Conf-780609--16

HEDL-SA-1424

MASTER

MASTER

ACID DIGESTION AND PRESSURIZATION CONTROL IN COMBUSTIBLE RADWASTE TREATMENT

C. R. Allen
R. G. Cowan
C. J. Grelecki

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

"COPYRIGHT LICENSE NOTICE"

"By acceptance of this paper, the publisher and/or recipient acknowledges the U.S. Government's right to retain a non-exclusive, royalty-free license in and to any copyright covering this paper."

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ACID DIGESTION AND PRESSURIZATION CONTROL IN COMBUSTIBLE RADWASTE TREATMENT

C. R. Allen
R. G. Cowan
C. J. Grelecki

Abstract

Acid digestion has been developed at the Hanford Engineering Development Laboratory (HEDL) in Richland, Washington, to reduce the volume of combustible nuclear waste materials, while converting them to an inert, noncombustible residue. A 100 kg/day test unit has recently been constructed to process radioactively contaminated combustible wastes. The unit, called the Radioactive Acid Digestion Test Unit (RADTU) was completed in September, 1977, and is currently undergoing nonradioactive shakedown tests. Radioactive operation is expected in May, 1978.

Because of uncertainties in waste composition and reactivity, the system was required to contain pressurizations. This led to the development of a simple and inexpensive system, which is capable of attenuating a shockwave from a full scale vapor detonation. The system has potential application in a wide spectrum of chemical reactors, since the fabrication materials are resistant to a very wide range of corrosive chemical attack.

Introduction

Acid digestion refers to a process developed at the Hanford Engineering Development Laboratory (HEDL) in Richland, Washington, to reduce the volume of alpha-contaminated combustible wastes by converting them into a noncombustible residue. Typical waste materials, such as polyvinyl chloride (PVC), polyethylene, paper and other cellulosic materials, ion exchange resin, and all types of rubber (Neoprene, latex, Hypalon) are digested in hot (230-250°C) concentrated sulfuric acid in the presence of nitric acid oxidant. The waste is converted to gases and an inert residue having less than four percent of the original volume.

Laboratory and nonradioactive engineering tests have led to construction of an engineering test facility for treating radioactively contaminated combustible wastes at rates up to 100 kg per day. The unit, called the Radioactive Acid Digestion Test Unit (RADTU), was completed in September, 1977. The unit is currently undergoing shakedown tests and is expected to be ready for operation using radioactively contaminated wastes in May, 1978.

The acid digester has been designed to handle chemically reactive materials, which may inadvertently be introduced with the waste. A pressure vessel is used in conjunction with vapor geometry control and a shockwave attenuation system. Based on laboratory and field tests, the system is designed to safely contain up to a full scale vapor phase detonation. (The probability of a detonation is almost zero, but because the contents of waste are undefined, it was considered desirable to design the digester to this standard.)

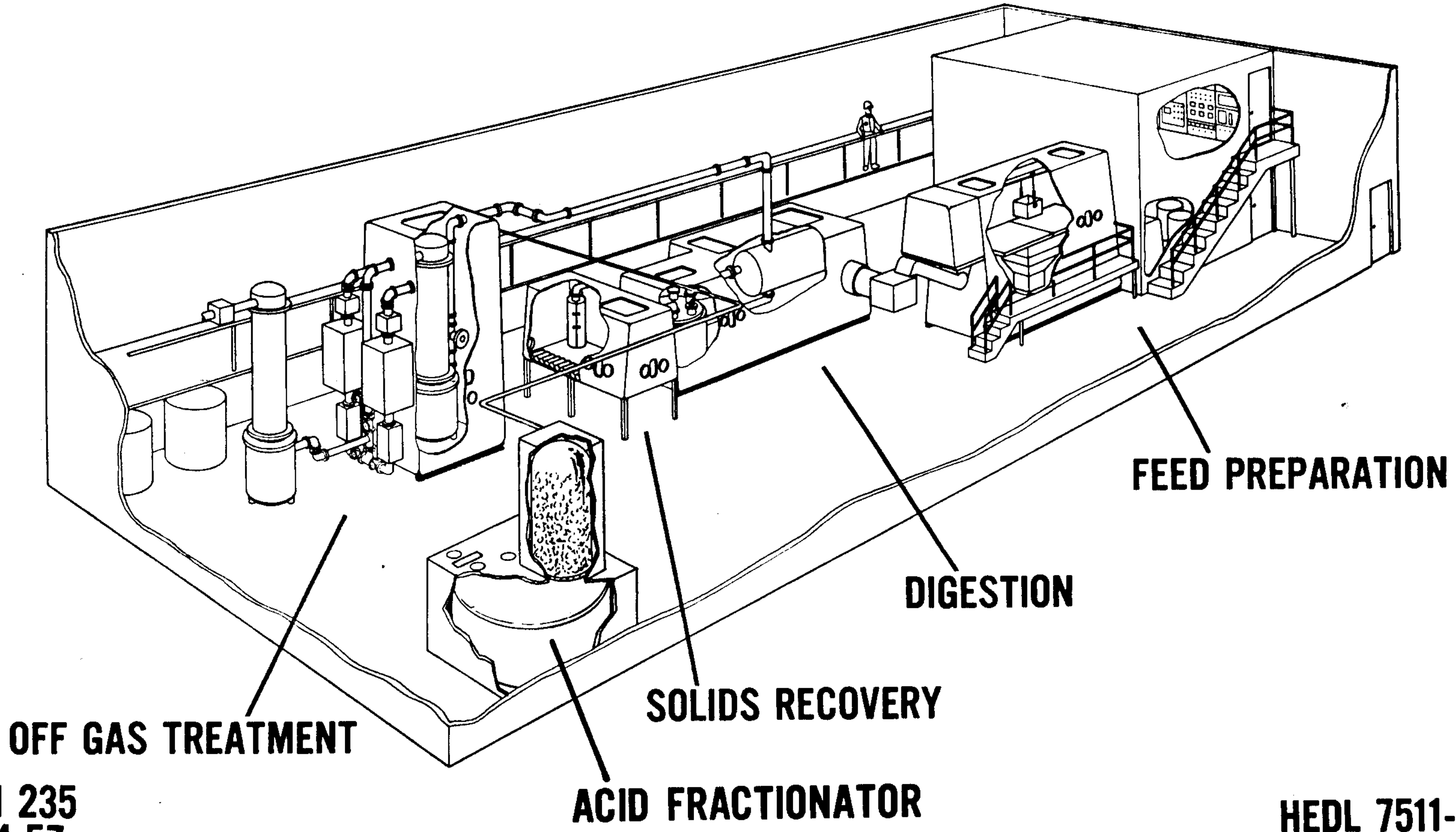
Description of Reactor System

The acid digestion system for combustible radioactive waste treatment consists of individual glovebox modules (Figure I), including the following:

1. Feed preparation module for sorting and shredding waste.
2. Digestion module for waste treatment.
3. Off-gas treatment modules to recover and recycle acids used in the process and clean exhaust gas stream prior to discharge.
4. Solids recovery module to recover solid residue from digestion process.
5. Chemical makeup module to provide process chemicals.
6. A transfer and storage module for contaminated chemicals.

We will only consider the digestion module in this report.

RADIOACTIVE ACID DIGESTION TEST UNIT (RADTU)



RM 235
234-5Z

HEDL 7511-102

FIGURE 1

Figure 2 shows a cutaway isometric drawing of the digestion system. It consists of a glass lined steel cylindrical pressure vessel in horizontal orientation (tray vessel). This vessel is connected to an annular shaped heating vessel by a glass lined steel drain pipe. The vessels are 11 mm thick and calculated to fail at 3 MPa pressure.

The tray digester vessel contains a flat tray 1.5 M long by 0.74 M wide and 50 mm deep (although acid on the tray is only 25 mm deep) made of foamed SiO_2 and held in place within a 75 cm diameter vessel by means of a hemicylinder shaped tantalum support. Waste is fed onto the surface of hot sulfuric acid in the digester tray. The hot acid chars the waste and breaks it into small carbonized particles which overflow the end of the tray and drain into the annular heating vessel.

The annular heating vessel features an inner glass lined steel vessel surrounded by an outer glass lined steel vessel sealed at the top using Teflon-asbestos gaskets. The annular space is 62 mm wide. The acid, inside the annular heating vessel, is heated to 240-260°C by means of external electrical resistance heaters, then nitric acid is added to the annular heating vessel to complete the oxidation of the charred waste overflowing the tray digester. The hot acid is gas-lifted back to the digester tray to complete the cycle. Off-gas generated from the digestion process is removed through a 15-cm diameter off-gas line to the off-gas module, where acid gases are oxidized and recovered for recycle to the digester. Residue is removed from the digester acid solution by transferring a portion of the acid from the annular heating vessel into an evaporator pot and evaporating the sulfuric acid back through the same stainless steel transfer line into the heating vessel, leaving the dry residue. Two pots are used in the process so that one can be removed to storage while the other is filling. The pots are fabricated from 316 stainless steel and will be 14.8 cm in diameter by 79 cm high. The heat to evaporate the sulfuric acid is provided by an 18 cm ID by 91 cm high three zone clamshell heater.

FIGURE 5.4-1

RADTU DIGESTER CONFIGURATION

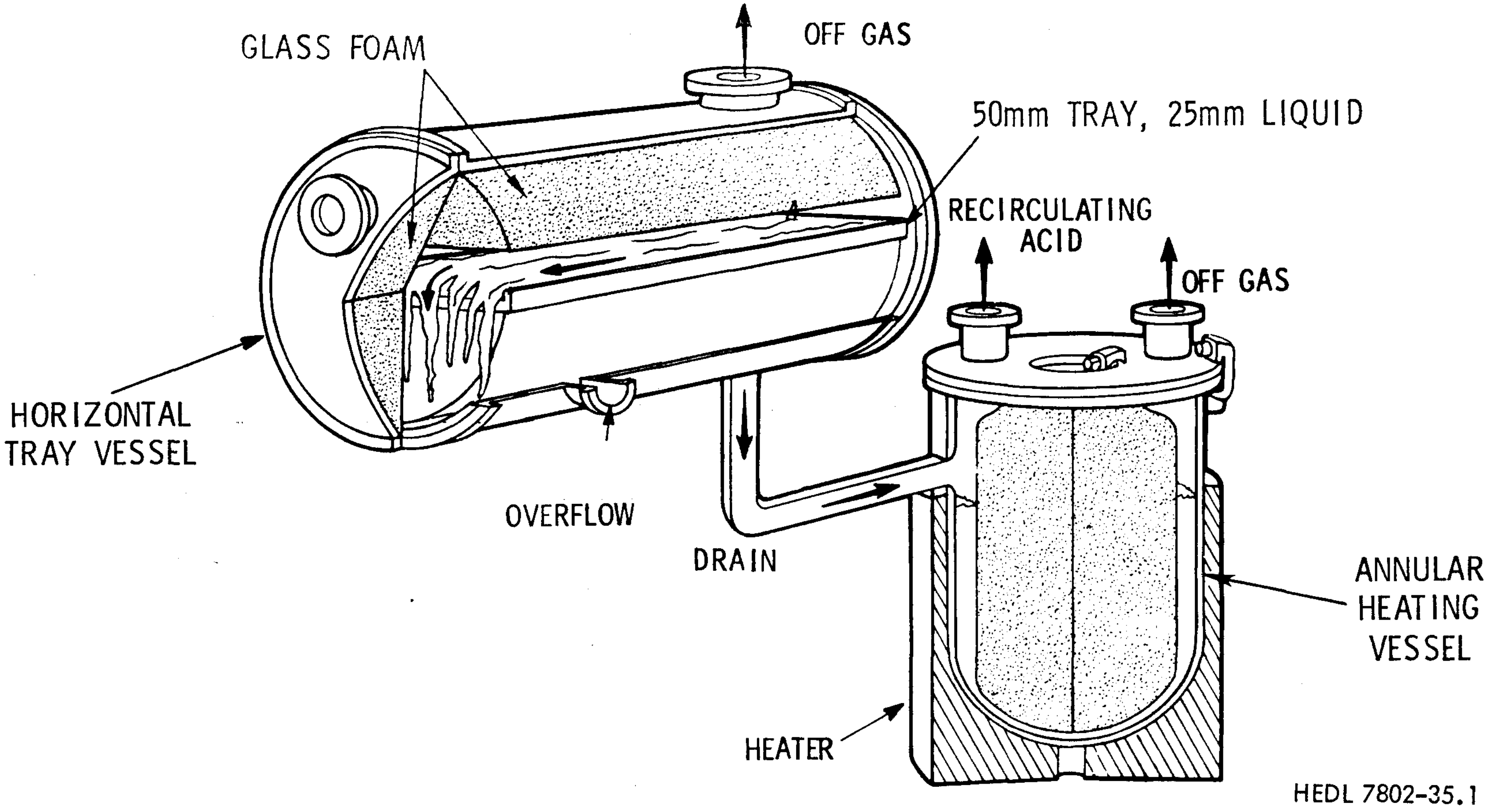
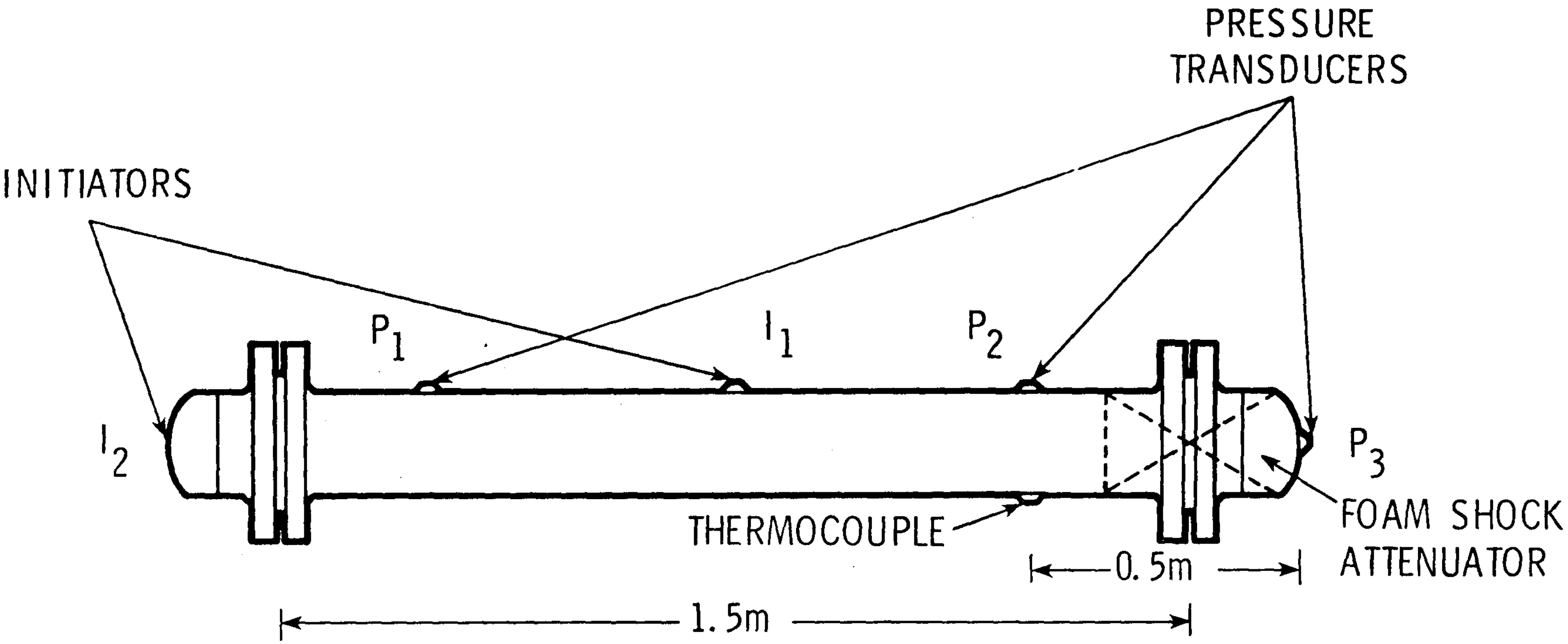


FIGURE 2: RADTU DIGESTER DESIGN



HEDL 7801-35.4

FIGURE 3: SHOCKWAVE ATTENUATION TEST EQUIPMENT

Process Description

The primary chemical reactions involved in the acid digestion process can be represented by the following four reactions:

$$C_mH_n + n/2\ H_2SO_4 \longrightarrow nH_2O + n/2\ SO_2 + mC \qquad (1)$$

$$C + 2\ H_2SO_4 \longrightarrow 2H_2O + 2SO_2 + CO_2 \qquad (2)$$

$$3C + 4\ HNO_3 \longrightarrow 4NO + 2H_2O + 3CO_2 \qquad (3)$$

$$5C + 4\ HNO_3 \longrightarrow 2N_2 + 2H_2O + 5CO_2 \qquad (4)$$

The sulfuric acid serves both to carbonize the waste material and to oxidize it to CO_2 as shown in reactions (1) and (2). Reaction (2) is somewhat slow, however, and nitric acid serves as a better oxidant, according to reactions (3) and (4). Thus, in many respects the sulfuric acid serves as a high temperature medium for carrying out the reactions. This is particularly necessary for digestion of plastic materials, such as PVC and polyethylene, where temperatures near 250°C are necessary to obtain complete oxidation of the waste.

The residue resulting from acid digestion of combustible waste materials consists primarily of sulfates and oxides of the inert "filler" materials in the wastes themselves. The residue accumulates in the digester acid and is readily separated from the acid by distillation of the sulfuric acid in a batch operation at 350-450°C. The resulting dried residue is similar in appearance to that resulting from direct incineration of combustible wastes. Differential Thermal Analysis (DTA) of the residue has shown it to be inert with no self-sustaining reactions (exotherms) occurring when the residue was heated to 800°C in the presence of air. Separate analyses have also shown no accumulation of unreacted carbon in the residue. The density of the residue is about 1.6 kg/liter.

Chemical Safety Studies

Because a wide range of extraneous chemicals and materials could be present in combustible waste, it was considered desirable to design the acid digestion system with intrinsic safety features not dependent on administrative controls. A study was made of alternatives that could provide intrinsic safety for all credible pressurization conditions. Consideration of these options led to the development of a shockwave attenuation system, which is discussed in the following sections.

Shockwave Attenuation

In the late 1950's Lieberman and Zaker[1,2] tested a number of materials for attenuating blast pressures. Hanna and Ewing[3] conducted detonation experiments in a spherical steel shell using fiberglass, hairfelt, and rubber foam as lining materials. Many of these materials were found to have some effect on shockwave properties and pressures, but the results were not dramatic. This report deals with a new material, glass foam, which very significantly reduces the pressure and impulse from an incident shockwave. It is believed that the unique material properties, closed individual pores and rigid structure, combine to effectively dissipate the shockwave energy; at the same time, some of the material at the surface is destroyed.

---

1. P. Lieberman, "Shock Impingement Experiments on Crushable Solids," Armour Research Foundation Report ARF 4132-10, June, 1959.

2. T. A. Zaker, editor, "Studies of Reactor Containment," Armour Research Foundation Report ARF 4132-14, August, 1960.

3. J. W. Hanna and W. O. Ewing, "Effectiveness of Lining Materials in Increasing the Blast Resistance of a Simulated Outer Containment Vessel for a Nuclear Reactor," Balistics Research Laboratories Memorandum Report No. 1341, April, 1961.

Propagating gas reactors are divided into two classes, depending on the mechanism by which energy is transferred from reaction zones into unreacted gases. The most common type of gas phase burning is a deflagration. Deflagration is defined as a propagating reaction in which the energy transfer from the reaction zone to the unreacted gases is accomplished through ordinary transport mechanisms. Final pressure inside a closed vessel, following a deflagration, is very close to that calculated for the diabatic constant volume reaction of the gases. Starting at atmospheric pressure with oxygen and common organic materials, the final adiabatic pressure are of the order of 10 to 15 atmospheres. It is easy to construct a vessel to withstand these pressures.

Detonation, on the other hand, is defined as a propagating reaction in which energy is transfered into the unreacted gases by a shockwave that adiabatically compresses the reactants. The static pressure in a detonation wave is approximately twice the adiabatic constant volume pressure. In the case of detonation, the resulting shockwave greatly complicates the design problem, because deflection from the vessel wall can result in an effective pressure at the wall, which is significantly higher than the incident pressure.

As a further complexity, when a deflagration initiates in a long closed cylindrical shape, the pressure in the unburned gases increases as the reactants are consumed, so that the last increment of gas burns at a higher local pressure than the first. This phenomenon is called pressure piling. During the course of the reaction, if the deflagration should transfer to detonation, then the pressure of the detonation wave is directly proportional to the local pressure when the transition occurs. If the transition takes place early in the process, then the static pressure of the detonation wave will be twice the adiabatic constant volume pressure. If the transition takes place toward the end of the reaction, when the local pressure is as much as 10 times the initial, then the static pressure of the detonation wave will be much greater, up to approximately 200 times the initial pressure. The total energy of the detonation wave decreases with the time delay before transition from deflagration despite the fact that the intensity of the shock increases. This is due to the fact that less material actually detonates when the transition takes place near the end of the process and so the duration of the shock is very short. If this energy can be dissipated or the shockwave decollimated, a vessel can withstand detonation that would normally destroy the vessel head. Both of these principles are employed in RADTU design.

Shockwave Attenuation Experiments

A series of experiments was performed to evaluate the ability of a foam material to attenuate a shockwave and prevent rupture of a steel vessel. The experiments were set up to use an explosive charge to give a shockwave similar to that from a vapor phase detonation in the RADTU acid digester vessel. The energy and destructive characteristics were designed so that they would be representative of what would be encountered in a worst case credible situation in RADTU.

In planning the program, extreme conditions were deliberately selected in order to allow an extra margin of safety. For example, a stoichiometric mixture of propane and oxygen at room temperature was selected as the reactive medium. In fact, such an energetic mixture could not form in the RADTU reactor.

Equipment

Figure 3 illustrates the test equipment used at Hazards Research Corporation to demonstrate the shockwave attenuation system. A long cylinder of schedule-40 pipe was filled with a detonatable gas mixture. Combinations of steel and nylon bolts that failed at specific strains (equated to pressure) were used to bolt the ends of the cylinder. Test attenuation materials were placed in the end of the pipe and the mixture was ignited. The candidate materials were corrosion resistant and compatible with the acid digestion system.

The equipment consisted of a 1.5 m steel pipe having an I.D. of 150 mm. At both ends a dished head (pipe cap) with flange was attached by steel or nylon bolts, making the inside overall length 190 mm. Pressure transducers were placed at two locations on the side of the pipe and also at one end on the dished head. Initiators were located, one on the nonfoam end and one at the center of the pipe. Foam was cut to fit and inserted in one end of the pipe into the dished head.

Results

A series of 18 runs was made with this apparatus under a variety of conditions, including those in which the explosive energy greatly exceeded that which could be expected in RADTU.

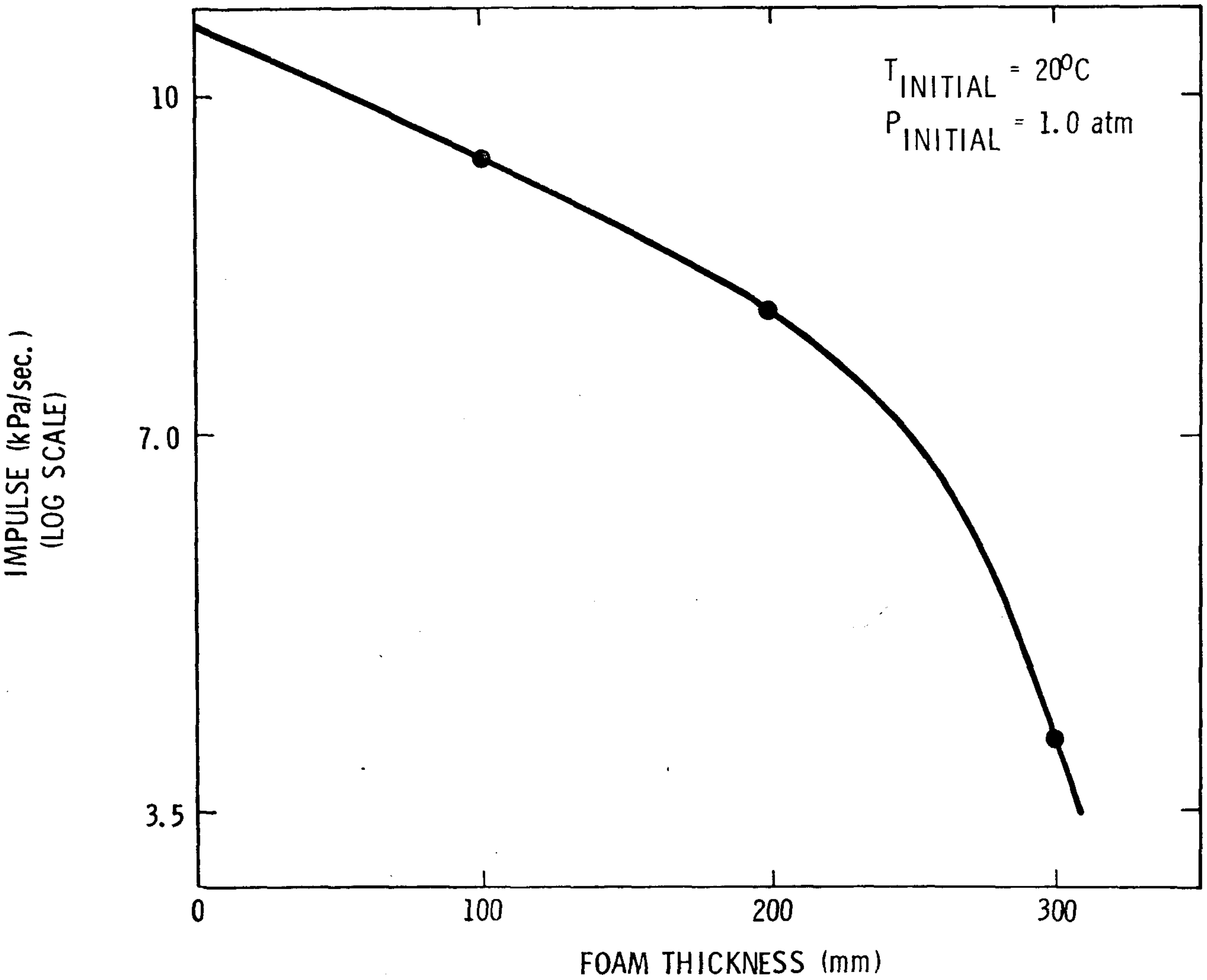
It was found that borosilicate glass foam materials only a few inches thick would prevent failure of the ends of the cylinder at mixtures and energies far exceeding those possible from a detonation in the RADTU reactor. This appears to be an ideal material for application in a chemical system, since the borosilicate glass is resistant to most corrosive chemicals. In addition, the material is inexpensive and easily fabricated into a variety of shapes.

The results obtained from the tests may be summarized briefly as follows:

1. With the reactor head designed to fail at 3.4 MPa, failure was not achieved with detonations of optimum propane-oxygen mixtures initially at one atmosphere. In order to get bolt failure, initial pressures of 1-1/2 atmospheres were required.

2. At initial pressures of 1-1/2 atmospheres with foam protecting only one end of the vessel, failure consistently occurred, presumably due to reinforcement from reflected shocks from the unprotected end. When both ends were protected with foam, failure did not occur.

EFFECT OF FOAM THICKNESS ON SHOCKWAVE ATTENUATION



HEDL 7801-35.2

FIGURE 4

3. Measure of the pressure time history of the shock as a function of foam thickness indicates a gradual decay in total impulse[1] initially up to about 100 to 200 mm with a much sharper decay after 200 mm. This effect is illustrated in Figure 4.

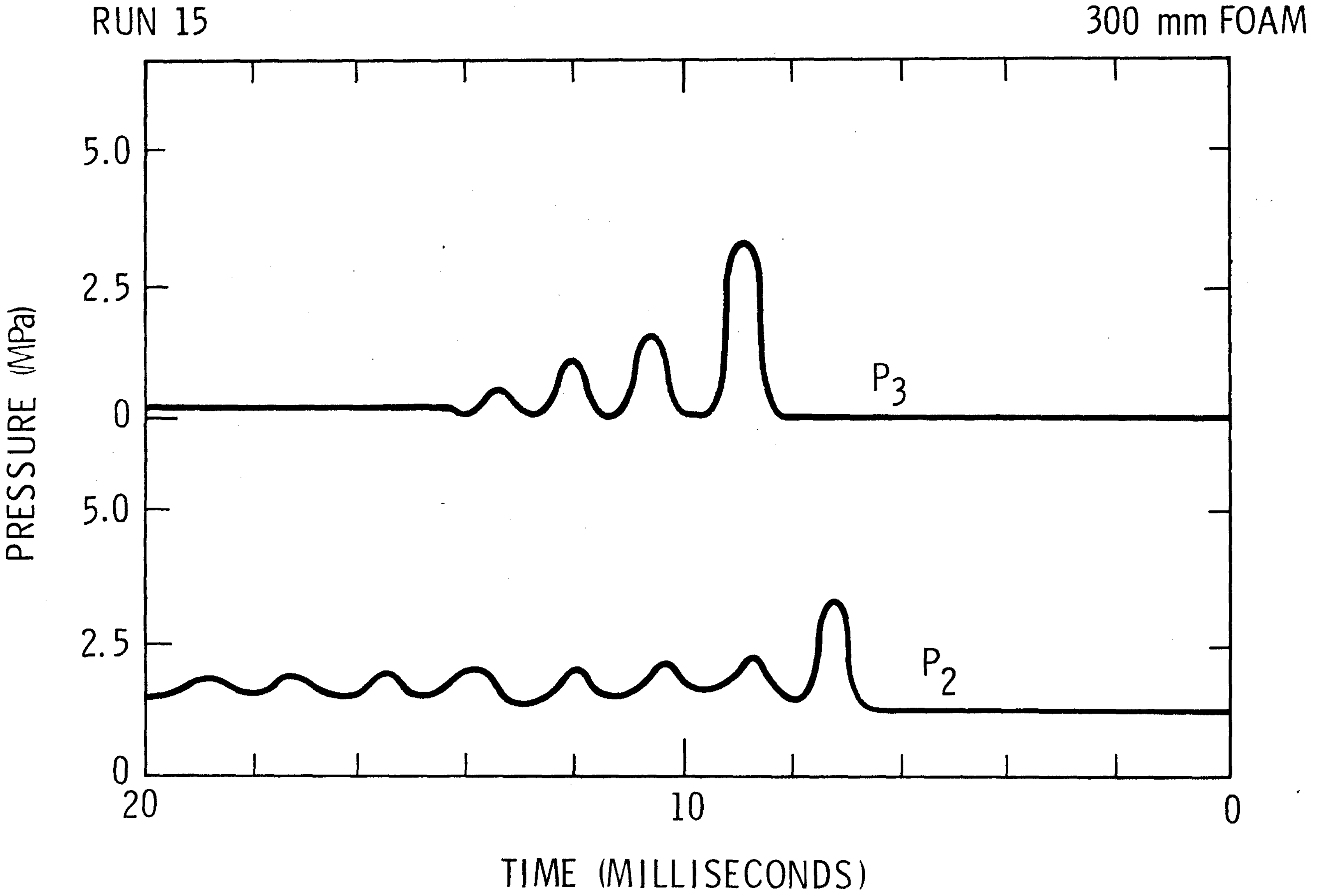
A typical pressure-time recording of an experiment shows two traces as illustrated in Figure 5. The lower trace is measured by the side pressure transducer P_2 (shown in Figure 2). The upper trace is measured by the end pressure transducer P_3. Time zero is at the right of the trace. These data were used to calculate the velocity of the pressure wave through the material as well as the impulse of the incident pressure wave. Figure 6 shows a plot of log velocity versus foam thickness. Note that the curve is almost linear while that of log impulse versus foam thickness (Figure 4) falls off sharply at foam thickness above 200 mm.

Theoretical Discussion

The primary purpose of this work was to design a waste processing system to safely contain internal chemicals and radionuclides under the worst conceivable conditions. Having achieved this goal, the press of continuing waste processing development has preempted any major efforts to further test or explore the mechanisms involved in shockwave attenuation. The use of a rigid closed pore foam is based on the idea that the pressure from a shockwave impinging on the foam will collapse the foam, if the pressure exceeds the compressive strength of the foam. Further, the collapse of the foam will require a substantial amount of work, which must come from the shockwave energy. For example, to collapse foam with a compressive strength of 1.4 MPa would require 1.4×10^6 joules

---

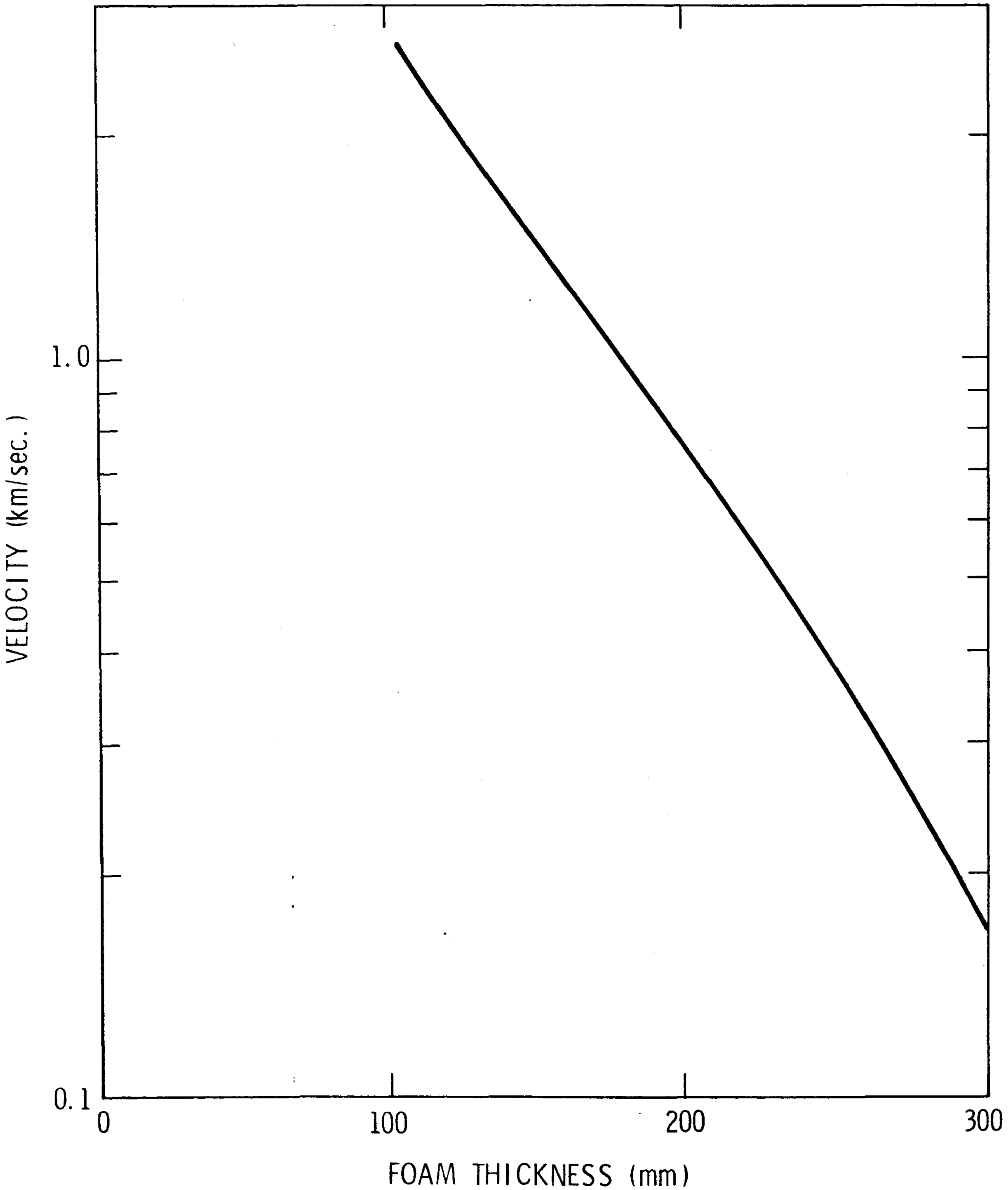
[1] Impulse is defined as the product of force (pressure) times the time. In this context it is representative of the destructive energy or momentum of the wave.



HEDL 7801-35.3

FIGURE 5

TYPICAL PRESSURE-TIME TRACE FROM DETONATION EXPERIMENTS



HEDL 7801-35.5

FIGURE 6

of energy per m^3 of foam. It is believed that a theoretical basis could be developed for changing pressure to work. This would be of great help in understanding this phenomenon and in designing new systems. However, in the present case, it was easier to run experiments in order to get design information. A theoretical discussion is presented in the appendix, solely for consideration in the hopes that further development may someday take place to shed further light on the materials requirements for design of systems to safely contain pressure excursions.

Application of Results to RADTU Safety

In view of the above work, it was concluded that the RADTU design as proposed was appropriate and could be expected to withstand any vapor detonation without failure and with an acceptable safety margin. This conclusion is based on the following:

1. The RADTU vessel design failure pressure of 5.9 MPa is considerably greater than the 3.4 MPa design of our experimental vessel. In addition, shocks produced at 250°C will be considerably less intense than those produced in our experiments at room temperature.

2. The RADTU design includes the packing of a considerable portion of the cylindrical section with foamglass, in addition to foamglass in the two dished heads. With this design, reflections are reduced and reinforcement due to reflections will be minimized.

This design also allows energy from the shock to be dissipated laterally, since the void channel is bounded on two sides by the frangible foam.

3. When the shockwave leaves the straight wall section, it will expand laterally in the dished head section so there will be some distribution of the force over the entire head section.

The cross section of the channel is 1/7 to 1/10 the area of the head. So the force acting on that area will be equivalent to a much lower pressure when distributed over a large area.

4. In applying the phenomenon of pressure piling to the reactor, three points need to be considered: (1) the reactor is not a closed volume. If a deflagrative combustion occurs, considerable venting will take place through the normal flow zones. (2) The design of the flow channel is not conducive to maintaining adiabatic conditions. To develop significant pressure the combusted gases must remain hot. To the extent that heat is transferred from the combusted gases the pressure will be less than calculated for the adiabatic case. (3) Finally, if a detonation occurs after a portion of the gas has reacted, the total energy of the detonation wave will be less. So while the intensity will be greater, the total impulse will not be, and the foam which is effective in absorbing the energy of the entire reactor charge will be sufficient to absorb the energy of a fraction of the charge.

APPENDIX

Theoretical Consideration

The gas phase reaction of concern is burning at or above sonic velocities. Under these conditions a shockwave can be produced, which stores a significant amount of work as moving gas. These reactions are referred to as detonations and in some cases can result in pressure as high as 100 times the initial pressure of gas. This pressure occurs where the shockwave interacts with the fixed wall of the vessel. The potential presence of a shockwave in a closed system makes the design of the vessel much more complicated. Designing a conventional pressure vessel for the maximum pressure from a detonative shockwave would result in a very heavy, costly vessel.

The rapid gas reaction produces shockwaves, which propagate at velocities in excess of the speed of sound.

A shockwave is a heat engine and can be visualized as a jet engine with no solid parts. The front of the wave is the compressor section, the center of the wave is the combustion chamber and the back of the wave is the exhaust nozzle. Because the vessel is a closed system, the thermodynamics of the system limit the efficiency of the heat engine and, thus, the stored energy in the shockwave. The lowest possible temperature in the closed adiabatic system after reaction is T_p (the constant pressure reaction temperature) the maximum temperature is T_v, thus, the maximum temperature difference is $T_v - T_p$ and the limit of efficiency for a heat engine is $(T_v - T_p)/T_v$. This is the initial efficiency limit but as the wave travels, the temperature behind the wave increases, thus, reducing the efficiency.

The gas density behind the wave (ρ_f) is lower than the initial density (ρ_1) by the amount of gas swept out by the wave. The limit of work from the isothermal expansion of a gas from ρ_1 to ρ_2 is $W = NRT \log (T_2/T_1)$. But the gas in the wave is moving at the apparent velocity of the wave less the velocity of sound at T_v and the expansion is the only source of this work in the system.

$$\text{Work Per Unit Volume} = 1/2\ (\rho_1 - \rho_2)\ (V_w - V_s)^2$$

Where V_w is the wave velocity and V_s is the velocity of sound.

By equating these two work terms, maximum work per unit volume of gas can be calculated, provided the velocity densities, the temperature, and heat capacities are known.

Although no calculation has been attempted, it is obvious that the efficiency will be very low and drops off as the velocity of the shockwave increases. This is also a limit, since it does not account for losses and nonideal conditions.

Measurements show that 200 mm of foam stops a shockwave, which had built up in a 1.5 m long tube filled with a stoichiometric, detonable mixture of propane and oxygen. The total chemical energy of the system was 316,000 J. The work required to collapse the foam (the strength above the P_v times the volume of foam) was estimated to be 2400 J or the efficiency of the shockwave was approximately 0.8% for the conversion of heat to work.