ANL/RE/CP-92759
CONF-970607--26

# AN EXPERIMENTAL STUDY OF STEAM EXPLOSIONS INVOLVING CHEMICALLY REACTIVE METAL

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## ABSTRACT

An experimental study of molten zirconium-water explosions was conducted. A 1-kg mass of zirconium melt was dropped into a column of water. Explosions took place only when an external trigger was used. In the triggered tests, the extent of oxidation of the zirconium melt was very extensive. However, the explosion energetics estimated were found to be very small compared to the potential chemical energy available from the oxidation reaction.

## I. INTRODUCTION

The potential for an explosive interaction between core melt and water has long been recognized as a concern in assessment of nuclear reactor severe accidents. Mechanical energy release from such an interaction is of interest in evaluating the structural integrity of the reactor vessel as well as of the containment. Usually, the source for the energy release is assumed to be the rapid transfer of heat from the melt to the water, producing steam fast enough to cause an explosive event ("steam explosion"). When the melt contains a chemically reactive metal component, however, there could be an additional source for the energy release, which is the heat release and gas (i.e., hydrogen) production due to the metal-water chemical reaction.[1] This chemical contribution to the explosion energetics could be important depending on the time scale of the chemical energy release.

In 1990-1991, Sandia National Laboratories conducted a series of tests investigating explosive interactions between aluminum melt and water as part of New Production Reactor safety studies.[2] These tests, typically involving 10-kg masses of aluminum melt, produced very energetic explosions. In fact, the estimated mechanical energy release was several times the maximum thermodynamic work potential for a pure steam explosion. The investigators suggested that 30-40% of the aluminum melt was oxidized on an explosion time scale during the tests. These findings generated considerable interest in the possibility of the steam explosion energetics being chemically augmented for melts containing a reactive metal such as aluminum and zirconium.[3,4] Zirconium is of particular interest, since it is a component of the core materials of the current nuclear power reactors. Accordingly, an experimental program was initiated at ANL in order to investigate the energetics of interactions between zirconium-containing melt and water. This paper describes the test apparatus and summarizes the results of four tests conducted using pure zirconium melt.

## II. APPARATUS

A schematic of the apparatus is shown in Fig. 1. Briefly, the apparatus consists of a melt furnace/release assembly and a test section. All components of the apparatus are placed in an inerted containment chamber that allows collection and measurement of the hydrogen generated in the melt-water interactions. The containment chamber also provides blast protection from the explosive interaction.

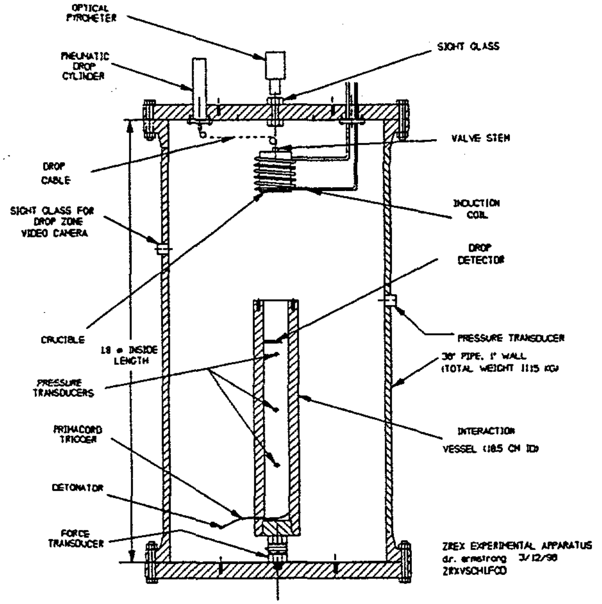

Fig. 1. Schematic of ZREX Apparatus

## A. Containment Chamber

The body of the containment chamber is a 1.8 m-long section of a 91.4-cm O.D., 2.54-cm thick carbon steel pipe. A small electric fan is placed in the chamber to circulate the atmosphere and help provide well mixed gas samples. Most of the electrical and mechanical penetrations are through the top lid of the chamber.

## B. Test Section

As shown in Fig. 2, the test section is a one-dimensional tube geometry and is located beneath the melt furnace/release assembly. It is a 98-cm long section of a 10-cm I.D., 3.8-cm thick carbon steel tube. The base of the test section is a welded carbon steel plug with a 3.2-cm diameter threaded hole for mounting of a force transducer.

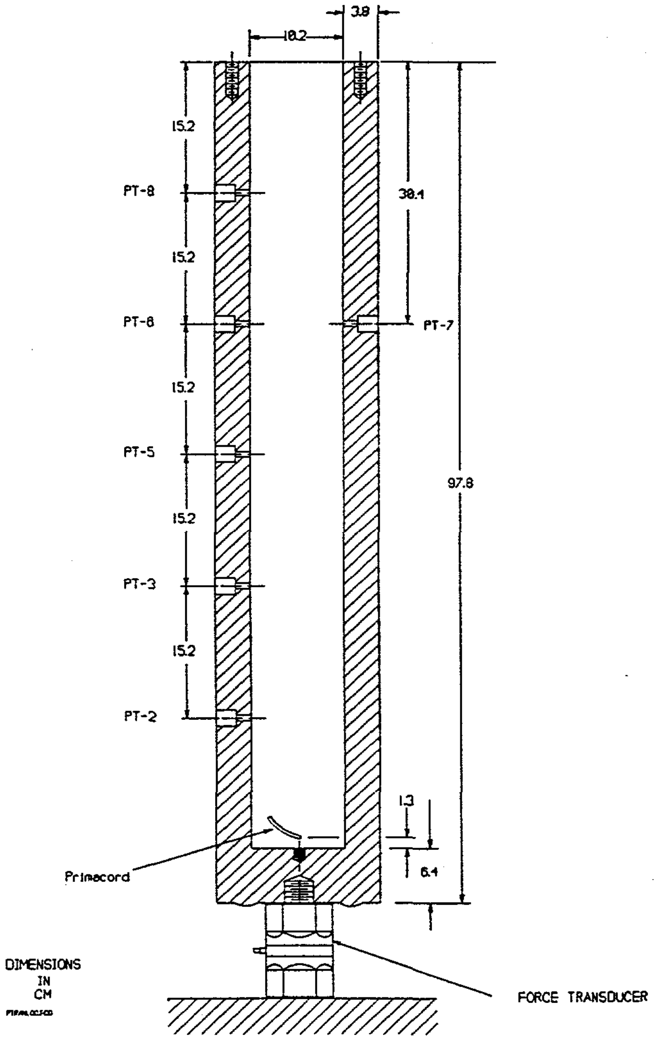

Fig. 2. ZREX Test Section

## C. Melt Furnace/Release Assembly

The melt furnace/release assembly is an inductively heated graphite crucible, equipped with an integral plug valve. To release the melt, the plug is pulled from its seat in the crucible base by a pneumatic cylinder mounted on the top lid of the containment chamber. The hole size of the crucible base is 2.54 cm in diameter.

## D. Trigger Device

The trigger device is a length of explosive detonating cord passed through a hole in the side wall of the test section into the water volume near the base. The initiating detonator is located outside the test section but inside the containment chamber. This location minimizes the effect of the detonator on the pressure transducers in the test section. The energy of the trigger can be easily adjusted by changing the length and type of detonating cord.

## E. Water Fill System

Water is added to the test section as the crucible temperature approaches melting so as to limit the time that hot graphite is exposed to water vapor. This is accomplished by using an external water tank connected to the test section through a pump and solenoid valve. The fill system is controlled manually from a remote location by an operator watching the water level with a TV camera.

## F. Gas Sampling System

The gas sampling system consists of one or two sample cylinders, with manual valves at the inlet and outlet, in the exhaust line from the containment chamber. The cylinders are placed between remotely operated solenoid valves that control the capture of a gas sample. When a sample is desired, the solenoid valves are closed, stopping exhaust flow and capturing gas in the cylinders. The manual valves are then closed and the cylinders removed and replaced with new ones.

## G Instrumentation System

An optical pyrometer is used to measure the melt temperature in the furnace. The pyrometer views the melt surface through a window in the top chamber lid, through a tube flushed with flowing argon, and through a hole in the top lid of the crucible. A TV camera is placed to view through the pyrometer alignment sight. This gives the operator a view of the melt during the experiment. A second TV camera, looking through a window in the side wall of the containment chamber, views the drop space between the bottom of the crucible and the top of the test section. A third TV camera views the top of the containment chamber, containing both the water fill tank and pneumatic cylinder for melt dump in its field.

A number of type-K thermocouples measure temperatures in the test section water, in the containment chamber gas space and in the exit water from the induction coil. An additional thermocouple controls test section heaters in those runs using preheated water.

Five piezoelectric pressure transducers mounted on the wall of the test section measure dynamic pressures during the melt/water interactions. A force transducer mounted on the bottom of the test section measures the reaction forces during the interactions. The reaction forces integrated over time provide impulses which, together with an estimated mass ejected from the test section, may be used to evaluate the interaction energetics. Pressure in the containment chamber is measured by both a static pressure transducer in the top lid and a dynamic pressure transducer mounted on the wall of the containment chamber. Strain gauges also are mounted on the wall and top cover of the containment chamber.

A melt drop sensor consisting of an array of wire grids supended in the test section water measures the velocity of the falling melt by indicating the time at which each grid is broken by contact with the melt. For those experiments where an external trigger is used, one of the grids is selected to serve as the trigger signal for the detonator firing cicuit.

The test section pressure and force measurements are recorded by high speed data acquisition boards in two PC computers. The drop sensor data is recorded by a separate PC while all other data is recorded through a multiplexer and DVM onto a fourth PC. A digital tape recorder is used for backup on critical data channels.

## III. EXPERIMENTAL PROCEDURE

A 1-kg batch of 1.3-cm diameter zirconium rod is loaded into the dropping crucible. The top and bottom of the crucible are insulated with zirconia board, and zirconia felt is wrapped around the side of the crucible. The crucible and insulation are placed in the induction heating coil and supported on a platform suspended from the containment chamber lid. A steel wire cable is attached to the crucible plug and connected to a pneumatic cylinder. The pyrometer and its associated TV camera are aligned with the crucible and window at this time.

If the experiment is to be triggered, the detonating cord and detonator are added to the test section. The containment chamber is assembled, and final connections and alignment checks are made. The chamber is pumped down overnight. Argon is backfilled into the chamber to a pressure a few kPa above atmospheric when the exhaust line is opened. An argon purge of 6 liter/min is continued throughout the experiment. The induction generator is turned on and crucible heating is begun.

When the luminosity of the melt is great enough to check the pyrometer alignment, a neutral density filter is placed over the pyrometer camera and all personnel leave the experiment bay. The water fill system is turned on, filling the test section with water. The temperature of the melt is monitored, and when the desired temperature is reached, the argon purge is stopped and the exhaust is closed, trapping a gas sample representative of the atmosphere at the time of melt dumping. Then the dump mechanism is actuated.

After the melt dump, the gas sample cylinders are removed and replaced with others. Fifteen minutes later (the internal fan is mixing the containment chamber atmosphere during this delay), the sample and exhaust valves are opened and the exhaust passes through the gas sample cylinders into an exhaust line that exits the building and enters the atmosphere in front of a fan 7 m above ground level. When the pressure in the containment chamber has dropped at least 3 kPa, the sample valves are closed and the gas sample cylinders are removed. Dummy sample cylinders are placed in the line and exhausting the containment chamber continues. When the pressure reaches about 110 kPa, the argon purge valve is opened and a cylinder of argon is purged through the containment chamber to remove any hydrogen generated during the experiment.

The following day, the apparatus is disassembled, gas samples are sent to an analytical lab, data is read out from the recording devices, and debris is collected and photographed.

## IV. RESULTS AND DISCUSSION

All four tests were conducted with one-kg masses of pure zirconium melt. Two of them were non-triggered experiments while the other two tests employed an external trigger made of one gram of chemical explosive (PETN). The experimental conditions and qualitative results are summarized in Table 1.

### A. Non-triggered Tests

Two non-triggered tests were conducted, one with 22°C water (ZREX-19)[1] and another with 70°C water (ZREX-23). The initial melt temperature in both of these two tests was 2000°C . In either of the tests, no explosions took place, and

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[1] ZREX for ZiRconium EXplosion

TABLE 1. Test Conditions and Results

| Test No. | Melt Composition | $T_{melt}$ (K)* | $T_{water}$ (K) | Test Objective | Results |
|---|---|---|---|---|---|
| ZREX-19 | Zr (100 w/o) | 2278 | 295 | • Non-triggered tests (baseline)<br>• Effect of water subcooling | • No explosions<br>• Rapid quenching of melt<br>• Moderate hydrogen production |
| ZREX-23 | Zr (100 w/o) | 2273 | 343 | | |
| ZREX- 20 | Zr (100 w/o) | 2373 | 296 | • Triggered tests<br>• Data on explosion energetics<br>• Effect of water subcooling | • Explosions<br>• Damage to apparatus<br>• Extensive hydrogen production |
| ZREX-24 | Zr (100 w/o) | 2373 | 367 | | • Similar to ZREX-20 |

* Initial value prior to melt drop

the melt dropped quenched rapidly. No dynamic pressures were registered by the test section pressure transducers. However, there was a spike in the containment chamber gas pressure (static). The rise time of the pressure spike was on the order of one second. The pressure spike was from 106 kPa to 121 kPa for ZREX-19 and from 124 kPa to 162 kPa for ZREX-23. These pressure spikes were probably caused by a combination of the generation of a hydrogen/steam mixture and the rapid heating of the containment gas atmosphere. It is believed that the primary cause was the containment gas heating brought about by the metal/water reaction.

The characteristics of debris observed in ZREX-19 and -23 were similar. In ZREX-19, a large amount (254 g) of the frozen melt was suspended from the top edge of the test section with the appearance of a cylindrical stalactite. A piece of frozen melt with the appearance of a folded ribbon and weighing 399 g was resting on the middle submerged burnwire (located at 39 cm from the top of the test section). This ribbon shape varied from 2 to 6 cm wide and a few mm thick. An additional 160 g of lump material also was on the middle burnwire. This burnwire was not significantly damaged. A small amount (5 g) of particles (several millimeters in size) were found in the catch can below the bottom burnwire. An additional 82 g of debris fell outside the test section and was mostly collected from the containment vessel floor. A photograph of the ZREX-19 debris is shown in Fig. 3. In ZREX-23, the debris was mostly in the form of a long, ropy, connected thin mass extending from the second to the fourth burnwire (located at 29 and 78 cm from the top of the test section, respectively) over a distance of 49 cm. A photograph of the ZREX-23 debris is shown in Fig. 4.

The gas samples of the containment chamber were analyzed by the Institute of Gas Technology Analytical Laboratory using a gas chromatographic method. Using the analysis results along with the measured temperatures and pressures of the containment chamber atmosphere, the amounts of hydrogen produced in the experiments were estimated.[2] The amount of hydrogen production for ZREX-19 was about 1.06 mole, which corresponds to about 4.8% of the total zirconium reacting with water. For ZREX-23, the amount of hydrogen production was about 3.75 mole, which corresponds to about 17.0% of the total zirconium reacting with water.

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[2] In this estimate, corrections were made for the oxidation of the graphite crucible producing hydrogen, primarily due to the water gas reaction, $C+H_2O \rightarrow CO+H_2$.

Fig. 3. ZREX-19 Debris

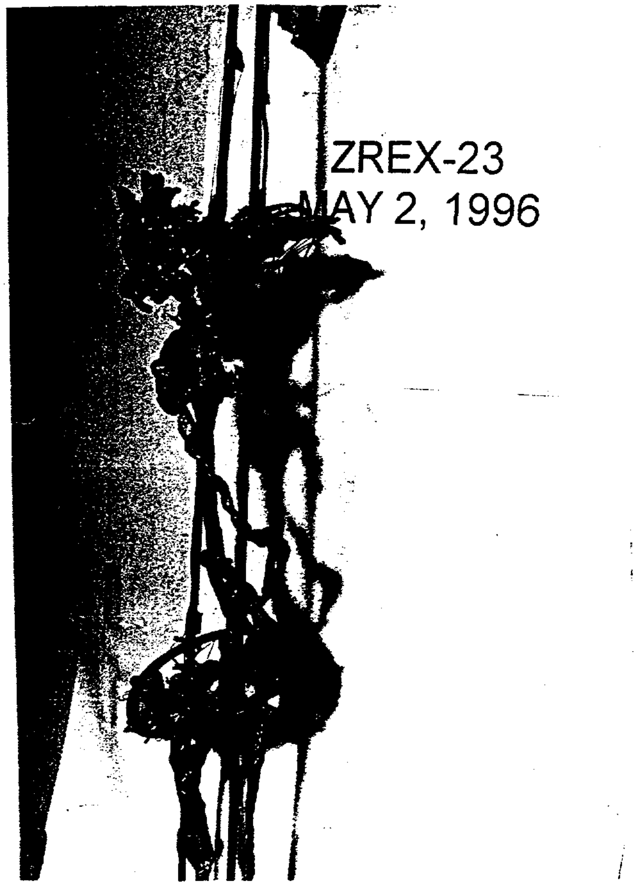

Fig. 4. ZREX-23 Debris

### B. Triggered Test ZREX-20

In this test, the initial melt temperature was 2100°C and the water temperature was 23°C. An external trigger was employed and it was the detonation of a length of Primacord containing 1 g of PETN placed near the bottom of the test section. The start signal for the trigger was generated by the melt burning through of a burnwire grid submerged in the water 20 cm below the top of the test section. (There was another burnwire grid 1 cm lower for redundancy.)

This choice of the location for the trigger start signal was made based on consideration of possible rapid quenching of the melt in the water. The results of ZREX-19 seemed to indicate that the melt could quench and freeze within a water depth of 39 cm. It was thought that the 20-cm water depth would be sufficient to submerge the 1-kg melt while minimizing quenching so that the melt is fully molten at the time of triggering.

After the melt dropped into the test section, the trigger was initiated and an explosive interaction took place. Post-test examination of the apparatus showed that much damage had been done. All of the mechanism hanging from the vessel lid was destroyed. The crucible was shattered. The induction coil, crucible support, valve opening gear, and sight tube were bent or torn. The lid and wall of the vessel were coated with a thick (~1 mm) layer of grey dust (36 g on the lid and 243 g on the wall). The bottom of the vessel contained large pieces of debris (probably crucible pieces, 1147 g) and was coated with a mud made up of water and more of the grey dust along with small pieces of debris (1354 g). A few fragments identifiable as zirconium were found in the bottom debris (47 g). The collector at the bottom of the test section had metallic-looking particles and thin flattened globules weighing a total of 98 g. When inspected under magnification (30x), the dust had the appearance of a collection of transparent fibers, small white spheres and small black spheres. The three types of insulation used in the experiment, namely, alumina board, zirconia board, and zirconia felt, consisted entirely of fibrous particles with no spherical parts. Thus, it may be assumed that all of the spheres are zirconium and zirconia from the explosion. (The diameters of these spheres varied over a wide range from under 10 μm to over 100 μm.) The total weight of solid debris after the experiment was 2990 g. This was 246 g less than the mass of crucible, zirconium, and insulation loaded into the experiment.

There were three burnwire grids in this test, the first one at the top of the test section and the second and third ones at 20 and 21 cm below the top of the test section either of which could generate the trigger signal. It was found that the first and second burnwire grids were destroyed, while the third one remained relatively intact. This probably suggests that the lowest part of the explosion zone was between 20 and 21 cm from the top of the test section.

The fast instruments, i.e., the force link and dynamic pressure transducers all produced signals, but it was later found that only two of the five pressure transducers in the test section were correctly functioning. (The locations of the pressure trans-ducers are indicated in Fig. 2.) One of the two working pressure transducers was located at 15 cm below the top of the test section and probably surrounded by a multiphase mixture in the interaction zone. The pressure trace of this transducer was so noisy that it was not possible to extract useful information from this trace. The other working pressure transducer was located at 30 cm below the top of the test section. The pressure trace of this transducer is shown in Fig.5. It shows a noisy pressure pulse of about 3 ms duration with a peak pressure of about 40 MPa. Probably the best data was obtained from the force transducer supporting the test section. It is shown in Fig. 6. It shows a force pulse, starting about 1.5 ms after the trigger (the trigger fired at zero time), with a width of about 3 ms and a peak force of ~ 360 kN. Immediately following the explosion, the containment chamber gas pressure (static) jumped from 108 kPa to 512 kPa, indicative of the rapid heating of the containment gas as mentioned earlier. Based on the results of analysis of the gas samples taken, the amount of hydrogen production in this test was estimated to be about 12.3 mole, which corresponds to about 55.8% of the total zirconium reacting with water.

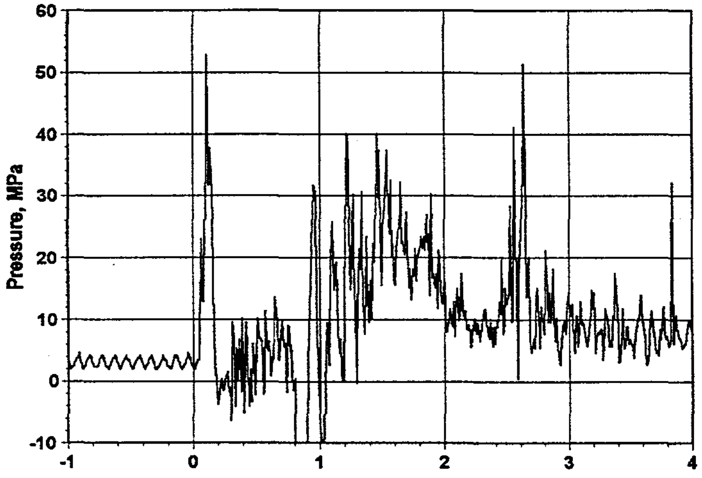

Fig. 5. ZREX-20 Test Section Pressure Trace

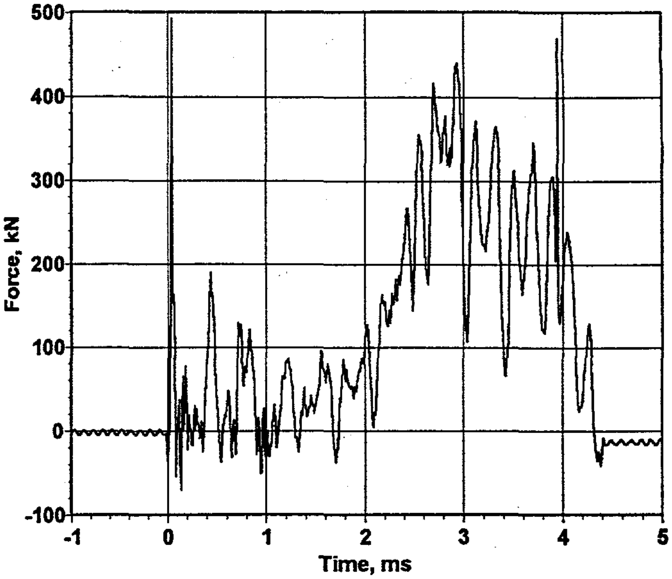

Fig. 6. ZREX-20 Test Section Reaction Force Trace

C. Triggered Test ZREX-24

In this test, the initial melt temperature was 2100°C, and the water temperature was 94°C. The external trigger used was the same as that for ZREX-20, i.e., a length of Primacord containing 1 g of PETN, which was placed near the bottom of the test section. The start signal for the trigger was generated by the melt burning through either of two burnwire grids located at 60.5 and 61.5 cm below the top of the test section. This choice of the burnwire location for the trigger signal was made based on considerations of the melt quenching in the test section as observed in the non-triggered test ZREX-23. It was thought that the quenching distance of the melt for nearly saturated water would at least be about 60 cm.

After the melt drop, the trigger was initiated and an explosive interaction took place, causing extensive damage to the apparatus. Post-test examination showed that the damage was very similar to that for ZREX-20 previously described, although it appeared to be somewhat more extensive. The debris characteristics also were very similar to those of ZREX-20.

An examination of the video and pressure records seems to indicate that the explosion took place immediately upon firing of the detonator (i.e., no perceptible time delay).

Figure 7 shows the pressure traces of three test section transducers located at 30, 46, and 61 cm from the top of the test section (i.e., the water surface level). These traces are somewhat incomplete , since the decay portions of the dynamic pressures are missing, probably due to signal cable failures caused by the explosion. Nevertheless, they reveal important details of the explosion characteristics. The pressure trace at 30 cm from the top of the test section (shown in Fig. 7) is remarkably similar to that for ZREX-20 (shown in Fig. 5) except that the peak pressure is somewhat higher (about 50 MPa vs. 40 MPa) and that the duration of the pressure is presumably somewhat longer. A close examination of the three pressure traces shown in Fig. 7 seems to indicate that the propagation velocity of the pressure pulse was about 450 m/s. The trace of the reaction force is shown in Fig. 8. The force peaked at 450 KN, but the transducer failed before it gave the full pulse. (It had a duration of about 2 ms before failure. The duration of the full pulse would have been longer.) Immediately following the explosion, the containment chamber gas pressure (static) exhibited a spike from 112 kPa to 672 kPa, again indicating the rapid heating of the containment atmosphere.

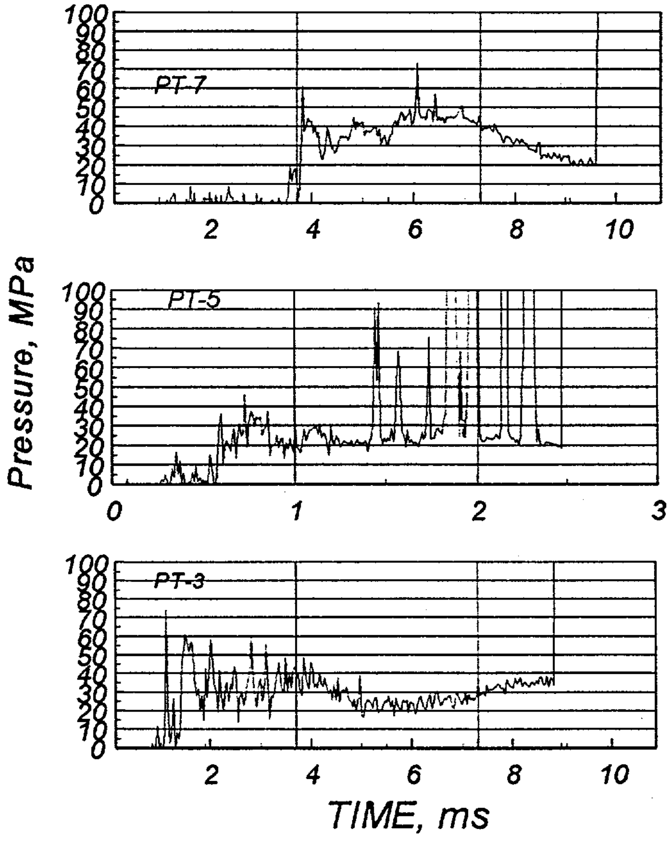

Fig. 7. ZREX-24 Test Section Pressure Trace

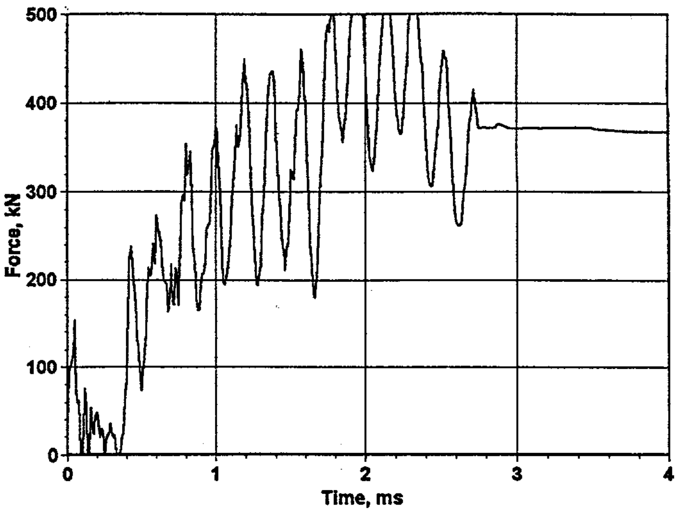

Fig. 8. ZREX-24 Test Section Reaction Force Trace

Another indication of the explosion event in ZREX-24 was the gas shock pressure recorded by the dynamic pressure transducer mounted on the wall of the containment chamber at the same elevation as the top of the test section. The gas shock had a peak pressure of about 1 MPa, as shown in Fig. 9.

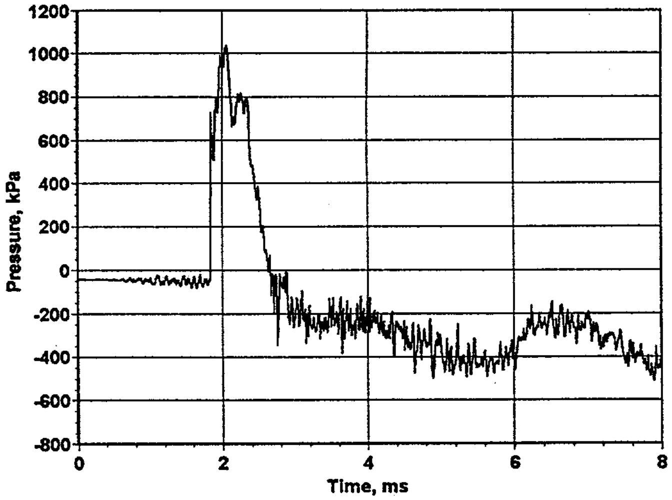

Fig. 9. ZREX-24 Containment Shock Pressure

Based on the results of analysis of the gas samples taken, the amount of hydrogen produced in this test was estimated to be about 20.3 mole, which corresponds to about 92.3% of the total zirconium reacting with water.

## D. Explosion Energetics

The force measurements at the bottom of the test section were used to estimate the mechanical energy release from the explosion. Considering one-dimensional acceleration of an inertial (rigid) mass caused by the explosion forces in the test section, the kinetic energy of the mass was given by $I^2/2M$, where M is the mass being ejected upward by the explosion and I is the impulse load on the bottom of the test section (which was obtained by integrating the force pulse over time). For ZREX-20, the impulse was estimated to be 650 N-s. Assuming an inertial mass of 2.5 kg (all of the zirconium melt plus the water above the trigger burnwire), the kinetic energy release was found to be 85 KJ. For ZREX-24, the impulse was estimated to be 1100 N-s (it was assumed that the force pulse was symmetric about the peak). Assuming an inertial mass of 5.7 kg (all of the zirconium melt plus the water above the trigger burnwire), the kinetic energy release was found to be 106 KJ.

The above estimates of the mechanical energy release may be compared to the stored thermal energy of the melt and to the potential chemical reaction energy of the melt. For both ZREX-20 and ZREX-24, the stored thermal energy of the melt was 890 KJ, whereas the maximum potential chemical reaction energy was 6400 KJ. Based on the hydrogen production measurements, it is estimated that a significant fraction of this maximum chemical energy was released in the triggered tests (about 3570 KJ for ZREX-20 and about 5910 KJ for ZREX-24). However, the estimated explosion energetics are seen to be very small compared to the potential chemical energy available from the oxidation reaction. No attempts have yet been made to determine the extent of chemical contribution to the explosion energetics relative to that of the stored energy.

A calibration test was conducted to characterize the external trigger used in ZREX-20 and ZREX-24. The trigger explosive (i.e., 1 g of PETN) was placed in the test section filled with water and detonated. The resulting pressure and force pulses were measured. The pressure pulses were sharp and narrow, having a peak of 30-40 MPa and a duration of about 100 μs. From these measurements, the trigger energy was estimated by using the shock wave energy formula given by Cole [5], viz

$$E = \frac{A}{\rho c} \int (\Delta p)^2 \, dt \qquad (1)$$

where $\Delta p$ is the overpressure, A is the test section cross-sectional area, $\rho$ and c are the density and the speed of sound of water, respectively, and t is time. Based on the above formula, the trigger strength was estimated to be about 400 J, which corresponds to 0.4-0.5% of the explosion energetics estimated for ZREX-20 and ZREX-24.

## IV. CONCLUDING REMARKS

In the triggered tests where explosions took place, the extent of oxidation of the zirconium melt was very extensive (55.8% in ZREX-20 and 92.3% in ZREX-24). As discussed above, however, the estimated explosion energetics were very small compared to the potential chemical energy available from the oxidation reaction. Modeling efforts would be needed to aid in understanding these results. Among the questions that should be answered is, what is the fraction of the total hydrogen production that took place over the explosion time period? It would seem possible that a significant fraction of the oxidation reaction occurred outside the test section after the melt and water had been expelled from the test section.

## ACKNOWLEDGMENTS

The authors wish to thank Mr. R. W. Wright for his support and guidance during the initial phase of this work. This work was performed under the auspices of the U.S. Nuclear Regulatory Commission.

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