energy-related chemical agents on man. Are sperm abnormalities temporary, disappearing once exposure to the mutagen is ended? Or are they permanent? Can sperm abnormalities caused by mutagenic compounds become hereditary traits in subsequent generations? Because the flow microfluorometer allows cell analysis at extremely high rates with statistical precision and sensitivity, it will be an important tool for finding answers to these and other questions about mutagenesis.

Key Words: biomedical research; cytochemistry, DNA — analysis; DNA — measurements; flow — measurements; flow microfluorometer; fluorescence analysis; fluorometry; histogram; mutagens; spermatozoa.

NSMERA

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SCIENCE AND TECHNOLOGY

NUCLEAR CHEMICAL MINING FOR COPPER RECOVERY

To meet projected domestic demand for copper, deeper ore deposits will have to be exploited and a technology developed for processing these ores. We have investigated combining nuclear technology and *in situ* leaching to recover copper ores from deposits too deep to be mined economically by conventional techniques. The chemical mining concept developed at LLL involves emplacing nuclear explosives below the water table in a deep-lying copper deposit, detonating these explosives to rubble the rock, and then passing oxygen and water through the rubble zone to leach out the copper as copper sulfate. The copper sulfate is then brought to the surface where liquid ion exchange and electrowinning are used to remove the copper.

Our technical evaluations of this chemical mining process have been favorable. In 1973, we teamed with the Kennecott Copper Corporation and ERDA to consider the feasibility of commercializing the process. The resulting joint study affirmed the technical feasibility of nuclear chemical mining and identified the process uncertainties that must be resolved before its commercial feasibility can be assured.

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To meet the nation's copper needs, lower-grade deposits have been progressively exploited and massive mining methods have been developed — for example, the introduction of large earth-moving equipment and improvements in ore processing. Although these deposits and methods appear adequate to meet demand for the next 10 to 15 years, new sources will be needed thereafter. Deeper or even lower-grade copper deposits must then be utilized, and a technology must be developed specifically to process these ores economically. Because of the long lead times to bring a new technology online, new mining techniques must be developed now to meet the projected copper requirements.

Chemical mining is a likely candidate for exploiting deep copper deposits. Over the past five years, we have worked extensively on one particular chemical process: nuclear rubbleization with subsequent *in situ* leaching of copper ores.¹⁰ More recently, we joined with the Kennecott Copper Corporation and ERDA to evaluate the commercial potential of this process. In general, although the process was judged technically feasible, we found several uncertainties that must be resolved before commercialization is economically advisable. We identified the most critical technical issues, however, and outlined an experimental program for investigating them.

COPPER SUPPLY AND DEMAND

Copper is one of several essential metals — crucial to industrial processes — in which the U.S. demand each year exceeds domestic production. Demand is growing and expected to continue so.¹¹ The annual shortfall presently is met by imports, but these have been beset in recent years by severe economic and political problems including nationalization of U.S.-owned production facilities. The international climate, plus widely fluctuating copper prices, keen competition for expansion capital, and higher plant and operating costs, have discouraged copper exploration and development.

The U.S. Bureau of Mines, in 1970, estimated our total domestic copper resources to be about 125 million tonnes. Of this, based on 1968 domestic copper prices, 75 million tonnes were considered economically minable. U.S. needs for the period 1968-2000 were projected at 70 to 90 million tonnes, depending on the copper-demand growth rate. The world demand forecast for the same period, exclusive of the U.S., was 230 to 365 million tonnes compared with economically minable reserves of 200 million tonnes (1968 international copper prices). Imports cannot be expected to meet U.S. shortages, over the long range, without driving copper prices to exorbitant levels.

Thus, concludes the Bureau of Mines study, discoveries of new reserves and the development of new technologies for economical copper recovery from presently submarginal resources appear necessary to meet forecasted U.S. and worldwide demands for primary copper.

Nuclear Chemical Mining

The LLL concept for nuclear chemical mining calls for copper minerals to be rapidly dissolved in a rubbleized ore column by operating the column at elevated temperatures and relatively high oxygen concentrations. First, a large rubble column is created well below the water table. Either conventional mining methods or nuclear explosives can be used, but the conventional approaches are estimated to be more expensive. Once created, the rubble column, or chimney, is then filled with water either artificially or by natural inflow.

When the chimney is full, oxygen is introduced into the bottom at pressures slightly above hydrostatic pressure. While the gas bubbles rise through the chimney, part of the oxygen dissolves and becomes available as an oxidant for the leaching process, as shown in Fig. 14. The rising undissolved oxygen provides a lifting force that induces a circulation cell within the chimney. As the liquids circulate within this cell, they carry the dissolved oxygen to all parts of

the chimney. This dissolved oxygen oxidizes the primary sulfide minerals to produce sulfuric acid and heat, which lowers the pH and raises the temperature. The net result is a relatively rapid dissolution of the copper minerals.

Leach solution is continuously pumped to the surface where it is split into two streams. One stream is diverted to the process plant for copper removal. The other is combined with barren electrolyte solution from the plant and reintroduced into the chimney along with added oxygen.

The solution diverted to the process plant is passed through a heat exchanger to lower its temperature to about 50°C. Afterward, a solvent extraction process strips the copper from the cooled leach solution. Electrowinning* is then used to recover copper from the electrolyte generated in the final stage of the

*Electrowinning is the term commonly used in the metals recovery industry for the electrolytic process of removing metal ions from an electrolyte solution.

Fig. 14. Schematic of LLL process for *in situ* leaching and surface recovery of copper.

solvent extraction process. Although other extraction methods may be feasible, solvent extraction and subsequent electrowinning appear the best.

Feasibility Study

Under ERDA sponsorship, we joined with Kennecott to consider the feasibility of commercializing our nuclear chemical mining process. This joint study focused specifically on the technical, economic, environmental, safety, and administrative considerations that arise when nuclear explosives are used to rubblize copper-sulfide ores for *in situ* leaching. A secondary goal was to provide the data for deciding whether an *in situ* copper-leaching experiment would be mutually advantageous, and, further, to provide detailed recommendations for such an experiment if deemed profitable.

In general, LLL concentrated on rubblization details, fluid circulation, leaching technology, and hydrology. Kennecott studied processing techniques and economics, and ERDA provided input on environmental and exploration concerns.

The first step was to establish a representative site as the basis for a reference case. We chose a hypothetical porphyry copper-ore body suitable to nuclear rubblization. Next, we set initial values for all process parameters based on available field and laboratory data and theoretical assumptions from extrapolations of commercial or analogous technologies. We then developed an operational plan, including schedules for rubblization, leaching, and process-plant operation. Finally, using these schedules, we refined our original assumptions and determined specific values for the reference case; the resulting dimensions are given in Table 3.¹² It should be emphasized that these are best-judgment values; those for a real site may differ significantly.

Once we arrived at the details of our reference case, we turned to its evaluation. This analysis had three objectives: (1) to estimate process economics, including capital and operating costs as well as return on investment, (2) to perform sensitivity analyses on process variables, and (3) to evaluate the environmental impact of nuclear chemical mining.

Process Economics. Cost estimates were based on data obtained from engineering companies, vendors, ERDA, and available literature. The entire mining and processing operation had an investment cost of \$113 million and an annual operating cost of \$26 million (1974 dollars). It would produce an annual gross

income of \$60 million. Further analysis yielded a discounted-cash-flow rate of return (DCF-ROR) on investment 18% for the reference case. Table 4 summarizes these economic results. Unfortunately, an 18% ROR is not sufficient to justify immediate commercialization of a high-risk technology. Subsequent sensitivity analyses also showed that the ROR could vary from 0 to 23%; some of the process uncertainties must therefore be resolved before commercialization is economically advisable.

Sensitivity Analyses. To consider uncertainties in all phases of the nuclear mining process, Kennecott made a series of sensitivity analyses. The purpose was to evaluate the economic effects of changes in the main

Table 3. Reference case dimensions of LLL's nuclear rubblization and *in situ* leaching concept for copper ores

Parameter	Dimension
Ore Body	
Length	878 m
Width	860 m
Thickness	386 m
Depth	844 m
Water table	91 m
Density	2.64
Ore grade	0.5%
Pyrite/chalcopyrite	1:1
Detonation Plan	
Yield	420 TJ (100 kt)
Depth	800 m
Chimney mass	4.6×10^6 tonnes
Rows	7
Shots/row	10
Schedule	1 row/3 yr
Leaching Schedule	
Chimneys in operation	20
Life of chimney	6 yr
Copper loading	4.8-9.3 g/litre
Oxygen flow rate	45 kg/min (100 lb/min)
Solution flow rate	4920 litres/min
Process Plant	
Copper production rate	38 000 tonnes/yr
Solution flow rate	9500-17 000 litres/min
Carrier	Kerosene
Extraction agent	LIX64N
Electrolyte loading	35-45 g/litre

Table 4. Economic summary for nuclear rubblization and *in situ* leaching of copper ores (1974 dollars)

Capital outlay and investment return			
Investment (millions of dollars)		Operating cost	
First year (mine development)	6.6	Annual	\$25.9 million
Regular (mine development)	22.0 ^a	Unit (copper)	67.4¢/kg (30.6¢/lb)
Last year	2.4	Startup cost	
Depreciable capital (surface facilities)	75.5	Periodic	\$1.5 million ^b
Working capital	8.5	Allocated unit cost for copper (annual average)	1.3¢/kg (0.6¢/lb)
Total over life of project (discounted)	136.5	DCF rate of return	17.8% ^c
Unit investment = \$2900 per annual tonne of copper (discounted)			

^aEvery 3 years for seven times.

^bEvery 3 years.

^cAssuming a depletion allowance of 15% and a copper selling price of \$1.50/kg (70¢/lb).

independent variables, which were grouped into four categories:

- Ore-body-related variables: ore grade, pyrite-to-chalcopryrite mole ratio, and the CO₂ content.
- Discretionary variables: yield of explosive, number of chimneys per row, size of pumping system for oxygen injection, and chimney life.
- Process variables: particle-size distribution and mixing behavior of the chimney.
- Economic variables: depreciable capital investments, investment expense, operating cost, and copper price.

The interaction of variables was not considered nor were they optimized to give the best results. Consequently, the analyses were qualitative rather than quantitative and only indicated trends.

Kennecott's analyses revealed that changes in most of the listed variables had little economic impact. However, a few of them — variables related to the amount of oxygen required — were extremely important. Certain parameters thus assumed increased significance: the effect of particle size on the pressure drop is crucial, the overall particle-size distribution must be clearly defined, oxygen must be efficiently transferred to all parts of the chimney, and the pyrite-to-chalcopryrite ratio must be known.

Environmental Impact. Finally, the environmental impact of the nuclear mining process was evaluated.

Ground motions, industrial-waste control procedures, radioactivity, plant safety, and plans for a decontamination plant were considered.

We found that ground motion and industrial waste problems can be managed with reasonable effort. Also, with proper controls and procedures, radioactivity is not expected to pose a significant environmental problem. All radioactive waste products will be returned to the chimneys. However, radioactivity will be encountered in all phases of plant operation, and safety procedures must ensure that exposures are below established standards for both workers and the public. Radioactivity levels are expected to be high enough in the liquid-ion-exchange and electrowinning plants to require careful study.

A major environmental concern was the possibility of radioactive solutions moving away from the rubblized ore body and into the biosphere. Accordingly, we closely evaluated the hydrologic condition expected around a nuclear chimney. Our analysis indicated that before the fluids can move a significant distance from the chimney, the radioactive components will have decayed to negligible levels, and the surrounding rock will have neutralized the fluids' acidity.

Furthermore, even if a prospective ore body has a hydrology problem — for instance, a large permeable fault in the ore zone — there are remedies. One of the more promising is to drill water wells in

appropriate places and, by pumping in water, change the local hydrologic gradient to produce a stationary water zone. This again would restrict the contents of the chimney to the vicinity of the ore body. Costs for such remedial steps were included in our economic analysis.

On a more positive note, we should point out that the LLL nuclear mining process also offers environmental pluses. The process eliminates a number of major environmental problems associated with most conventional copper recovery techniques. Open pits, SO₂ emissions, waste dumps, and tailing ponds, for example, are all avoided.

Study Results

Our joint study affirmed that the LLL concept for nuclear rubblization and *in situ* leaching of copper ores is technically feasible. It also identified the most critical technical issues that must still be resolved.

The amount of oxygen needed to stir the liquids in the chimney is a major uncertainty. Process economics are so sensitive to oxygen requirements that this uncertainty must be resolved before further commercialization work is undertaken. Excess oxygen provides the fluid circulation needed to carry oxygen to all parts of the chimney. This circulation is generated when the undissolved oxygen, acting as extra void space, lowers the liquid density and thus creates a buoyancy force that drives a circulation cell within the chimney. In this circulation model, flow resistance or frictional drag encountered in a packed bed, or chimney, is the critical parameter. The key issue in establishing the total oxygen requirement, therefore, is this resistance, which is a function of effective average particle diameter, rubble porosity, and particle shape factor.

A second uncertainty is the movement of radioactivity through *all* phases of the copper recovery process. Radioactivity levels in the leach solution and chimney gases have been studied in some detail; we used the results of these studies to plan surface and subsurface mining operations. However, solvent extraction and electrowinning processes need similar study before safety and operating procedures can be defined for the complete recovery operation. Rigorous documentation of radioactivity levels is also needed to expedite the licensing procedure. Licensing, an important phase of commercialization, may take time; it cannot begin until radioactivity data are complete.

The question of how many ore bodies are compatible with LLL's recovery process is another

unknown. Although geological evidence suggests many large, deep copper-ore deposits, the information needed to verify this contention resides in company files, is purely speculative, or has not yet been systematically sought. Many prospective sites remain unexplored because there have been no economic incentives or guidelines for exploration at the depths suited to nuclear rubblization. Documentation of these sites is needed to put our recovery process in perspective.

Given favorable resolution of the above uncertainties, the next step would be to verify the leaching rates and conditions for a large rubble column. A demonstration experiment using chemical explosives in a porphyry copper-ore deposit could be a useful intermediate step in the scale-up from laboratory autoclave work to nuclear rubblization. Data on particle-size distribution, frictional drag resistance in a rubble column, and leaching rates for large rubble volumes could be thus obtained with less time and money than in a nuclear experiment.

Only a full-scale experiment, however, will prove the feasibility of nuclear rubblization: nuclear detonation in a copper-ore body at the proper depth. Any full-scale experiment should be conducted according to the conditions given in our reference case. After detonation, the chimney parameters, diameter, and height would be verified first. Before leaching began, rubble zone characteristics would also be measured — for example, particle-size distribution and porosity. Finally, leaching should be continued until enough data are taken to verify the predicted leaching curve.

Some important leaching data, however, should be obtained before extensive field tests are under way and could be compiled from work in small laboratory autoclaves. Almost all of today's leaching data are for San Manuel ore, which severely limits the selection of prospective sites for our nuclear mining process. We need data for other ore types, in which mineralization, ore grade, pyrite-to-chalcopyrite mole ratio, or carbonate minerals differ from San Manuel ore.

The two remaining uncertainties are symmetry of collapse and containment. These phenomena are well understood for single detonations but become serious unknowns when closely spaced multiple explosions are planned. Symmetry of collapse is a problem if the chimney of one explosion is markedly changed because of proximity to an existing chimney. For containment, a problem develops if the presence of a nearby chimney decreases the probability of containing

radioactivity. Initial study of these uncertainties can be done theoretically. Eventually, however, both will have to be proved with a full-scale experiment incorporating at least two, and perhaps three, nuclear explosions.

There are, therefore, several issues that must be resolved before the commercial potential of nuclear rubbleization and *in situ* leaching of copper ores can be assured. The most important technical uncertainty is the oxygen injection requirement. The prime commercial uncertainty is market acceptance and

government certification of a copper product that contains trace amounts of radioactivity. The LLL nuclear mining concept has been shown technically feasible, and our joint study with Kennecott and ERDA has identified the next logical steps in developing this concept.

Key Words: copper; copper ores; copper ores - effects of nuclear explosions; copper ores - leaching; electrowinning; liquid ion exchange; nuclear mining.

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