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Lawrence Livermore National Laboratory

October 1983

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Energy and Technology Review

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An Overview of Oil-Shale Retorting Processes

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The Laboratory is playing an important role in the research and development of oil-shale retorting technology through its studies of the relevant chemical and physical processes, mathematical models, and new retorting concepts. The LLNL cascading bed process is an outgrowth of this effort.

Shocked Fluids at High Densities and Temperatures

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We have been investigating the properties of dense molecular fluids at high pressures and temperatures to improve our understanding of high-explosive behavior, giant-planet structure, and hydrodynamic shock interactions.

Computer-Controlled Triple-Quadrupole Mass Spectrometry

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By totally computerizing our triple-quadrupole mass spectrometer system, we have produced a *general-purpose instrument of unrivaled speed, selectivity, and adaptability* for the analysis and identification of trace organic constituents in complex chemical mixtures.

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About the Cover

Computer simulation of crushed shale particles tumbling down the sloping chutes of an oil-shale retort of novel design. The tumbling motion causes the smaller pieces to work their way underneath the larger chunks just before the stream of shale falls off the end of the chute. The fall inverts the stream, placing the smaller pieces on top again as the process repeats. This rapid mixing is important to the retorting process as it promotes rapid heat exchange between the retorted shale, heated by combustion of the char, and the cold raw shale fed into the system. When the *retorted and raw shale are well mixed*, the stream falls into the pyrolyzer portion of the retort where the product oil and gas are extracted and removed. For more information on oil shale retorting, see the article beginning on p. 1.

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An Overview of Oil-Shale Retorting Processes

We are playing an important role in the research and development of oil-shale retorting technology through our studies of the chemical and physical processes that occur during retorting, the development of mathematical models of the retorting process, and our assessments of new retorting concepts. The LLNL cascading bed process is an outgrowth of this effort.

The United States has vast quantities of oil shale, enough to supply our liquid fuel needs for centuries. Oil can be obtained by simply heating the shale to convert the organic material it contains to shale oil. The challenge is to do this at a cost that makes the shale oil competitive with conventional petroleum. Shale oil has, in the past, competed successfully with petroleum (e.g., Scotland until the 1940s). Yet in recent times, no one has demonstrated a shale oil process that is economically competitive with the current world prices of petroleum.

Experience gained by government laboratories and commercial industries with present oil-shale retorting processes varies in scale from small laboratory experiments to larger pilot and semi-works plants that can process as much as a few hundred tonnes per day. For example, Union Oil Company reportedly will soon begin production in its new 10 000-barrel/day plant in Colorado.

Industrial development of oil shale retorting is still in its early stages, and there is substantial room for technical advances and accompanying reductions in cost. We expect progress both in improvements of present processes and in the development of new retorting processes.

At LLNL, we have been involved in the research and development of oil-shale retorting technology for more than a decade. Our early work concentrated on retorting technology applicable to in-situ processes. This work has been successfully concluded, although commercial application awaits the development of low-cost methods of constructing suitable shale rubble beds on a large scale. Research interest, especially for government-supported work, has shifted from in-situ technology to the broader field of advanced aboveground retorting processes. The emphasis at LLNL has been on aboveground concepts for the past several years.

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Currently, we are studying the chemical and physical processes believed to occur during retorting, developing mathematical models with which to calculate and analyze the retorting process, and devising and assessing new retorting concepts. The LLNL cascading bed process is the latest outgrowth of our continuing effort.

Pyrolysis and Oxidation of Oil Shale

This country's most extensive oil shale reserves are found in the Green River geologic formation, which is located in the western United States. This oil shale is an impure marlstone (a clay/carbonate rock) consisting mostly of inorganic mineral matter. In a typical shale, the solid organic constituent is kerogen and constitutes about 15% of the rock by mass and 30% by volume. The rock itself has such a fine-grained structure as to preclude any process for grinding it into particles to physically separate the kerogen from the mineral matter (see Fig. 1). Because the raw shale is essentially impermeable to fluids and the kerogen is not soluble, liquid extraction processes are likewise inapplicable.

To retort oil shale to produce shale oil, we must break the shale into pieces small enough to permit good heat transfer. (In any shale mining and crushing operation, this requirement is easily met, although the size range and content of fine particles present some handling difficulties.) The shale pieces are then heated to about 500°C, at which temperature the kerogen pyrolyzes (i.e., decomposes) rapidly, producing oil vapor and gas and leaving behind solid char. The amounts, compositions, and energy resulting from the combustion of the various components produced by the pyrolysis of kerogen are shown in Fig. 2.

Heat for the retorting process is provided most efficiently by burning some of the pyrolysis products—preferably the less valuable ones. The oil is the most valuable product, and the gas is potentially valuable as a source of hydrogen for upgrading the shale oil or as a source of marketable gas. Char is the least valuable product and, hence, is the fuel of choice for providing the process heat.

In addition, in most retorting processes, the mineral matter in the shale is not inert. The carbonate minerals, dolomite and calcite, are major components of these shales, and

Fig. 1

Microstructure of oil shale, showing the physical relationship between the organic (kerogen) and inorganic (mineral) components.

dolomite especially is subject to decomposition at temperatures and times typical of the combustion processes. Reactions between mineral matter and gases are also important, both in the reducing conditions typical of pyrolysis and in the oxidizing conditions typical of the combustion portion of the process. Participation of the mineral solids in the retorting process is undesirable when it consumes a large amount of energy, as in carbonate decomposition, but welcome when it removes sulfur-containing gases from the gas stream and thus reduces a source of air pollution.

Some of the oil produced may be destroyed within the processing cycle before it is recovered. For example, oil

in the vapor phase will crack if it is subjected to high temperature, producing mostly lighter gaseous hydrocarbons (exposure to 550°C for only 2 s will result in a loss of about 10% of the oil). In addition, oil in the liquid phase will coke at elevated temperature, producing mostly solid hydrocarbon products; fortunately, the loss in oil yield from this mechanism is insignificant at the rapid heating rates characteristic of aboveground retorting processes. Oil and oil vapor also can be destroyed by burning if they are exposed to oxidizing conditions during the retorting process.

The challenge we are faced with, then, is to devise a simple and efficient oil-shale retorting process that operates at low cost. This requires an accurate

Fig. 2

Typical decomposition products from kerogen. When heated, kerogen decomposes into the mass fractions of oil, gas, and char shown; the chemical composition of each is indicated. The percent combustion energy obtained by burning each component is also given.

Hot Gas Retorting Processes

The Paraho internal combustion retort: a moving bed of shale travels downward and is heated by hot gas flowing upward through it. The hot gas is provided by combustion of hydrocarbon gas and char within the retort. Oil produced from the pyrolysis process is carried out of the retort by the gas stream in the form of vapor and oil mist (liquid).

The Union B and the Petrosix retorts: the hot gas is provided by heating the hydrocarbon gases produced by pyrolysis in an external heater. The hot gas flows opposite to the direction of the shale particles. In the Union B process, the shale is pumped upward and the gas flows downward; in the Petrosix process, the shale flows downward and the gas flows upward. Fuel from an external source must be supplied to operate the heater.

The NTU batch process: one of the earliest oil-shale retorting concepts. Oil shale is dumped into a retort, heated by hot gas produced by the combustion of hydrocarbons within the retort, and then removed. Processes similar to this have been used in the past and are still used or considered where a simple though inefficient process is acceptable.

The Superior process: something of a hybrid in which shale is loaded onto a moving circular grate to form a fixed bed that is carried through a hot-gas retorting zone; the hot gas is supplied by an external heater. The fixed bed then is carried through an oxidizing zone where some heat is produced by combustion of char and used to preheat gas.

The modified in situ (MIS) process: a fixed-bed retort is constructed underground by some combination of mining and blasting. Downward-flowing hot gas is provided by burning the char in the retort. However, because of the method of construction, little control over particle size is possible, and the bed contains particles less than 0.5 cm in diameter as well as particles larger than 10 cm in diameter. As a result, the retorting rate is slow and oil yield is reduced. Another serious problem is the difficulty in obtaining uniform permeability, which reduces the fraction of the bed that is swept by the retorting front.

and thorough understanding of the important physical and chemical processes that occur during retorting and of their interactions in a complex system, mathematical modeling to obtain the necessary information logically and efficiently (rather than by trial-and-error experimentation), and sophisticated engineering to design a retorting process at minimum cost.

Different Retorting Processes

Over the years, many processes have been proposed for retorting oil shale. For the most part, they have evolved from different methods for heating solid particles (in this case, oil shale particles). Either hot gas or hot solid material may be used to supply heat to the shale. (Hot liquids are not practical for temperatures near 500° C.) The classification of the retorting processes described below is a useful means of identifying and evaluating the many oil-shale retorting processes. The processes referred to by company name are simply convenient examples that illustrate the generic process types. Many other process variations are possible within each class described, and other processes exist that are not listed as examples.

Heat Transfer from Hot Gas

If hot gas is chosen as the heat-transfer medium, the broken-up shale is distributed in a packed bed through which we pump hot gas to heat the shale particles. The various types of hot gas retorts have certain characteristics in common. For instance, the mass of gas required to process a unit mass of shale ranges from 0.6 to 0.8, a ratio that derives from the relative heat capacities of the shale and the gas. As a result, large volumes of gas are required and the resistance of the bed to the flow of gas must be minimized to avoid large gas-pumping costs.

Fine particles are undesirable in packed beds because they restrict the flow of gas or increase the pressure drop across the bed. Therefore, shale particles with diameters less than about 0.5 cm must be discarded or processed

Table 1 Classification of hot gas processes for retorting oil shale. Hot gas is passed through a packed bed of shale particles to heat and retort the shale.

Packed bed retorts		
Fixed bed	Moving bed	Gas heater type
MIS NTC	Paraho	Internal combustion (direct)
Superior	Union B Petrosix	External combustion (indirect)

in some other way. Large particles, on the other hand, require a relatively long time to heat, adding to the cost by increasing the residence time of shale in expensive equipment and by loss of oil through coking, which occurs if the heating is very slow. The maximum practical size limit for shale particles in hot gas retorts is probably a diameter between 5 and 10 cm.

Table 1 lists the various kinds of hot gas retorts. Packed shale beds may be either fixed or moving. The gas may be heated either internally by combustion of fuel within the retort (direct) or externally in some kind of heater (indirect). A brief description of six representative hot gas retorts is given in the box on p. 4.

Heat Transfer from Hot Solid

The second option for heating the oil shale is to use a hot solid material. In this case, the various processes may be classified according to the method of mixing the solid with the raw shale and the method of heating the solid (Table 2). The transfer of heat from the hot solid to the raw shale depends mainly on the convection of the gas that is present and only to a small extent on conduction and radiation. The oil vapor and gases produced during pyrolysis play a significant role in the heat transfer. In all these hot solid processes, the raw shale is crushed to a size small enough for rapid heat transfer. Either shale itself (retorted) or another solid may be used for the heat-carrying medium. When retorted shale is used as the heat-carrying solid (by burning the char that remains on the shale particles) the need to separate two solids is avoided by using more hot retorted shale than raw shale and then discarding the excess solid somewhere in the process. If another solid is used (e.g., ceramic balls), it must be easily separated from the shale. In these processes, large solids are separated from fine shale by screening and are reheated in a packed bed or ball heater of some kind; hot gas is used as the heat transfer agent. The box on p. 5 presents a short description of five hot solid retorts.

Hot Solid Retorting Processes

The Tosco II process: hot ceramic balls are mixed with smaller shale particles in a rotating drum. After the shale is pyrolyzed, the balls are separated out and reheated in a ball heater using gas as fuel. The retorted shale is discarded.

The Shell SPHER process: hot balls fall through a fluidized bed of small shale particles. The balls are then separated from the shale and reheated in a manner similar to that used in the Tosco process. Mixing is provided by the fluidized bed and by the falling balls.

The Lurgi process: hot burned shale is rapidly mixed with raw shale in a screw mixer and then held in a surge bin for a few minutes to complete the pyrolysis. After pyrolysis, the shale is fed to a lift pipe (dilute fluid bed) where it is burned as it is pneumatically lifted up in a stream of air. The hot burned shale exiting from the lift pipe provides a continuous source of hot solid.

The Chevron process: raw shale and hot burned shale are mixed in a fluidized bed and held there until pyrolysis is complete. Although a fluidized bed (a suspension of solid particles in a gas) provides good vertical mixing, the residence time of solids is not uniform. To correct this problem, a number of stages are introduced into the fluid bed to provide a more uniform residence time. In addition, a lift pipe is used to burn the retorted shale and provide hot solid, as in the Lurgi process. The use of a lift pipe for burning shale in both of these processes limits the maximum particle size that can be processed to a diameter of about 0.5 cm.

The LLNL cascading bed process: mixing occurs in a few seconds as the solids—recycled retorted shale and raw shale—flow down a series of chutes that invert and redirect the flow. Pyrolysis is completed in a few minutes as the hot shale particles flow through a bin. The char is burned to produce hot solid in a cascading bed burner rather than in a lift pipe. Solid particles cascade down a series of chutes that slow their fall and provide sufficient residence time for combustion. Oxygen is provided by air flowing across the tumbling solid particles. The maximum particle size may be as large as 1 or 2 cm in diameter because the vertical pneumatic lift pipe is not restricted to the operating conditions required for char combustion.

Table 2 Classification of hot solid processes for retorting oil shale. Hot solid particles are mixed with shale particles to heat and retort the shale.

Stirred bed retorts		
Mechanical mixing	Fluidized bed	Solid heater type
Tosco II (drum mixing)	Shell SPHER (gas mixing)	Packed bed, large solid particles, gas fuel
Lurgi (screw mixing)	Chevron STB (gas mixing)	Fluidized bed or cascading bed, fine solid particles, char fuel
LLNL (gravity-flow mixing)		

Analysis and Evaluation of Four Generic Retorting Processes

Faced with this variety of retorting processes, we must answer the question: Which one is the best? Although we are a long way from knowing the answer, we do know it will depend on the cost to produce shale oil from any given shale feed. None of these retorting processes has been operated on a commercial scale. Cost estimates are based on engineering designs of widely varying detail and reliability. Some of the designs are very tentative, being based on concepts that have not yet been implemented, whereas others represent actual experience with large-scale pilot or semi-works plants. In no case has even a single full-scale module of a commercial retort been operated. An additional problem is that details of both the technology and the cost estimates are considered to be proprietary by most companies and, hence, are not publicly available.

Although cost estimates, even comparative cost estimates, must be viewed skeptically, we believe technical evaluations and comparisons of the generic retorting processes are worthwhile and informative, even if complete technical operations data are not available. By this means, the state of the art may be more clearly defined, advantages and disadvantages of various processes may be identified, and opportunities for improving the present processes may become

apparent. In the course of this analysis, we have developed a new process concept, the LLNL cascading bed process, that may offer advantages over the other processes evaluated.

We selected four representative generic retorting processes for evaluation—two hot gas processes and two hot solid processes (see Table 3):

- A moving-packed-bed retort with hot gas supplied by internal combustion. Example: the Paraho process.

- A moving-packed-bed retort with hot gas supplied by an external combustion heater. Example: the Union B process.

- A fluidized-bed retort with hot solid supplied by the combustion of retorted shale in a lift pipe (a dilute phase fluid bed). Example: the Chevron staged-turbulent-bed (STB) process.

- A gravity-mixed retort with hot solid supplied by a cascading bed burner. Example: the LLNL cascading bed process.

These retorting processes are not at an equal stage of development. The Paraho process has been operated at a semi-works scale, and engineering design has been prepared for scale-up to commercial size. The Union B process is under construction as the first full-scale module of a commercial plant and should begin operation this year. The Chevron process has been operated at a laboratory scale, and a pilot plant is under construction. The LLNL process concept is being tested in the laboratory.

Analysis and Evaluation Method

In order to make comparisons of the various generic processes, a detailed description of each process is required. We must know the amount and rate of flow of all material (gas, solid, and liquid) and the amount of energy entering and leaving each process component. This, in turn, requires that we know the chemical reactions occurring in each component, the pressure drops, and the energy needed to move material through the equipment.

Table 3 Summary of the four generic oil-shale retorting processes selected for analysis and evaluation.

Generic process		
Abbreviation	Name	Modeled example
HGIC	Hot gas, internal combustion	Paraho
HGEC	Hot gas, internal combustion	Union B
HSIB	Hot solid, fluid bed	Chevron
HSCB	Hot solid, cascading bed	LLNL

We are somewhat hampered in making the comparisons by incomplete knowledge of the processes. The existing understanding of the generic processes is not always sufficient to provide us with the detailed description of each process that we need, and, in some cases, the required information is proprietary and, thus, not publicly available. Fortunately, qualitative descriptions of many processes are available, and we can begin our comparisons with these. Furthermore, a substantial amount of data on the chemical and physical processes important in oil shale processing has been obtained in recent years at LLNL and at other laboratories. We have developed mathematical models incorporating this understanding and have used them to construct detailed descriptions of each process.

We constructed models of each generic retorting process using the following information:

- LLNL mathematical models of the retorting process based on kinetic and thermodynamic data for the relevant chemical reactions and physical processes.
- Our interpretation of the qualitative information available about each proprietary process.
- Our designs for additional components where required.
- Our designs for process optimization as suggested by model calculations. (These changes improve the process without changing the concept.)

For all four processes, we assume a shale feed grade of 125 l/tonne and a production of 50 000 bbl/day of crude shale oil (no upgrade) or the equivalent energy content of oil plus gas.

In our opinion, these models are suitable for evaluating and comparing the four generic processes. Although it is convenient to list "proprietary" examples of each of the generic processes, these examples almost certainly differ from the processes we describe here. The differences, however, should not be large enough to affect our general evaluation and comparison of the generic processes.

The model calculations allow us to construct flow diagrams of mass and energy and to understand each generic process well enough to make some useful comparisons. The calculations also help us to identify problem areas and research opportunities.

HGIC Process

The Paraho process was used as a starting point in modeling the hot gas, internal combustion (HGIC) concept. In the Paraho process, raw shale is fed into the top of the retort and moves downward through it. About 15% of the raw shale is smaller than 1.2 cm in diameter and is rejected. Recycled gas is introduced at the bottom of the retort, and mixtures of air and recycled gas are introduced at an upper and a lower distributor within the retort. Combustion of the recycled gas, char, and some oil vapor occurs above the two distributors, providing a supply of hot gas that heats and pyrolyzes the shale. The oil mist and vapor are transported to a condenser where oil is collected.

Our model for a moving-packed-bed retort with hot gas supplied by internal combustion includes the chemical reactions and physical processes shown in Table 4. The model calculations have been validated by comparison with many laboratory experiments at LLNL and with data from Paraho retort runs. The excellent agreement between the calculated and measured temperatures in the Paraho semi-works retort (2.4 m diam, 8.2 m high) is illustrated in Fig. 3 for typical operating conditions. The calculated oil yield, gas composition, and spent shale composition also compare well with the experimental results.

Using the model to simulate a larger scale retort (10 by 40 m in cross section and 8.2 m high), we found that some operating changes might be desirable. The predicted oil yield can be significantly improved if the separation between the combustion zone and the retorting zone is increased. This can be done by moving the air distributors 1 m downward and increasing the flow of recycled gas into the bottom of the

retort by 55%. The peak temperature is substantially higher than in the semi-works retort because of the lower heat loss from the surface and because the higher flow of recycled gas captures more of the sensible heat of the outlet shale. The peak temperature can be limited, however, by reducing the air flow by 35% at the top distributor. This change also reduces the outlet gas temperature, thereby reducing the heat load on the oil condenser. We assume that oil would be condensed from the outlet gas at 10°C in a commercial process rather than at 60°C as in the semi-works plant. This would reduce the amount of oil vapor that is recycled with the gas and then burned in the retort.

Mass flow in this HGIC process is shown in Fig. 4. The widths of the streams in the figure are proportional to the mass flowing in the process. The mass of the raw shale is reduced by pyrolysis of the kerogen, combustion of the char, and decomposition of the carbonate minerals. Inasmuch as most of the energy produced from the burning char is absorbed in the decomposition of the carbonates, the fuel contained in the recycled gas is essential. The HGIC process is thermally efficient in that solids and

gases enter and leave the retort at relatively low temperatures. However, because the gas cycle is diluted by nitrogen from the introduced air, it may not be practical to use the fuel value of the gas outside the retort, and it is not practical to condense all the liquid product from the large volume of recycled gas.

HGEC Process

The Union B process was used as the starting point for the hot gas, external combustion (HGEC) model. In this process, shale is pushed upward through the retort by two alternating pistons. Gas heated in an external heater flows downward through the retort, and oil may be removed as either vapor or mist or may flow downward as a liquid. We used the LLNL moving-packed-bed model to simulate the HGEC process. Our calculations are somewhat simplified

Fig. 3

Comparison of measured and calculated temperature profiles in a Paraho retort. The good agreement between the calculated and measured temperatures from the bottom of the retort (left) to the top of the retort (right) confirms and verifies our understanding of this retorting process.

Table 4 Mathematical model elements used in analyzing three of the generic oil-shale retorting processes, HGIC, HGEC, and HSCB.

Chemical reactions in shale particles

- Release of bound water.
- Pyrolysis of kerogen and coking of oil.
- Pyrolysis of char.
- Decomposition of carbonate minerals.
- Oxidation of char and sulfur.
- Reaction of carbon with carbon dioxide.
- Reaction of carbon with water.

Chemical reactions in gas stream

- Combustion and cracking of oil.
- Combustion of H_2 , CH_4 , CH_3 , and CO .
- Water-gas shift.

Physical processes

- Axial convective transport of heat and mass.
- Axial thermal dispersion.
- Axial pressure drop.
- Heat transfer between gas stream and shale particles.
- Thermal conduction within shale particles.
- Water evaporation and condensation.
- Movement of shale opposite to flow of gas.

compared with the HGIC process because we do not have to consider oxidation reactions within this retort.

Only that portion of the shale feed material that is smaller than 3 mm is rejected (approximately 6%). By choosing to process more of the finer shale particles than the Paraho process, the Union B process rejects less material but at the cost of higher resistance to the flow of hot gas. According to published information, the walls of the retort diverge upward to permit the shale to be pushed upward by the rock pump. The angle of this divergence has an important additional influence on the pressure drop through the retort. We calculated that, for a given cross section at the top of the retort, walls with a 15-deg divergence from vertical would increase the pressure drop in the retort from 20 to 63 kPa. In our calculations, we assume a divergence of 10 deg and calculate a pressure drop of 40 kPa. Although a significant amount of the product oil may be present as oil vapor in the gas stream leaving the retort, it need not be condensed and separated from the gas stream because only a negligible amount of oil vapor is lost to cracking when it is heated and recycled through the retort. The remaining gas stream is condensed at 10°C to remove product oil. Although gas is being used as heater fuel in the first module under construction, coal is assumed to be used in our model of a commercial process.

The mass flow in this HGEC process is shown in Fig. 5. Use of an external heater avoids dilution of the circulating gas with nitrogen from air and allows collection of almost all the liquid and hydrocarbon gas. Fuel must be provided from an external source to run the heater. In addition, the spent shale exits at a much higher temperature than in the HGIC process, yielding a lower thermal efficiency. However, carbonate decomposition is eliminated, and the char remains on the retorted shale.

HSFB Process

The starting point for our model of the hot solid, fluid bed (HSFB) concept

is the Chevron STB process. Here, raw shale is mixed with hot burned shale in a fluidized bed and retained in the bed until pyrolysis is essentially complete. To provide a uniform residence time for the shale particles in the fluidized bed, stages are added to ensure that the mixture moves downward more or less uniformly. The mixture of retorted and partially burned shale then is introduced into a pneumatic lift pipe. As the particles are lifted in a column of air, the fuel (i.e., char) remaining on them is burned, raising the temperature. The heated solid material

Fig. 4

Mass flow diagram for the HGIC process (hot gas, internal combustion). The relative masses flowing in the process are represented by the widths of the streams. The mass of gas flow required is almost as large as the mass of solid being processed. Shale leaving the retort is completely retorted, and one fourth of the char produced has been burned. Product oil must be separated from a large mass of waste gas.

Fig. 5

Mass flow diagram for the HGEC process (hot gas, external combustion). The amount of gas required is comparable to the amount of solids processed. No air enters the retort, and the char is not burned. No waste gas is mixed with the product oil and gas.

is separated from the gas stream at the top of the lift pipe. At this point, some of it is discarded, but a major fraction of the heated solid material is mixed with new raw shale in the retort, completing the cycle.

A model was developed to calculate the major processes in this retort, including fluidization of the solids, pressure drop, kerogen pyrolysis, and the release of bound water. This allowed us to select reasonable operating conditions and to calculate mass and energy flow in the retort. We also modeled the processes occurring in the lift pipe, including combustion of char and sulfur, combustion of the pyrolysis products from fine shale particles blown out of the retort, decomposition of carbonates, pneumatic transport of solids, pressure drop, and particle attrition. The pneumatic transport of a mixture of particles of widely varying size is not well understood, thus reducing confidence in our lift pipe calculations. For example, the most optimistic interpretation of recent data could result in a 40% decrease in the required height of the lift pipe. We also calculated the compression of gas streams, carbonate decomposition in a surge bin at the top of the retort, and the heat exchange required in the process.

Figure 6 shows the mass flow in this HSFB process. The ratio of hot solids to raw shale is 3.5. The solids leave the

Fig. 6

Mass flow diagram for the HSFB process (hot solid, fluid bed). A large mass of solid flow must be handled compared to the mass of raw shale processed. No waste gas is mixed with the product oil and gas. Char is efficiently burned to provide the heat for the process. [The mass flow diagram for the HSCB (hot solid, cascading bed) process is essentially the same.]

retort at 500°C and are heated to 665°C in the lift pipe. Maximum particle size is 6 mm. Most of the shale (98%) is retorted, with a residence time in the retort of 3.6 min. The required height of the 8.4-m-diam lift pipe is 49.4 m, providing a residence time of about 11 s. The constraints of residence time and particle size make it difficult to reduce the height requirement without increasing the pressure. If it is economically practical to increase the pressure from 80 kPa (ambient at the site) to 200 kPa, the height of the lift pipe can be reduced to about 15 m. Another alternative may be to burn part or all of the char in a dense-phase fluidized bed.

Although more solids must be handled than in hot gas processes, the high throughput and relative ease of handling them in the HSFB process may be advantageous. Only a small amount of gas is required for fluidization, and both oil and hydrocarbon gas may be readily recovered. Char left on the retorted shale can provide all the energy required in the process.

HSCB Process

The hot solid, cascading bed (HSCB) concept was developed at LLNL. In modeling the hot solid processes, we realized that there might be some inherent advantages in using hot solids over hot gases, especially the relative ease of handling solids and the efficiency of using char as fuel. Our model calculations specify the essential requirements of a hot solid process:

- Rapid mixing of solids.
- Residence time of 2 to 5 min for pyrolysis.
- Rapid removal and cooling of the product to avoid cracking of oil vapor.
- Residence time of 10 to 20 s for the retorted shale in a combustor.

While the first and third conditions are easily met in a fluidized bed retort, the second condition is not. A fluidized bed provides mixing during the residence time, which not only is unnecessary but also results in a nonuniform residence time. In the Chevron hot solid process discussed

above, the unnecessary mixing is accepted and, to compensate, attempts are made to keep the residence time more uniform by introducing stages into the bed.

The lift pipe is an adequate way of lifting and burning shale, but the constraints are tight. The interrelationships between particle size, residence time, gas velocity, oxygen concentration, and combustion kinetics require a very high lift pipe and a small particle size. Moreover, control of a lift pipe during operation may prove to be difficult.

Our cascading bed process is a way of working around these problems of the fluidized bed process (see Fig. 7). Raw shale from the feed supply and hot shale from the cascading burner enter the mixer, where they are rapidly mixed in an alternating series of chutes. The shale mixture flows into and through a pyrolyzer; several minutes are allowed in the pyrolyzer to obtain complete pyrolysis of the kerogen. Gases and oil vapor are removed through vents in the pyrolyzer. The mixture of retorted and burned shale is then introduced into a short lift pipe, whose only purpose is to transport it to the top of the cascading burner. Only an unimportant amount of combustion occurs during transport. The shale is separated from the gas at the top of the lift pipe and distributed into the top of a cascading burner, where alternating chutes retard its fall and provide the residence time required for combustion. Temperature is controlled by adjusting the lateral flow of air across the burner, which is about 5 m high.

The computational model developed for the HGIC process was adapted to simulate both the retort and the cascading burner for the HSCB process; it includes all the chemical and physical processes listed in Table 4. In addition, we used a model of the lift pipe to calculate the small amount of combustion (about 25% of the total combustion) that occurs during the pneumatic transport.

As a first step in the development of this concept, we have built and successfully operated a laboratory-scale

Fig. 7

Artist's rendering of a commercial-scale cascading bed retort. Raw crushed shale from the mine is mixed with hot burned shale from the cascading burner. The mixing occurs in a few seconds as the two streams of shale fall into the pyrolyzer. Gas and oil vapor products are evolved rapidly, especially at the top of the pyrolyzer, and are removed and cooled. Retorted shale at the bottom of the pyrolyzer is carried, first horizontally and then vertically, to the top of the retort by a blast of air. After air is removed in the cyclone separator, the shale flows down through the cascading burner; a lateral flow of air burns the char on the shale, raising its temperature. This hot shale is then mixed with more raw shale and the cycle is repeated.

burner that measures about 4 m high and 8 by 15 cm in cross section (Fig. 8).

Comparison of Retorting Processes

Many features of the four generic processes are presented for comparison in Fig. 9. Each retorting process is represented as a site containing the shale-processing facilities required to produce 50 000 bbl/day of shale oil or its energy equivalent; for three of the four processes, an optional electric power generating plant is included. The daily flow of materials in and out is shown on the same mass scale so that amounts may be compared. The unlabeled numbers are tonnes per day. To show the large masses of solid material (i.e., shale) on the same scale as other materials, we show them stacked ten units deep. Energy flow is given in megawatts electrical except for the fuel required for the HGEC process, which is measured in megawatts thermal. The mass of the fuel is not given; it will depend on what fuel is used and the efficiency of the gas heating system.

The shale-processing facility is shown by three columns representing the major components of the plants. The first is the volume of the reaction vessels required for handling the shale. For the hot gas processes, this is the volume of the retort itself. For the hot solid processes, it includes the pyrolysis vessels and the shale combustion vessels. Differences in the volume of this equipment should give qualitative ideas of capital cost differences for this portion of each process. The second column shows the heat exchange capacity for each process in megawatts divided by the log mean temperature difference, a number roughly proportional to the surface area required and related to cost. The third column is the rotating machinery capacity in megawatts, which represents the electrical power requirement for the process plant. Power plants to generate electricity from hot shale are optional in three of the processes (all but the HGIC process). Both heat exchange capacity

and power generating capacity are shown for these.

In addition to the shale oil produced, hydrocarbon gas and hydrogen are recovered in all the processes except the HGIC process. (In that process, most of the gas is used as fuel, and it is not practical to recover the rest because it is diluted with nitrogen and combustion products.) The recovered gases may be sold after they are upgraded to pipeline quality or they may be used to make hydrogen. Hydrogen collected on site or produced from hydrocarbon gases will be used to upgrade the shale oil.

The two hot solid processes use all the shale that is mined, whereas the two hot gas processes must reject some of the fine shale particles. The HGIC process requires the largest mine because of the amount of fine particles rejected and the inability to recover the hydrocarbon gas and all the oil vapor. The HGIC process also requires the largest reaction vessel volume (9440 m^3), with a correspondingly large cross-sectional area (1157 m^2). In the HGEC process, the volume required (3800 m^3) is substantially reduced, even though fewer of the fine particles are rejected. This is possible because combustion in the retort has been eliminated, along with the related control problems. Gas, therefore, can be moved through the retort much faster, although at the expense of higher pumping costs, as is apparent in the large machinery capacity and power requirement in the HGEC process.

In the HSF process, a similar reduction in vessel volume is obtained without an increase in the pumping capacity and power required, even though a mass of solid 3.5 times as large as the raw shale input is being continuously recycled (see Fig. 6). The high efficiency with which solids can be processed in fluid beds makes this possible. Even so, a major fraction of the volume required (3760 m^3) is in the lift pipe combustor (2720 m^3). The height of the lift pipe combustor (50 m) and the difficulty in operating it with oil shale are problems that have yet to be overcome.

In the HSCB process, the vessel volume has been reduced to 1130 m³ by substituting a cascading bed combustor for a lift pipe, and a gravity-flow mixer and pyrolyzer for a fluidized bed. The mechanical equipment and electrical power requirements for the HSCB process are slightly lower than those for the HGIC and HSFB processes. The problem in the HSCB process is to learn how to design and build a very large cascading bed combustor and mixer.

Clean-Up of Waste Gases

In all retorting processes, waste gas will be discharged into the atmosphere. Both the concentration of pollutants and the total amount of waste gas will have to be controlled to meet legislated levels. The waste gas from an HGIC retort contains large amounts of sulfur in the form of hydrogen sulfide and lesser amounts in other forms. It also contains hydrocarbons and some nitrogen compounds. Hydrogen sulfide must be removed, the gas must be oxidized, and additional sulfur in the form of sulfur dioxide may have to be removed. The cost of this clean-up processing will be an important part of the overall process cost. The hydrocarbon content of the waste gas is low, equivalent to approximately 88 kJ/mol, but it may be practical to make power from the combustion of this gas. If so, the cost of cleaning the gas may be somewhat reduced. The waste gas produced in the HGIC process (approximately 10 000 tonnes per day) will almost certainly be more difficult to clean than that from the other processes.

In the other three processes, only a relatively small amount of waste gas comes from the pyrolyzer, and it is not diluted with combustion products or nitrogen. Hence, it may be used as a source of hydrogen for hydrogenation of the shale oil or cleaned and upgraded to pipeline quality. (Hydrogen from some source will be needed to upgrade the shale oil.) In the HSEC process, most of the waste gas is produced by combustion of whatever fuel is used in the gas heater. If the fuel

Fig. 8

Diagram of the cascading bed combustor. Air flowing from left to right burns the char on the shale as the fall of the shale is delayed by the chutes. The temperature in this combustor is controlled by adjusting the air flow.

Fig. 9

The four generic retorting processes. (a) Hot gas, internal combustion (HGIC) e.g., Paraho process. (b) Hot gas, external combustion (HGE), e.g., Union B process. (c) Hot solid, fluid bed (HSFB), e.g., Chevron

process. (d) Hot solid, cascading bed (HSCB), e.g., LLNL concept. In these diagrams, the masses of materials entering and leaving a plant site are given by the numbers (in tonnes per day) and are shown to

(b) HGEC

(d) HSCB

scale. Energy flow in megawatts is shown, as is the net potential energy export from the site if the optional power-producing plants are provided. Major components of the retorting plants are shown, as are

the components of the optional power plants. Water required relative to oil produced is small for all four processes. Large volumes of solid must be handled in all processes.

is natural gas, the waste gas will be clean; if the fuel is coal, the clean-up equipment used in coal-burning plants will be needed. Use of a local fuel for the gas heater rather than an imported fuel probably is desirable. For example, burning char left on retorted shale would be preferable if it could be done economically, including the cost of cleaning up the waste gas.

In both hot solid processes, large quantities of gas are produced by the combustion, in air, of char on retorted shale. In both processes, combustion occurs under conditions that seem to be advantageous for the removal of sulfur from gas by reaction with the hot shale.

In general, nitrogen oxides in the gas are less important than the sulfur compounds but will require attention. In spite of the large amount of waste gas produced in oil shale retorting, the hot solid processes appear to have an advantage in requiring no clean-up of sulfur in the gas. The waste gas from the HGIC process may be the most expensive to clean, even though the volume is the smallest.

Water Requirement

The water required for each retorting process is divided into two categories—shale disposal water and process water. The water needed for heat exchange or cooling is shown in Fig. 9 as process water; the daily requirement is given in cubic metres. We note that the process water requirement is, in every case, less than the amount of oil produced.

The temperature of the waste shale emerging from the retorting process also is shown in each diagram. In the HGIC process, the temperature is relatively low (70°C) because of the high thermal efficiency. The water consumed in cooling this shale to ambient temperature, plus an additional 10% for wetting and compaction, is also shown in Fig. 9. The other three processes are not as thermally efficient as the HGIC process and thus the waste shale temperatures are higher. The higher temperatures, however, provide an option for converting some of this energy to electricity before final cooling and wetting. The electrical

generating capacity and the heat exchange capacity of the optional plants are shown, as is the water consumed in cooling and wetting the shale (i.e., for shale disposal), with and without the power plant. If a power plant is installed, there is a reduction in the amount of water consumed. Because the amount of water reduction is not economically significant, the question of whether to include the power plant will be determined by the cost of the plant and the value of the power. The power plant can make each of these three sites a net producer of electrical power.

Conclusion

In our opinion, there is no clear choice for a "best" process for large-scale, low-cost production of shale oil. Oil-shale process technology is neither highly developed nor mature, and substantial improvements will result from further research and development and from industrial experience. The hot gas processes may be viewed as first-generation technology, and the hot solid processes, if they can be successfully developed, may be second-generation technology.

Valuable engineering experience at the hundreds-of-tonnes-per-day scale has been obtained with the HGIC and HGE processes, and the technology is moderately well developed for proceeding to the next step. The first module of an HGE process plant (10 000 bbl/day) is being constructed by Union Oil Company with initial operation planned for late 1983. Natural gas will be burned as fuel in the first module, thus avoiding problems with waste gas clean-up. Later versions probably will use some other less expensive fuel. Industrial operating experience with this process, supported by continued research and development, should make possible further improvements in efficiency and reductions in cost.

Scaling up the HGIC process to commercial-size plants may be a greater technical risk than scaling up the HGE process because of the difficulty of controlling the combustion

process and the flow of solid material in a large retort, and the expense of cleaning up the waste gas.

The hot solid processes are not as highly developed as the hot gas processes, in many respects, because retort operating experience with these processes is limited to laboratory-scale operations or, on a larger scale, to short tests of some of the process components. Much information must yet be obtained on these hot solid processes. In particular, we need to learn more about the important chemical reactions and physical processes that take place during retorting. The hot solid processes, however, do offer the advantages of high throughput, low-sulfur waste gas, and reduced gas-pumping requirements. Potential difficulties center about our lack of experience in handling large quantities of fine shale particles in both the combustor and the pyrolyzer, and some uncertainty about oil cracking in the pyrolyzer.

The HSCB concept offers several potential advantages over the HSFb process by substituting a mixer and a gravity-flow pyrolyzer for the fluidized bed, and a cascading bed combustor for the lift pipe combustor. Elimination of the fluidized bed and of the need for controlled combustion in the lift pipe should permit the use of coarser material and reduce the amount of fine material to be handled. At this stage of development, however, the HSFb process may have an advantage in scale-up because of industrial experience with fluidized beds comparable in size to that of the pyrolyzer. The larger lift pipe combustor, however, may prove more difficult to operate.

From our survey of these oil-shale retorting processes, it is evident that a balanced program of research and development in oil shale technology is

needed, together with industrial development on an appropriate scale. This will lead to the technical advances that will make possible significant reductions in the cost of producing shale oil. Such an approach, however, will require the cooperation of government and industry in providing continuing support during the next decade.

We at LLNL are playing a particularly important role in researching and developing this technology. We are studying the chemical and physical processes important in oil shale retorting (including the chemistry of potential pollutants and their relation to process variables), developing mathematical models of the retorting processes, and investigating and assessing new process concepts. The concept for the LLNL cascading bed process is an outgrowth of this effort. We have constructed and are operating an experimental working model of this process that will establish its feasibility. We also are conducting a study of the chemistry of recycled shale solids, the results of which will be applicable to other hot-solid retorting processes as well.

A major problem—if not *the* major problem—for our cascading bed concept involves scaling up the process from the laboratory experiment to the larger pilot or semi-works plants. Advances in our understanding of solid flow in the cascading bed combustor, in the mixer, and in the pyrolyzer are needed. With the aid of a new computer model to calculate the flow of large numbers of discrete solid particles, we are making progress in this area. □

Key Words: hot gas-external combustion (HGEC), internal combustion (HGIC); hot solid-cascading bed (HSCB), fluid bed (HSFB); kerogen; LLNL, cascading bed process; oil shale retorting; shale oil.

Shocked Fluids at High Densities and Temperatures

We have been investigating the equation-of-state properties of dense molecular fluids at high pressures and temperatures to improve our understanding of the behavior of high explosives, the structure of the giant planets, and the applications and effects of hydrodynamic shocks.

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As they explore the universe around us, astronomers and geophysicists encounter many phenomena so far beyond our experience with conditions on Earth that we are unable to verify our theoretical descriptions of them. One group of such phenomena concerns the behavior of matter at extremely high temperatures and pressures. We have been exploring these phenomena using shock-wave compression techniques with which we can produce, momentarily, conditions that exist continuously only in such places as the interiors of Jupiter and Saturn.

The shock compression of molecular fluids is of particular interest because of the phenomena that occur at high densities and temperatures, e.g., strong intermolecular repulsion, molecular rotation, vibration, and dissociation, electronic and molecular ionization, and

chemical decomposition and reaction. Shock compression is thermodynamically irreversible and is therefore accompanied by an increase in temperature. For example, water shocked to 30 GPa is compressed more than twofold in density¹ and heated to 2000 K.²

The mathematical expression that relates temperature, pressure, and density for a material is called its equation of state. The three principal applications for the information we gather concerning the equation-of-state (EOS) properties of dense molecular fluids at high pressures and temperatures are:

- Predicting the performance of high explosives.
- Modeling conditions in the interiors of the giant planets.
- Understanding the effects of hydrodynamic shocks.

In addition, the experimental data we

obtain provide a valuable test of the validity and accuracy of our theoretical equation-of-state models.

Applications of EOS Data

Explosive Performance

The postdetonation products of solid high explosives include nitrogen (N_2), water (H_2O), carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), ammonia (NH_3), methane (CH_4), and solid carbon (C). To understand the forces exerted by a detonating explosive well enough to model them, we must know how the density of each of these chemical products responds to changes in pressure and temperature.

The explosive benzotrifuroxane (BTF), for example, is thought to decompose according to the reaction,⁵

Suppose we start with a 10-cm-thick slab of BTF bonded to a 0.7-cm-thick copper plate and detonate the explosive uniformly over its free surface. A detonation wave moves rapidly through the BTF at 8.5 km/s and strikes the copper plate. When the shock wave gets through the copper, the plate is accelerated by the expanding reaction products.

We simulated this hydrodynamic flow using our KOVEC computer code⁴ with a Jones-Wilkins-Lee (JWL) equation of state for BTF³ and a Grüneisen equation of state for copper.⁷ Figure 1 shows the initial configuration and the pressure histories in two thin zones 3 cm and 0.3 cm from the copper plate (zones I and II, respectively). The initial pressure jump (to 36 GPa) and pressure release is the same in both zones. In zone II, however, 0.5 μ s after arrival of the detonation front, the reflection from the copper plate reshocks the detonation products to 53 GPa. The corresponding density histories (not shown) have similar shapes with peaks at 2.5 and 2.9 g/cm³, and the temperatures reach several thousand kelvin. Conditions in this and other explosives are comparable to those achieved in

shocked and double-shocked liquids like nitrogen and carbon monoxide.

In the 1960s, equations of state derived from shock-compression data for water,¹ nitrogen,² and carbon dioxide⁶ were combined to obtain empirical equations of state for mixtures like high explosives.^{7,8} Recently, we have derived equations of state for detonation products from shock-compression data for the individual liquids via quantum statistical mechanics and a mixture theory based on the minimization of the free energy with respect to concentrations of the species present. This mixture theory extends theories based on our work on carbon monoxide and hydrocarbons and is in satisfactory agreement with experimental measurements for three explosives: liquid nitrous oxide (NO), RX-23, and hexanitrobenzene (HNB). This work suggests that we will eventually be able to predict high-explosive behavior by a statistical-mechanics treatment of dense molecular fluids at high temperatures.

The Giant Planets

Each of the outer planets in our solar system is thought to consist of a rocky core covered with a thick layer of "ice" (metallic hydrogen and helium for Jupiter and Saturn, and ammonia, methane, and water for Uranus and Neptune) and surrounded by an envelope of molecular hydrogen and helium (about 20 wt%).^{9,10} The

Fig. 1

Calculated pressure histories at two locations in a 10-cm-thick planar slab of the explosive BTF, bonded to a 0.7-cm-thick copper plate and initiated simultaneously all over its free surface. The second pressure peak at zone II is a reshock caused by reflection from the copper plate.

condensed gases are believed to have been compressed isentropically starting from low atmospheric densities and temperatures.

Because these planets are so massive, their interior temperatures are very high. The calculated temperatures and pressures in Jupiter's envelope, for example, are as much as 20 000 K and 200 to 500 GPa (100 GPa = 1 Mbar). Such conditions are unattainable with static compression techniques but can be approached by shock-wave experiments.

Figure 2 shows the isentropes for what we believe to be the material composition of Jupiter and Saturn, together with the equation of state of hydrogen on a temperature-pressure plot.¹¹ The principal Hugoniot of liquid hydrogen crosses the isentropes of the giant planets near 20 GPa and 4000 K. Reflected-shock Hugoniot points exist at higher pressures and temperatures near the planetary isentropes. (See the box on p. 25 for a description of the Hugoniot curve.) Thus, shock-wave equation-of-state data starting from the liquid state are useful for calibrating theories for the fluids thought to exist in the outer planets.

Other experiments are useful for probing the nature of the planetary interiors. For example, the high electrical conductivity of shocked water and ammonia suggests that the fluids in the interiors of Uranus and Neptune are chemically ionized.

Hydrodynamic Shocks

Equations of state of fluids also are useful for investigating technological applications of dynamic high pressures.

For example, shock waves have been studied in liquid hydrogen under planar, cylindrical, and hemispherical loading.¹² In experiments using planar geometry, a layer of liquid hydrogen is used as a buffer between an impactor and a copper baseplate to investigate metallurgical effects in single-crystal copper compressed both quasi-isentropically and by a single shock to 57 GPa.¹³ The copper close to the liquid hydrogen buffer experiences multiple shocks; the copper far from the buffer receives a single strong shock.

Because the copper is initially chilled to the temperature of liquid hydrogen (20 K), the residual temperatures (i.e., those obtained because of the shock) calculated for these pressure histories are only 170 and 375 K, respectively. Hence, shock-induced defects, which would otherwise be destroyed by the annealing caused by shock heating, survive to be examined and characterized. As a result, we know experimentally that the shock-compressed region is denser than the quasi-isentropically compressed region.¹³

Measuring the EOS

To generate planar shock waves for material studies, we can use high explosives or single- and two-stage light-gas guns to hurl high-velocity impactors against target specimens. Maximum velocities reached by the impactors are about 8, 5, and 2 km/s for two-stage guns, plane-wave high-explosive systems, and single-stage guns, respectively. Most recent results for fluids have been obtained with a two-stage gun¹⁴ that achieves about twice the shock pressure and temperature possible with plane-wave explosive drivers.

Shock-wave equation-of-state experiments, also called Hugoniot experiments (see the box on p. 25), are based on the Rankine-Hugoniot relations and shock impedance matching.¹⁵ The measured quantities are impactor velocity, shock velocity, and initial density. The Rankine-Hugoniot relations link the measured quantities to the thermodynamic

Fig. 2

Thermodynamic paths for hydrogen (after Ref. 13). The principal Hugoniot is the locus of pressure-temperature points that can be reached by single-shock experiments from standard conditions (100 kPa pressure in the liquid state). It crosses the isentropes of Jupiter and Saturn near 20 GPa and 4000 K. The solid black curve near the bottom of the figure is the solid-liquid melt line.

variables of pressure, specific volume, and specific internal energy.

These equation-of-state experiments are rather complex. The gas guns and high-explosive systems used to accelerate the impactors to high velocities are complicated apparatuses. It is also quite difficult to make experimental measurements of some of the materials of interest, especially the liquid gases. For example, for our measurements on liquid helium, we had to maintain a sample of liquid helium at 4 K in the target chamber, which was at a temperature of 300 K, for nearly 30 min. This challenge, similar to keeping an ice cube in a blast furnace, could be met only with careful cryogenic design of the experimental apparatus (Fig. 3).

Once we have determined pressure-volume points on the material's Hugoniot, it is then possible to measure

other properties, such as shock temperature, electrical conductivity, and Raman spectra, for a characterized state. Shock impedance matching also is performed in these experiments to determine the pressure-volume-energy state of the material with the measured property.

Experimental Configurations

Figures 4a and 4b illustrate the experimental set-ups for single- and double-shock Hugoniot experiments for liquid specimens. In the former, we measure shock velocity in the liquid; in the latter, in an anvil behind the liquid.

Figure 4c illustrates a shock temperature measurement in a transparent liquid. Thermal radiation emitted from the shock front goes through the unshocked part of the specimen and is detected in a multichannel time-resolved pyrometer.

Fig. 3

Design and operation of the two-stage gas gun. (a) Hot gases produced by gunpowder drive a piston down a pump tube 10 m long containing a light gas (usually hydrogen). (b) When the compressed gas reaches its peak pressure, a valve releases the gas, and an impactor is accelerated along an evacuated barrel 9 m long to strike a target containing the specimen liquid. The inner diameter of the pump tube is 90 mm and that of the barrel 28 mm. (c) Target assembly mounted in a specially designed cryogenic holder, which consists of an aluminum cylinder surrounded by two chambers containing coolant. The gaseous specimen is cooled to a liquid in the target cavity. Shock detectors mounted through the rear of the target cavity are placed to form two detector planes at two distances from the rear wall, enabling us to measure the shock transit time. The shock of the impactor is transmitted through the baseplate into the sample liquid. The shock velocity is determined by dividing the interplanar distance by the shock transit time.

The measured intensities are fitted to a graybody or blackbody spectrum to determine the radiating temperature of the shock front. Under the assumption that the radiating temperature of the shock front is also the temperature of material in thermal equilibrium behind the shock front, the data can be compared with theory. This assumption is probably valid for simple fluids with optically thin shock fronts, but it may have to be modified for complex systems, such as those in which chemical reactions take place in the shock front.

Fig. 4

Schematic diagrams of various kinds of impact-shock experiments. (a) Single-shock equation-of-state experiment. (b) Double-shock equation-of-state experiment. (c) Shock-temperature experimental arrangement for a transparent liquid. (d) Electrical-conductivity experimental configuration for a liquid.

Figure 4d illustrates a two-probe experiment for measuring the electrical conductivity of a shocked liquid. A constant-current power supply is connected across the shunt resistor, and an oscilloscope displays the time-resolved voltage across the electrodes.

Experimental configurations to measure the Raman spectra of shocked fluids are also in use.

Data Uncertainties

Among the sources of uncertainties in the reduced data are experimental uncertainties in the measured quantities as well as systematic uncertainties in the shock impedance matching method. Experimental uncertainties are typically 1% in shock velocity, about 0.3% in initial density, and 0.1% in impactor velocity. The accuracy of impedance matching depends on the accuracies of the Hugoniot curves for metal impactors, baseplates, and anvils, and the release isentrope for the baseplate. The Hugoniot curves for metals are measured in separate, accurate experiments and introduce small uncertainties into the data analysis. Because the release isentropes are calculated, not measured, they introduce the largest systematic uncertainty.

Typically, for liquid specimens, total uncertainties are 1 to 2% in pressure and 2 to 3% in volume for single-shock Hugoniot experiments, and 4 to 5% in pressure and 8 to 10% in volume for double-shock experiments. Uncertainties in the radiating temperatures of a shock front are about 200 K out of 3000 to 6000 K. Uncertainties in two-probe electrical conductivity measurements are probably 10 to 20%, which is acceptable because conductivity changes by several orders of magnitude for the strongly shocked fluids under investigation.

Experimental Results

Pressure, Density, and Temperature

Table 1 lists the maximum pressures and densities we have achieved in

equation-of-state experiments with liquids. The corresponding calculated and, in a few cases, measured maximum temperatures are in the range 5000 to 30 000 K. The assumption is generally made that the results are for material in thermal equilibrium on the 200-ns time scale of the experiment. Theoretical calculations for comparison with experiment are also performed for material in thermal equilibrium.

The assumption of thermal equilibrium is reasonable because relaxation times to thermal equilibrium are faster than experimental times for most of the phenomena that occur at such high temperatures and densities. Nonequilibrium molecular-dynamics simulations¹⁶ and solutions of the Navier-Stokes equations¹⁷ both show that shock widths are on the order of 1 nm for strong shock waves in a dense, simple fluid with the fluid in thermal equilibrium behind the front. However, the question of equilibrium does have to be continually addressed, especially if phenomena might be occurring on a time scale comparable to the experimental time (e.g., chemical reactions).

Shock-temperature measurements have been performed on a number of fluids, including water, argon, and nitrogen. The temperature of the shocked material is an important thermodynamic parameter because this

is the parameter that tells us how much of the internal energy is absorbed into internal degrees of freedom and how much appears as thermal energy.

We also have measured the electrical conductivity for shocked water and ammonia in an attempt to determine the mechanisms of electrical conduction. In so doing, we obtained information about the physical nature of the shocked fluid that cannot be obtained from measurements of state variables alone. For example, the conductivity of shocked water indicates that a significant fraction (probably 10 to 100%) of the water molecules is chemically ionized at a shock pressure of about 30 GPa.¹⁸

The ramifications of this result are that the "ices" inside the giant planets probably are chemically ionized and that ionic species probably exist in high-explosive reaction products. In fact, this raises the question of how the ionic nature of fluids at high density and temperature affects results that are calculated on the assumption that all the molecular species present are un-ionized.

Raman Spectra

Backward stimulated Raman-scattering experiments have been performed on shocked benzene.¹⁹ The shift in the benzene ring-stretching-mode vibrational frequency was

Table 1 Summary of shock-compression experiments for fluids: T_0 is initial temperature, ρ_0 is initial density, $\rho_{\max}$ is maximum density, and $P_{\max}$ is maximum shock pressure (100 GPa = 1 Mbar).

Liquid	T_0 , K	ρ_0 , g/cm ³	$\rho_{\max}$, g/cm ³	$P_{\max}$, GPa
Deuterium	20	0.17	0.96	76
Hydrogen	20	0.07	0.23	10
Nitrogen	77	0.81	2.8	64
Oxygen	77	1.2	3.3	86
Carbon monoxide	77	0.81	3.0	69
Methane	111	0.42	1.6	92
Benzene	295	0.89	2.4	70
Polybutene	295	0.89	2.7	210
Argon	87	1.4	3.8	91
Xenon	165	3.0	9.6	130
Ammonia	230	0.69	1.8	64
Water	295	1.0	3.5	220

measured up to 1.2 GPa using a pulsed laser timed to probe a few millimetres behind the shock front. The observation of this mode provides confirming evidence that benzene molecules exist behind the shock front at low shock pressures, as opposed to higher pressures where decomposition occurs.

Recently, we also have measured the pulsed, spontaneous Raman spectrum of water shocked to 7 GPa. Both of these measurements offer the exciting possibility of experimentally investigating, on a microscopic scale, the molecular and ionic processes in shocked fluids.

Verifying Our Theoretical Models

The dominant effect in the EOS at high densities and temperatures is intermolecular repulsion. The rare (noble) gases are the simplest materials to study in this respect because, when electronic thermal excitation is negligible (i.e., "cold"), their physical properties are determined by the repulsive potential.

In liquid argon, for example, the upper limit of the "cold" range is a single-shock pressure of 36 GPa, a compression to half the initial volume, and a calculated temperature of about 12 000 K. The pair potential derived from argon shock-wave data is in excellent agreement with the pair potentials derived from molecular-beam scattering results, indicating that two-body interactions dominate.

Molecular Fluids

It has been shown that shock-compression data for nonpolar molecules can be calculated by using an intermolecular potential scaled from argon and by taking into account molecular vibrational and rotational degrees of freedom. This procedure is approximately and systematically valid to a compression of about 2.5 times liquid density for xenon (another rare gas) and for nitrogen, oxygen, carbon dioxide, methane, and carbon monoxide (postdetonation products of high-explosive materials).

Figure 5 illustrates the excellent agreement between theory and experiment for liquid nitrogen at pressures below 40 GPa. The divergence between theory and experiment above 40 GPa probably is due to dissociation of the nitrogen molecules and electronic excitation at the high pressures and temperatures. A fundamental conclusion of this systematic study is that, since our measurements are in good agreement with potentials scaled from the pair potential of argon, in which two-body interactions are dominant, effective two-body interactions must also dominate in the molecular fluids we have studied.

Hydrogen and Deuterium

Hydrogen in its molecular form is an important postdetonation product of many high explosives; in its liquid and metallic forms, hydrogen is believed to be one of the major constituents of the giant planets. We have shock-compressed hydrogen and its isotope deuterium up to 90 GPa. An effective pair potential has been derived for molecular hydrogen by achieving agreement between theory and an extensive body of shock-wave and static-compression data.

Because of the high shock temperatures, the theory treats both hydrogen and deuterium molecules as free rotors, making it possible to use a spherical approximation for the effective pair potential. We take the vibrational frequency as a constant because the measured change in the

Fig. 5

Shock pressure vs relative volume for liquid nitrogen. Data from previous work⁶ (open circles) follow closely the solid theoretical curve up to about 40 GPa; our data at higher pressures (solid circles) show a divergence that is probably due, at least in part, to dissociation of the nitrogen molecules (not included in the theory).

vibrational frequency up to 60 GPa in solid hydrogen at 300 K is insufficient to influence the calculated thermodynamic parameters.²⁰

The calculated shock temperatures are 4800 K at 20 GPa on the principal

Hugoniot of liquid deuterium and 6500 or 7100 K at a double-shock pressure of 75 GPa, depending on whether or not dissociation is included in the theory. Calculations show that dissociation is negligible in the single-shock regime

Generating the Hugoniot Curve

A shock wave suddenly changes the pressure in a medium and travels with a supersonic velocity u_s that is a function of the pressure P . When the shock wave has negligible thickness, it can be characterized by discontinuous changes in pressure, volume, and energy (top figure).

If we do a series of shock-wave experiments, each time compressing matter from a fixed initial pressure, volume, and energy to a different pressure, each shock will produce a different change in volume. A plot of pressure-volume pairs (P and V) of the final states is called a Hugoniot curve. As indicated by the arrow in the middle figure, the change when a material is shocked to a given pressure is discontinuous. The Hugoniot curve represents the locus of all the points, each of which can be reached with a single shock from the given starting conditions.

Using the Rankine-Hugoniot relations, we can calculate a given point on the Hugoniot curve if we have measured the shock velocity and the impactor velocity in a target-impactor experiment. The Rankine-Hugoniot relations are:

$$P - P_0 = \rho_0(u_s - u_0)(u_p - u_0), \quad (1)$$

$$V = V_0[1 - (u_p - u_0)/(u_s - u_0)], \quad (2)$$

and

$$E - E_0 = 1/2(P + P_0)(V_0 - V), \quad (3)$$

where

- P_0 = initial pressure,
- ρ_0 = initial density,
- E_0 = specific initial internal energy,
- u_0 = velocity of the unshocked liquid,
- $V_0 = 1/\rho_0$ = initial specific volume,
- P = the first shock pressure,
- V = specific volume,
- E = specific internal energy,
- u_s = shock wave velocity,
- u_p = mass velocity behind the shock front.

In our experiments, the initial velocity u_0 of the target liquid is zero, and we measure P_0 and the initial temperature T_0 . The values of ρ_0 , V_0 , and E_0 are obtained from the known equation of state of the

liquid near its saturation curve at 100 kPa. The value of u_s is measured. The value of u_p is inferred by the method of shock impedance matching. This method relies on the continuity of pressure and mass velocity across an interface. (If the target and impactor are made of the same material, then the material velocity u_i at the interface is exactly half the impactor's velocity.) We then calculate P , V , and E from Eqs. (1), (2), and (3), respectively. The result defines one point on the Hugoniot curve of the liquid.

To explore conditions off the Hugoniot curve, we can use some form of multiple shock. In a double-shock process, the final state of the first shock is the initial state of the second shock (points 1 and 2 in the bottom figure). The double-shock process attains higher pressures and compressions than are possible with a single shock.

and produces only a 1% decrease in volume in the double-shock regime. This effect is small in comparison with the 8% uncertainty in the data on experimentally derived volume.

The theory also is in excellent agreement with the 5-K isotherm for solid hydrogen to 37 GPa.²¹ Figure 6 compares the present and previous shock data^{22,23} and theory. The theoretical two-body potential for hydrogen is significantly stiffer than the effective one. The difference represents a real, attractive, many-body contribution to the effective potential.

A major purpose of our deuterium shock-wave experiments was to improve our knowledge of the equation of state of the insulating molecular phase in order to refine estimates of the insulator-to-metal transition in crystalline hydrogen at 0 K. Our estimate remains in the range of 310 to 360 GPa.

Helium

Helium, one of the elements believed to exist in quantity in the giant planets, is extremely difficult to examine experimentally, especially in its liquid form. We have performed three Hugoniot experiments on liquid helium at an initial temperature of

4.3 K, a pressure of 100 kPa, and a molar volume of 32 cm³/mol. We had to improve the design of our cryogenic target substantially to allow for liquid helium's very low heat of vaporization. From these experiments, we obtained the first-known shock-wave data for liquid helium. We achieved shock pressures from 1.2 to 16 GPa and calculated temperatures of 800 to 12 000 K and obtained threefold compressions.

These preliminary data are in good agreement with our theoretical results in which we use an effective pair potential obtained from a fit to the 0-K isotherm from band theory calculations at high pressures and densities. Thus, preliminary results indicate that many-body effects (included in band theory) occur in helium as well as hydrogen. We find we can neglect electronic excitation because the lowest electronic excitation energy for helium is about 25 eV, large in comparison with the shock temperature of about 1 eV.

Xenon and Argon

Xenon and argon, being rare or noble gases, are simpler to calculate than other, more reactive, gases; by comparing experimental data on these gases to calculated results, we can assess the validity of our models. Electronic excitation in shocked fluids is clearly demonstrated in xenon and argon. We measured the Hugoniot of liquid xenon up to a pressure of 130 GPa, a molar volume of 13.7 cm³/mol, and a calculated temperature of 29 000 K. The data are in excellent agreement with theory that includes an effective pair potential and electronic excitation across a density-dependent energy gap.

The sensitivity of these data to electronic excitation arises because strongly shocked xenon is heated to temperatures comparable to its excitation energy. Enough electrons are excited to reduce the thermal pressure by up to a factor of three from what it would be without electronic excitation. The present and previous data²⁴ are plotted in Fig. 7 as shock pressure vs molar volume. Curves A and B are two

Fig. 6

Shock pressure vs molar volume for liquid deuterium. Data from various sources are compared with theoretical equation-of-state curves described in the text.

theoretical curves taking into account electronic excitation; curve C was calculated neglecting electronic excitation.

These data are also consistent with our theory, which indicates that xenon undergoes an insulator-to-metal transition at $9 \text{ cm}^3/\text{mol}$ and 0 K at 130 GPa or greater. A similar result was obtained for argon. A fundamental conclusion of this study is that high shock temperature is a very useful probe of the electronic structure of these noble gases at high densities and pressures.

Water and Ammonia

Frozen ammonia and water are thought to form the inner layers of Uranus and Neptune. We know that chemical ionization takes place in shocked fluids like water and ammonia. A sizable body of shock-wave data and theoretical work exists for water, including single- and double-shock equations of state, shock temperatures, and electrical conductivities.¹⁵ A theoretical treatment of water is complicated because the water molecule is polar (i.e., has an electrical dipole moment), making the intermolecular potential nonspherical. Hydrogen-bond interactions also have a strong influence on the structure of water, especially at low pressures.

Above a few gigapascals of shock pressure, our model places water definitely in the fluid state because the shock temperature is higher than the melting temperature of ice VII. At a shock temperature of about 1000 K, all the hydrogen bonds are broken because the bond energy is about 0.1 eV. For temperatures between 1300 and 3000 K, the intermolecular pair potential for water is effectively spherical, and thermodynamic properties can be derived from a central pair potential, from the vibrational frequencies of the isolated water molecule, and from a temperature-dependent rotational contribution to the free energy. Above 3000 K, significant molecular ionization occurs:

The experimental evidence for ions indicates a high electrical conductivity ($20 \Omega^{-1} \cdot \text{cm}^{-1}$) above 30 GPa and measured shock temperatures about 17% below those calculated by treating water as a molecule and neglecting ionization.

Benzene

Many organic high explosives have a benzene-like basic structure. Thus, to understand the behavior of these explosives, we start by studying the simpler benzene. Chemical decomposition is known to occur in hydrocarbons like benzene at high shock pressures and temperatures (Fig. 8).²⁵ The dashed line in Fig. 8, the

Fig. 7

Shock pressure vs. molar volume for liquid xenon. The calculations of theoretical curves A and B take into account electronic excitation. The calculation of curve C does not.

Fig. 8

Empirical curve relating shock velocity and mass velocity in benzene. The incipient plateau region indicates the onset of decomposition and the formation of dense carbon phases.

extrapolation of the linear fit to the lower velocity data of Ref. 25, shows excellent agreement between the two sets of data. The linear fit at lowest velocities corresponds to a region below 13 GPa where optical experiments²⁶ show that benzene retains its C_6H_6 molecular structure.

A theory based on corresponding-states scaling for the C_6H_6 intermolecular potential of benzene is in good agreement with this nonreactive portion of the Hugoniot. The plateau region is the onset of decomposition and volume decrease caused by the formation of dense carbon phases.²⁷ The upper linear region can be described by a model in which benzene decomposes into a two-phase mixture of carbon in a dense diamond-like phase and hydrogen in the condensed molecular phase.

Calculation of the measured shock temperatures of benzene requires a heat capacity substantially larger than can be accounted for by the two-phase model or any other. It appears, rather, that the effective radiating temperature of the shock front is not the equilibrium temperature of the shocked benzene. The difference probably is caused by chemical reactions in the shock front. Chemical equilibrium calculations that include up to twelve chemical species suggest, in addition to the two phases, the presence of small concentrations of several high-molecular-weight species. Hence, the two-phase model is an approximate description for shocked hydrocarbons, but it neglects other chemical species that might be present without greatly affecting the calculation of the Hugoniot curve.

Summary

We have been investigating the properties of dense molecular fluids at high pressures and temperatures to improve our understanding of the behavior of high explosives, the structure of the giant planets, and the applications and effects of hydrodynamic shocks. With our two-stage gas gun, we can accelerate projectiles to generate hypervelocity

impacts on cryogenic targets and achieve shock-wave compressions approaching pressures of 100 GPa and temperatures of 30 000 K. Our techniques enable us to obtain valuable experimental data with which we can test the validity and accuracy of our theoretical equation-of-state models.

Key Words: dense molecular fluid; equation of state; giant planet; high explosive; hydrodynamic shock; hypervelocity impact.

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Computer-Controlled Triple-Quadrupole Mass Spectrometry

We have developed a totally computerized triple-quadrupole mass spectrometer system of unrivaled speed, selectivity, and adaptability for analyzing and identifying trace organic constituents in complex chemical mixtures.

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Accurate and comprehensive information on the identity and molecular structure of chemical compounds is extremely important in environmental, biomedical, and industrial research. The growing awareness of the need for this kind of data has prompted a large demand for rapid, economical, unambiguous identification and quantification of a wide variety of very complex sample types. These challenges to modern measurement science have been addressed by a number of analytical techniques, one of the most powerful of which is triple-quadrupole mass spectrometry (TQMS).¹⁻⁶

Basically, a mass spectrometer separates ions according to their different responses to electric fields, magnetic fields, or both. (If each ion had the same charge and velocity, separation would depend only on mass.) Mass spectrometry involves ionizing a sample under high vacuum, passing the ions through electric and magnetic fields to separate them, and finally detecting them.

A variety of means is used to ionize the sample and then to analyze and detect the ions. In the most common method of ionization, electron impact, the sample is vaporized in a vacuum and bombarded with a beam of electrons. The usual means of detection is with a channel electron multiplier; each ion that enters the detector causes the emission of at least one secondary electron. The secondary electron is accelerated by the electrostatic field (several thousand volts) within the channel until it hits the interior surface of the channel. If it has accumulated enough energy from the field, the secondary electron's impact causes other electrons to be released. This process occurs ten to twenty times a second, resulting in a multiplying cascade of emitted electrons.

In the past, the traditional method of analyzing the ions was with a powerful magnetic field (Fig. 1). Quadrupole analyzers have become popular recently because they eliminate electromagnets (and problems connected with their

inherent hysteresis), they are smaller and cheaper than magnetic mass spectrometers, and they are faster and much easier to automate.

A single quadrupole analyzer is useful for many purposes, but it is unable to distinguish between ions of different composition that share the same mass/charge ratio (see the box on p. 37). The triple-quadrupole mass spectrometer (TQMS) can overcome this limitation by acting like two mass spectrometers in tandem. It preanalyzes ions in the first segment, breaks apart those the first segment selected by collisionally activated dissociation in the second segment, and analyzes the fragments in the final segment. Since it is almost impossible for ions of different composition to produce identical sets of fragments, this system enables us to identify structurally the originally selected ions and provides clues to their origin.

The first and third quadrupoles analyze the ions by separating them according to mass. The second quadrupole functions as a combination electrical collimator and dissociation chamber. In this second quadrupole region, the ions are centrally confined while they are exposed to collisions with neutral gas molecules (argon or nitrogen) that break the ions apart into characteristic sets of "daughter" fragments.

A principal advantage of TQMS is the operational flexibility inherent in its design. Each of the three quadrupoles may be operated in various modes, providing at least five different combinations (see Fig. 2). For example, the TQMS may be set to analyze the primary ions formed by electron impact (a normal mass spectrum), to analyze the fragments of a specific primary ion (daughter mode), to find all the primary ions that can produce a given fragment (parent mode), to find all the parent ions that have lost a particular amount of mass (specific neutral loss), or to monitor the production of a single chemical species in an ongoing reaction (single reaction monitoring).

The TQMS is more specific, selective, and sensitive for components of a

complex mixture than a conventional mass spectrometer. The TQMS also improves our ability to study solids or insoluble materials such as oil shale and high explosives because it combines the separation and identification functions in a single instrument.

The analytical capabilities of such an instrument seemed ideal for our work, but the available commercial instruments were not. These instruments are designed to analyze large numbers of similar samples for a small number of known constituents. Furthermore, their computer control covered only a few of the operating parameters, which would have forced us to spend substantial time in manual tuning. Additionally, the data acquisition and manipulation were controlled by a single computer, making the results inaccessible for on-line, real-time changes of instrument parameters.

For our operation, we required the capabilities of TQMS in support of widely dissimilar activities, such as fossil fuel research, polymer synthesis, and high-explosives research. Hence, our instrument would have to be both rapid and versatile in handling a large variety of sample types rather than a large number of similar samples. In addition, the data generated would have to be transportable to our large main-frame computer systems for statistical analysis and modeling studies. Further, we wanted the instrument design to allow for real-time, self-adaptive modification of run

Fig. 1

Schematic representation of a general mass-spectrometer system. The sample is vaporized and ionized in the source, the ions are accelerated to high energy and separated (analyzed) according to their various masses, and ions of a particular mass are passed to a detector that registers their intensity.

parameters based upon data display and interpretation of analytical results.

We had investigated previously the concept of totally automated, self-adaptive instrumentation for process control and enzyme characterization.⁷

Since our final goals in the TQMS development were self-adaptive experimentation and artificial-intelligence-guided interpretation (i.e., semiautomated research), it seemed logical and desirable to extend these

Mode	Quad 1	Quad 2	Quad 3	Results
Normal	Separated by mass	All masses passed, no gas	All masses passed	Normal mass spectrum
Daughter	Fixed on specific mass	All masses passed, collision gas	Separated by mass	Spectrum of all daughter ions from the selected parent ion
Parent	Separated by mass	All masses passed collision gas	Fixed on specific mass	Spectrum of parent ions that fragment to give specific daughter ion
Neutral loss	Separated by mass	All masses passed, collision gas	Separated by mass	Fixed mass difference between two scanning quads gives specific neutral mass loss
Reaction monitoring	Fixed on specific mass	All masses passed, collision gas	Fixed on specific mass	Single or multiple reaction monitoring

Fig. 2

The triple-quadrupole mass spectrometer combines three quadrupoles to obtain a higher order of sensitivity, selectivity, and flexibility. The first quadrupole serves primarily to separate out the unwanted ions and secondarily to collimate and focus the ion beam. The second quadrupole serves as an ion collimator, holding ions selected in the first quadrupole on axis while exposing them to disruptive collisions

with neutral gas molecules (argon or nitrogen). Anywhere from less than 1% to 90% of the ions can be broken up. The third quadrupole analyzes the fragments produced in these collisions, removing the unwanted daughter ions and yielding a distinctive "fingerprint" of the selected ion. These instrument elements may be selected in a variety of ways for various kinds of analyses.

concepts to the multitude of instrument operational parameters and multidimensional data output from the TQMS system.

In pursuing this development, we found it far less expensive to provide two interacting LSI-11 computers than to do the entire job with one. One computer handles the task of instrument control and data acquisition; the other simultaneously does data manipulation, filing, sorting, and display. This division of labor makes it much easier to develop and modify the necessary codes than it would be with a system using a single computer to perform all functions.

Mechanical and Electronics Design

To develop a totally computerized TQMS system, we solved a number of technical problems, including⁶:

- Interfacing a source, three analyzers, and a detection system with our LSI-11/23 computers.
- Designing the computerized ion-focusing lens assemblies.
- Designing operational circuits for controlling the field axis voltage on all three quadrupoles and linking the second quadrupole to the appropriate first or third quadrupole when scanning.
- Developing interactive instrument operational algorithms.
- Developing a file-handling structure for managing the scientific data.
- Implementing and extending existing mass spectral computer programs to handle the additional operational characteristics of a TQMS system.

Figure 3 shows, schematically, the basic mechanical and electronic design. The source is a totally digital design (all

Fig. 3

Functional diagram illustrating the interconnections among the various components in our completely computerized TQMS system. Brown indicates mechanical components, beige indicates electronic power supplies, gray indicates the instrument-control computer and its peripheral equipment, gray-brown indicates the data-processing computer and its peripherals.

voltages are set digitally); all source parameters (electron energy, repellers, focus, draw-out, and temperature) are under computer control. This enables us to obtain useful analytical data, for example, by relating ionization voltage and subsequent ion appearance (Fig. 4), a form of experiment that is impossible on commercial systems with analog sources.

We were able to purchase fully computerized rf and dc controllers for the first and third quadrupoles. The corresponding unit for the second quadrupole is much simpler because it need only supply rf voltage.

We designed a sweep circuit to link the second-segment power supply with that of either the first or third quadrupole. Computer control of the field axis voltage enables us to optimize sensitivity, selectivity, and resolution for a given sample type (Fig. 5).

A series of ion lenses precollimates the ion beam as it enters each quadrupole. The computer interactively tunes these lenses to maximize ion intensity and thereby increases the number of ions reaching the detector. The detector can count both positive and negative ions, and the instrument can be rapidly switched during an analysis to form and pass one or the other. Either an electrometer or pulse

counting can be used with the detector. Such automated optimization of the instrument operational parameters is impossible on any currently available commercial system.

Although mass spectrometers are inherently low-pressure analytical instruments, our TQMS system requires a certain amount of neutral gas in the second quadrupole to break up the parent ions. The system, therefore, is differentially pumped to maintain the different pressure levels required in its various parts. The source, quadrupole analyzers, and detector each have a turbo-molecular pump, of 510-, 270-, and 110-l/s capacity, respectively.

Computer Design

Computer design in mass spectrometry has evolved in a series of phases. The initial phase was the "programmed switch/recorder," in which the computer replaced manually operated switches to open and close valves, turn power supplies on and off, change voltage or current in discrete steps, and record peak intensities. Such operations are very repetitive, operator-defined, and programmed in at the start.

The second phase was the "feedback switch/recorder," wherein the computer made preprogrammed choices based on input from sensors of temperature, pressure, etc. This allowed for automatic adjustment of inlet pressure, recording of peak intensities based on magnetic field strength or accelerating voltage, and accurate mass determination.

Our instrument is at phase three, the "controller" phase, in which the computer reads all important operational parameters and sets all the instrument controls. In this system, any voltage, pressure, current, temperature, etc., can be read and varied to an accuracy of up to 1 part in 64 000 using digital-to-analog (D/A) and analog-to-digital (A/D) converters. Thus, we are free to use the instrument in ways that would be impossible or extremely slow and tedious under manual operation.

We are currently working on phase four, which is the "self-adaptive

Fig. 4

Appearance-potential curves indicating how the electron-bombardment energy in the ion source influences the intensity of mass fragment 52 from parent ion 78 (benzene). The appearance of mass 52 in the primary spectrum indicates that benzene is being dissociated (as well as ionized) by electron impact in the source. The potential at which this ion appears is a clue to the strength of the bond being broken.

controller" phase. In this phase, the computer "learns" to adjust the operational parameters of an experiment according to rules developed through the interaction of the scientist (expert) and the computer. This development is part of the concept referred to as "expert systems" in the field of artificial intelligence.

As may be anticipated, the initial design of the computer system is crucial in determining how sophisticated the instrument can become. A computerized instrument system originally designed as a feedback switch/recorder system cannot readily be upgraded to function as a controller, much less a self-adaptive or expert system. Since the anticipated benefits of self-adaptive control are so attractive, we have directed our design of both hardware and software toward the phase-four stage.

Hardware

Our TQMS system uses two LSI-11/23 minicomputers, one running under the RT-11 V4 operating system for instrument control and data acquisition and the other under the RSX-11 M operating system for data processing, manipulation, and storage. Each computer can operate independently in parallel and can also transfer data to the other through a direct-memory-access (DMA) interprocessor link.

The instrument-control computer consists of a DEC-11/23 processor with and 32 000-word memory, a hard disk storage device, an assortment of parallel line cards, D/A converters, 10- μ s A/D converters, programmable clocks, a floppy disk, a DMA link, and terminals. The data-processing computer contains (in addition to another DEC-11/23 processor) a 128 000-word memory, a 300-Mbyte hard disk, a tape unit, a DMA link, and an assortment of printers and terminals.

Software

We have designed and written the software for our TQMS specifically to take advantage of a totally computer-

controlled system. At present, 37 major machine parameters are under computer control and available to software management.

The two major goals of our software have been flexibility and speed. Although all instrumental parameters can be set by the computer, we provided flexibility by allowing simultaneous manual control over many of them. For example, the electron multiplier voltage or any number of other instrument parameters may be manually changed (and computer recorded) while the field axis potential (or some other parameter) is being scanned by the computer.

Speed in data acquisition is very important for tracking thermally induced reactions or decompositions. To save time, we use peak jumping (i.e., skipping automatically from the top of one peak to the top of the next one of interest) instead of continuously scanning the entire mass range (including all the valleys and unessential peaks). The rf/dc settles to the exact mass desired within 100 μ s to provide very rapid scanning.

Another factor in reducing the data-acquisition time is the data-conversion rate. We are currently using a 100-kHz 12-bit A/D converter (10 μ s per reading). This improves our signal-to-

Fig. 5

Curves showing the influence of third-quadrupole bias on the intensity of the ion beam transmitted from the second quadrupole. The bias of the second quadrupole is varied from -50 to $+20$ V. In one case (brown), the third-quadrupole bias is fixed at -25 V; in the other three cases, it is offset a fixed amount from the second-quadrupole bias. Computer control of the voltage enables us to optimize the instrument's sensitivity, selectivity, and resolution for a given sample type.

noise ratio because we average 100 or more readings per peak. The inherent speed of the A/D converter, coupled with its direct-memory-access (DMA) capability, enables us to take 100 readings scaled to the right gain in 1.0 ms, giving a total time of 2.9 ms per peak.

Gain selection is needed to improve dynamic range. For this function, we use built-in 10× and 100× amplifiers on the electrometer output, fed into separate channels of the multiplexed A/D converter. The software examines the outputs of these amplifiers and selects the one whose signal is in the right range.

On some commercial TQMS systems, the data are acquired by adding many scans together but without dividing by the number of scans. Thus, even if a peak shows only once per 100 scans (which means that it

probably is an artifact instead of a real measurement), it is still counted. With our system, however, we spend all our data-acquisition time on one peak or another (via peak jumping) and spend the same amount of time on each peak. Since our data are automatically averaged, all counts represent the peak in a statistically significant manner.

The software for this instrument carries out five major functions: tuning, recording, and modifying of all instrument parameters, mass-scale calibration, and intensity-data acquisition (Fig. 6). The instrument-tuning subroutines (SEGSCN and MTUNE) display an oscilloscope trace of a chemical standard while source, lens, and field axis parameters are

Fig. 6

Functional diagram indicating the relationships among the various subroutines (some of which are described in the text) used in processing the data from the TQMS.

Basic Operation of the TQMS Analyser

A quadrupole analyzer consists of a strong-focusing field established by applying radio-frequency (rf) potentials to four carefully aligned metal electrodes, thereby concentrating all of the ions moving through it (whatever their charge, mass, or initial velocity) into a narrow beam. The quadrupole fields focus ions axially by alternately pushing them toward the axis and pulling them away. Because the push is more effective than the pull, the net effect is to collimate the ions into a narrow beam.

This focusing system works as a result of the unusual configuration of the quadrupole field. The two sets of electrodes alternate rapidly in polarity as the ions pass between them. At any instant, the ions are being repelled by one pair of electrodes and attracted by the other. Before the ions can move far, however, the polarities reverse. The net effect is a strong tendency for the ions to cling to the axis, regardless of their mass, charge, or (within limits) their initial velocity (see figure below, a).

If we superimpose a dc potential along the quadrupole electrodes (rods), the system becomes selective (see figure below, b). The rf field, instead of oscillating about zero, oscillates about a fixed value of

the electric field. The ions follow complex trajectories that are a function of their mass/charge value, the radio frequency, the magnitudes of the rf and the dc voltages, and the geometry of the rods. By controlling the ratio of the dc to rf voltages, the field can be established to pass ions of only one mass/charge value (the mass/charge ratio is proportional to the magnitude of the rf voltage divided by the radio frequency). Ions with a mass/charge ratio smaller or larger than the specified value will strike the rods. By simultaneously adjusting the dc and rf amplitudes, ions of various mass/charge ratios can be allowed to pass through this "mass filter" and on to the detector in a single quadrupole analyzer or to the next stage in the TQMS.

In the second stage of the TQMS, only the rf field is imposed on the rods. Thus, no separation occurs, just collimation of the ions that are being fragmented by low-energy collisions with neutral argon or nitrogen gas. These newly formed daughter ions are collimated and passed to the third quadrupole stage, where both rf and dc potentials are applied to separate the ions on the basis of their mass/charge ratios. Those ions finally selected then are passed on to the detector.

varied. When optimum tuning is achieved, the values of the parameters are stored in a disk file for subsequent use. Many different tuning files can be created this way and then used sequentially while an experiment is continuously running.

The technique of peak jumping requires a very accurately calibrated mass scale. To do this, the MSCAL program jumps to a known peak of a calibration gas, determines its center by stepping to 75% of maximum intensity on either side, and records the D/A setting for the center. Linear equations are calculated from the peaks used in each range, i.e., from mass 31 to 119, mass 119 to 219, mass 219 to 364, etc. (these peaks are the major peaks of our trifluorobutylamine standard). Each quadrupole is calibrated independently to an accuracy of at least one sixteenth of an atomic mass unit (amu), and the equations are stored in disk files.

With a fully computerized instrument, it is desirable and easy to record the values of all instrument parameters before and during a run as they change, for later reference. This forms a computerized notebook that is important for subsequent data analysis.

Since acquiring intensity data is the key function of any computer-controlled mass spectrometer, we wrote the intensity recording portion of our data-acquisition program in assembly language to maximize speed. These assembly language routines are called by programs written in Fortran for instrument control and data acquisition.

Data-Management System

We have developed a data-management system to handle this flood of multidimensional data. Three files are recorded with each experiment, the header file, the pointer file, and the data file. The header file is essentially a computer notebook, storing all starting parameters as well as comments entered before, during, and after the experiment. The pointer file stores five separate pieces of information for every scan:

- A pointer to the particular scan in the data file.

- The number of data pairs.
- The time the data were taken.
- The sum of the intensities.
- A code for the scan.

The data file contains the values for any set of selected parameters and the data pairs for each scan.

These files are written "on the fly" after each scan (using the DMA interprocessor link) so data can be accessed in real time. The extracting routine takes advantage of the speed and flexibility of the data-management system used to file data. It can rapidly search data from a particular experiment and create a new file of the pertinent data to be plotted. We can extract information from any plane of data, allowing almost any parameter to be plotted against any other while holding one or more other parameters constant. Using previously developed programs, we have developed a very powerful routine, PLOTMS, with which we can display data in real time.

Applications of the TQMS

Trace Sulfur Compounds

We first applied our TQMS to the analysis of trace sulfur compounds in the pyrolysis of oil shale. Depending upon the shale source and processing conditions, sulfur compounds are released primarily as hydrogen sulfide (H_2S). There are, however, poorly characterized trace sulfur compounds, such as carbonyl sulfide and mercaptans, present in amounts ranging from 0.1% down to a few parts per million, that must also be removed to reduce the sulfur gas content to environmentally acceptable levels. It is necessary to determine the concentrations of these and other trace compounds in order to select and optimize gas clean-up procedures.

The case of thiophene, one of these trace sulfur compounds, clearly illustrates the power of the TQMS in separating a trace component from an interfering species. Thiophene has a molecular weight of 84 and so does cyclohexane, a hydrocarbon present in large amounts. An ordinary mass spectrometer cannot separate these two

compounds in a complex mixture because their masses are identical.

Figure 7a shows the daughter fragments, produced by collisions in argon gas, from an analysis of a pure thiophene standard. In addition to the parent at mass 84, this scan shows daughter products at masses of 69, 58, 45, and 39. Figure 7b shows a similar analysis of a pure hydrocarbon standard, cyclohexane, with a great many daughter ions (at 78, 69, 68, 67, 56, 55, 43, 42, 41, and 39) but none at 58 and 45. Because these two ions appear in the one spectrum and not in the other, they are definitive for thiophene.

We analyzed the complex gas mix from oil-shale pyrolysis in the same way as the standards, selecting for mass 84 in the first quadrupole and displaying the daughters (Fig. 7c). In addition to the major cyclohexane peaks, we also see small peaks at 58 and 45 that are specific for thiophene.

We made this analysis quantitative by comparing the digital data from the standards and the sample. In this way, we determined that the thiophene and cyclohexane concentrations in the sample were 63 and 1900 ppm, respectively. Our detection limit for thiophene in this complex gas mix is 0.3 ppm. We also have determined the detection limits for eight other sulfur compounds suspected to occur in oil-shale pyrolysis gas in trace amounts.

The High Explosive HMX

In another set of experiments, we investigated the thermal decomposition kinetics of the high explosive HMX (1,3,5,7-tetranitro-1,2,5,7-tetrazacyclooctane).^{8,9} During thermal decomposition, HMX breaks up into a number of major ions, and there is a large variation in their relative abundances that depends on the thermal environment of the molecule before ionization in the source.¹⁰ In fact, it is very difficult to distinguish between ions formed by fragmentation in the electron-impact ionization source of the mass spectrometer and those ions formed by the thermal decomposition of HMX. Additionally, it

is important to resolve the true identity of fragment ions to identify the decomposition pathways that are important in calculating the molecular energetics of the high explosive.¹¹⁻¹³

We introduced a 1-mg solid sample of HMX into the TQMS via the direct inlet probe and raised the temperature from 100 to 300°C (at 14°C/min). Again, we used argon gas to cause collisionally activated dissociation in the second quadrupole and took spectra of the daughter fragments from several different parent ions. One parent (mass 176) showed interesting variations with probe temperature and illustrated the possibilities of studying thermal fragmentation kinetics with the TQMS.

Fig. 7

Spectra indicating the method of analyzing for thiophene in the presence of large concentrations of cyclohexane, an impossible task with conventional mass spectrometers because both substances have the same molecular mass (84). (a) Pure thiophene daughter spectrum, showing peaks at 39, 45, 58, and 69. (b) Pure cyclohexane daughter spectrum, showing peaks at 39, 41, 42, 43, 54, 55, 56, 67, 68, and 69, but nothing at 45 or 58. (c) Oil-shale gas-mixture daughter spectrum. The small peaks at 45 and 58 indicate the presence of thiophene (63 ppm), determined despite the much larger concentration (1900 ppm) of cyclohexane.

In Fig. 8, we can see how the intensity of mass-176 ions varies as a function of probe temperature. The appearance of mass-176 peaks at two distinct temperatures (around 150°C and near 300°C) indicates that this ion either is formed by two thermal processes or has two separate molecular structures.

To distinguish between these two possibilities, we measured the intensities of the key daughter fragments (masses 42, 44, 58, and 75) throughout the entire temperature rise. The traces for daughter ions at masses 44 and 58 (Fig. 8) show that these two ions are produced from the 176 parent

only in the high-temperature regime. In addition, the differences between the 176 line and its daughters at masses 75 and 42 (Fig. 8) further substantiate the theory that the structure of the mass-176 ion is different at different temperatures. This also appears to support the proposition that we are observing true thermal decomposition of the HMX instead of source-induced electron-impact decomposition.⁹

This experiment shows how TQMS can aid in the calculations involving the decomposition kinetics of high explosives. By knowing which fragments are associated with each parent at different temperatures,

Fig. 8

Intensities of various fragment ions from the thermal decomposition of the explosive HMX as a function of decomposition temperature. The double hump in the total ion intensity demands explanation, suggesting that there may be two different decomposition mechanisms. TQMS analysis shows that daughter ions of mass 44 and 58 (gray) appear only at the high temperature, whereas ions of mass 42 and 75 (brown) are more prominent at the low temperature. This information affords clues to the decomposition mechanisms.

researchers can conduct more accurate fundamental studies of the molecular energetics of high explosives.

A major advantage of our TQMS system is its speed. In the experiment from which we generated Fig. 5, we entered 23 different sets of field axis conditions and three sets of parents for each condition, and scanned all daughters for all field axis conditions for each parent. A thousand readings were averaged for each mass unit. In all, we recorded 26 082 separate masses for each run, taking only 282 s (4.7 min).

Furthermore, this speed is available for any kind of data, not just specific types. We can do normal analysis as well as kinetics studies or component analysis of a rapidly changing gas stream. Allowing 1.9 ms for electrometer settling time and ranging, we can scan ten parents and all daughters from 20 to 100 amu and take 1000 readings for each amu in just 9.52 s. By peak jumping, we can look at five selected daughters for each of ten parents and average 1000 readings for each parent and daughter in only 595 ms. The data extraction requires only 40 s for a finished plot, including information input, terminal plotting, and copying time.

Conclusion

Our completely computer-controlled triple-quadrupole mass spectrometer has unique capabilities for chemical analysis. The use of two interacting computers, one to control the instrument and acquire the data and the other to manipulate and display the data, provide the flexibility to do many different types of experiments as well as the power to do them rapidly and efficiently.

The implications of this speed for analytical chemistry are tremendous. The ability to vary, acquire, extract, and plot any of the experimental parameters while averaging 1000 to 10 000 readings per data point makes it possible to acquire enough statistically valid data

for quantitative, triple-quadrupole mass spectrometry analysis.

Furthermore, the rapidly diminishing cost of powerful minicomputers has enabled us to use two of them and thereby bypass the need to develop expensive, time-slicing software. We also were able to provide, in the initial design of the instrument, the operational characteristics essential for future experiments with self-adaptive automation and the development of a TQMS "expert system." □

Key Words: artificial intelligence; computer code—MSCAL, MTUNE, PLOTMS, PLTIB, SEGSCN; environmental pollution—salut; expert systems; explosives—decomposition; HMX; mass spectrometer; oil shale; triple-quadrupole mass spectrometer (TQMS).

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