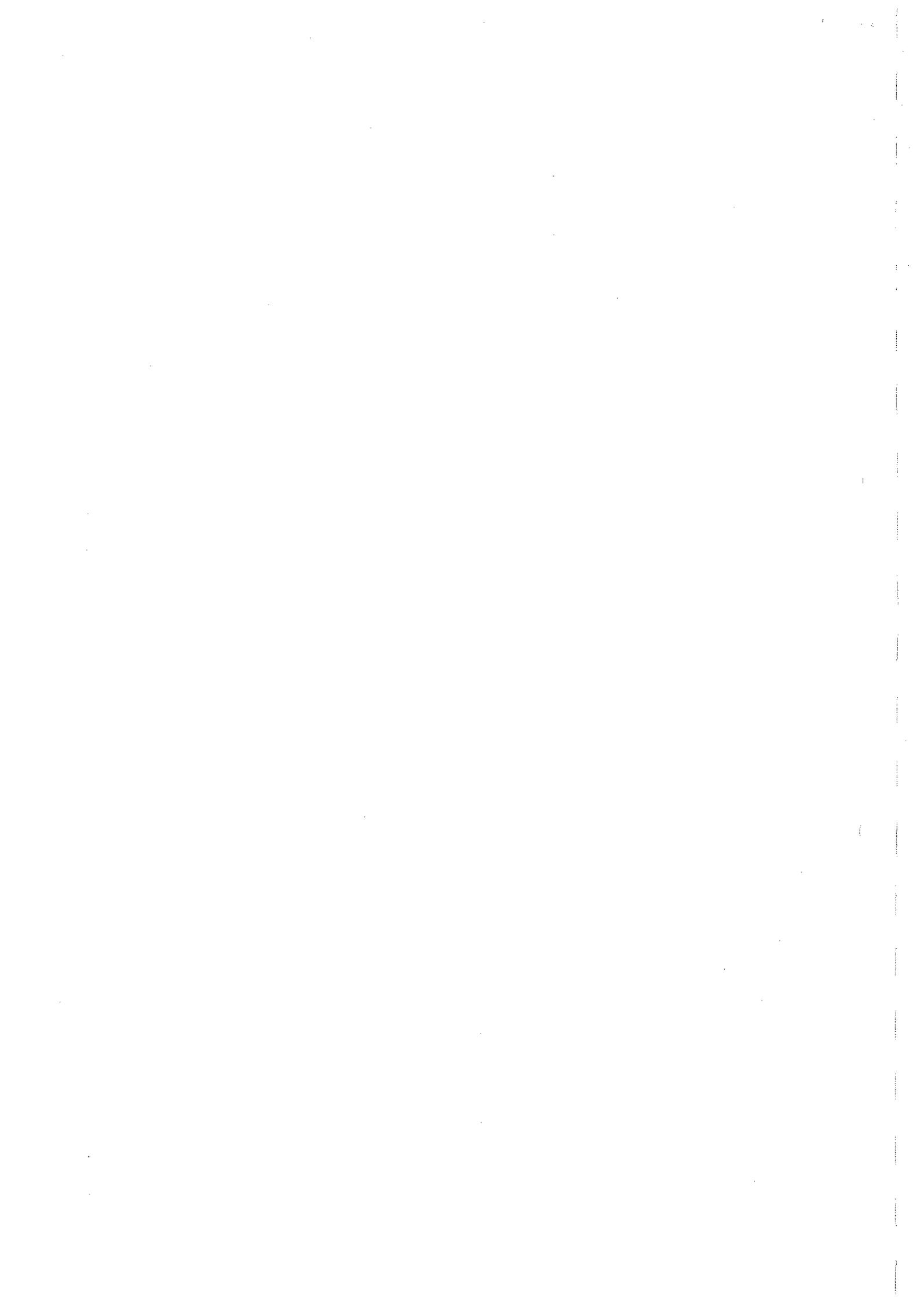


AEAT-6155

HOT CELL FACILITY FOR HYDROGEN ANALYSIS

P Ramsay

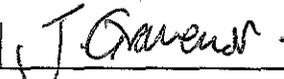
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Executive Summary

The hydrogen content of irradiated zircaloy cladding and the associated formation of brittle hydride particles is an important consideration with respect to achieving improved fuel performance. Although zircaloy itself becomes only slightly activated during neutron irradiation, significant dose rates may be associated with cladding samples owing to the presence of fission products and bonding layers at the inner surface, particularly in high burnup fuel. A hot cell is necessary for analytical work on these samples and has been constructed and commissioned at the AEA Technology Hot Laboratory.

Of the methods available for hydrogen analysis, the hot vacuum extraction (HVE) technique was chosen as being most suitable for hot cell use. Hydrogen analysis using HVE depends on the virtually complete evolution of hydrogen from zircaloy at temperatures of 1100°C and low pressures of the order of 10^{-4} Pa or better. The hydrogen is collected and its mass determined by volume and pressure measurements. Since fundamental physical quantities are measured, there is no need for calibration against standards of known hydrogen content, although standards are used to check correct operation of the equipment.

The HVE equipment incorporates a radio frequency (RF) induction furnace and high vacuum system of compact design to facilitate installation and to occupy minimum floor space in the hot cell. RF induction was chosen for rapid heating of the sample while minimising heating, and therefore outgassing of nearby components. The vacuum is maintained by a dual turbopump system having a compression ratio of 10^6 for hydrogen. The offgas is pumped into a collection volume and the hydrogen subsequently diffused out through a palladium membrane. The pressure change is then used to calculate the mass of hydrogen.

The facility is capable of the measurement of blank hydrogen levels better than ± 0.2 μg (1 standard deviation) which is the source of repeatability errors. Comparison with standard samples obtained from international standards organisations indicates that the accuracy of hydrogen determination within samples is within the ± 1 $\mu\text{g/g}$ requirement determined at the design stage. A programme of hydrogen analyses on samples of irradiated zircaloy cladding has been successfully completed.



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1 Introduction

The mechanisms of oxidation and hydriding of zirconium alloys are closely interrelated and have been widely investigated⁽¹⁾. Oxidation in water produces hydrogen, which may then recombine with oxygen, be liberated as gas, or diffuse into the underlying metal through the oxide barrier. If the hydrogen content of the metal becomes large enough, hydrides may precipitate.

The formation of hydride platelets in zirconium alloys has an adverse effect on the fracture toughness, which in the presence of stress may cause brittle failure such as the well-known phenomenon of delayed hydride cracking (DHC). The formation of hydrides depends on the hydrogen concentration and the temperature and is likely to be more pronounced at lower temperatures where the solid solubility of hydrogen in zirconium is less. At elevated temperature hydrogen has considerable mobility and may migrate down temperature gradients and to regions of higher tensile stress, such as stress concentrating features or residual stress locations, leading to enhanced hydride formation there when the temperature is reduced as a consequence of reactor shutdowns. Consequently the measurement of hydrogen concentration is an important consideration in LWR fuel performance and safety assessments.

For certain applications it is required to measure hydrogen in zirconium in the presence of fuel material, with the attendant issues of high sample activity and the effects of fission product release. This required the building of a facility that could be operated within a fully shielded cave and could achieve the desired accuracy requirements of $\pm 1\mu\text{g/g}$ (2σ) for levels less than $50\mu\text{g/g}$.

2 Method principles

After investigation into the various methods available for the determination of hydrogen, it was decided to pursue a Hot Vacuum Extraction technique for the removal of the hydrogen from the sample. A palladium membrane is used to directly measure the hydrogen released by differential pressure determination.

This method was considered the most suitable since the mass of hydrogen is measured directly. It was expected to be less affected by the release of fission product gases from irradiated fuel compared with other techniques such as thermal conductivity measurement.

2.1 REQUIRED CONDITIONS

Hydrogen has a strong affinity for zirconium, requiring both a high temperature and high vacuum to ensure that all the hydrogen is extracted from the sample. However, it is not necessary to melt the sample, an important consideration with respect to minimising fission product release from fuel samples.

The solubility of hydrogen in zircaloy obeys Sievert's Law⁽²⁾ and so the conditions required to remove the hydrogen from the sample can be determined. Using the actual offgassing leak rates obtained during tests, the overpressure in the furnace was 8×10^{-6} Pa and the temperature used was 1200°C, so that the remaining hydrogen concentration in the sample was 0.022µg/g.

3 The Rig Arrangement

The HVE rig arrangement is shown in Figure 1. The equipment comprises three main parts: a RF induction furnace for heating the sample, a collection volume for receiving the offgas, and a palladium thimble for extracting the hydrogen. Two turbopumps are provided, one for evacuating the furnace and compressing the offgas into the collection volume, and the other for prior evacuation of the collection volume. A rotary pump provides backing vacuum. A number of air actuated valves enables control of the flow of gases between each component.

3.1 FURNACE

The gas analysis vacuum furnace was supplied by Stanelco Products Ltd and uses RF induction heating of a tantalum crucible about 25mm dia. and 25mm deep to raise the sample to the required temperature. The RF energy is concentrated in the electrically-conducting crucible giving high heating rates. The furnace consists of two concentric quartz glass cylinders that are sealed by O-rings at the top and bottom, so allowing the interior to be evacuated to high vacuum and the interspace between the cylinders to carry cooling water. The induction coil surrounds the glass vacuum chamber and is far enough away from the stainless steel end fittings to avoid any significant heat losses to them.

3.1.1 Air Lock

To maintain low outgassing rates it is essential to keep the system under vacuum continuously, and so a Parker airlock is used to transfer the sample to the crucible which only allows a small quantity of air to enter the vacuum system during the transfer process. The airlock consists of a rotatable piston sealed by O-rings which has a pocket in it to receive the sample. Pushing the piston forward and rotating it takes the sample past the O-ring seals and allows it to fall into the alumina drop-tube which guides the sample into the crucible. This piston is operated by a linear air actuator which is switched on and off by the operator's manipulator. The drop tube also affords a view into the top of the crucible for an infrared pyrometer, via a quartz glass window mounted in the top of the furnace assembly.

3.1.2 Lifting Furnace

The normal arrangement for a Stanelco furnace would be that the furnace is fixed with the base being lowered to allow access to the crucible for emptying or replacement. This would not have been acceptable since the working height would be above the reach of the in-cave manipulators. The solution was to keep the crucible mount fixed and raise the whole furnace. All the components required for

the furnace are mounted on a Hepco slide, which is driven vertically up and down by a small electric motor/gearbox/screw thread arrangement.

The furnace was supplied within an aluminium frame containing only the furnace itself and the slide mechanism. The size of this frame was determined by access to caves and available floor area. Additional components were then allocated an area within the space remaining within the frame. The space constraint required careful attention to detail during rig development and assembly.

3.1.3 RF Heating Arrangement / Miller Cable

The system used to heat the sample consists of a Stanelco 18kW RF generator connected by a flexible Miller coaxial cable routed through the cave wall to the induction coil. The power pack, Miller cable and furnace are cooled by recirculated water from two separate heat exchangers, so that if an in-cave cooling pipe is ruptured any contamination egress will be confined to the one heat exchanger only. The secondary cooling water from the two heat exchangers is circulated through a large air-blast cooler located outside the cave facility that discharges the waste heat to atmosphere.

3.1.4 Service Connections

The furnace crate requires a number of supplies to enable operation, the glass walled furnace tube requires cooling water, and the valves require compressed air. Various electrical connections are required including the RF power. The constraints on these connections are:

- All these services needed to be supplied to the furnace crate in such a manner that they all can be disconnected using manipulators.
- No parts can protrude outside the frame's external dimensions
- The supplies need to move vertically when the furnace is lifted during crucible maintenance.

3.1.5 Replacement of glasses

It was apparent that the furnace glass tubes should be replaceable remotely since it was possible for a layer of vaporised metal to be deposited on their cold surfaces. If this layer is allowed to build up, it could cause an electrical RF discharge, possibly cracking the glass. This layer would also be highly radioactive following use with fuel and the replacement of these glasses was a major area of concern. The solution was found by motorising the furnace lift. If the furnace's bottom metal support block is disconnected from the motored section, then the motor pulls the glasses out of the support blocks O-rings. With the addition of tapered lead-ins to guide the replacement glasses back into the seals, the motor can be used to push the furnace back together. This technique has been successfully used to replace the pair of furnace glasses within the cave, using manipulators only.

3.2 COLLECTION CRATE

With the arrangement of the furnace crate being determined by other constraints it was decided to mount all the remaining equipment needed for the rig in a similar sized aluminium frame. The collection crate needed to contain a volume to store the sample offgases, the palladium finger to extract the hydrogen and turbo pump plus backing rotary pump to evacuate the system prior to a measurement. This crate

also contains pressure transducers, valves, cold trap, mass spectrometer, which again had to fit within the constrained dimensions. All the components used in the collection volume were 'constructed' from standard vacuum fittings, mainly incorporating the CF type connection. The bolted flanges with copper O-rings gave the arrangement much strength, so limiting the need for support mountings.

3.2.1 Palladium Finger

The palladium finger consists of a tube, 5mm diameter, 100mm long and 0.3mm wall thickness. The bore of this tube is connected via a valve to the collection volume. The outside of the palladium tube is connected to the backing vacuum to maintain a low partial pressure of hydrogen there. The whole finger assembly is then heated to 400°C by cartridge heater units.

The mechanism for the transfer of hydrogen across the tube wall⁽³⁾ involves the catalytic reaction of a hydrogen molecule with an available site on the surface. This new dissociated atom then diffuses through the metal to the low concentration side where it converts back to free hydrogen. It was found that the time taken to extract the hydrogen from the samples would progressively increase with time. This occurs when all the available reaction sites are already filled and further hydrogen extraction is limited to the slower diffusion rate through the metal. To maintain an extraction time of approximately 15 minutes it was found that after a measurement, introducing air for a period would regenerate all the reaction sites on the internal palladium surface in preparation for the next test.

It is believed that the chemical reaction sites on the surface of the palladium are susceptible to poisoning by hydrocarbons and elements such as iodine. Some of these poisons can be removed by the reaction with oxygen, but some could be permanent and so the design of the finger is such that it can be replaced in cave Figure 2.

3.2.2 Crate coupling

The first option examined for the coupling of the furnace and collection crates was to use a flexible hose and standard vacuum connectors modified for manipulator use. This was abandoned when it was realised that a suitably size vacuum hose was not very flexible and would be difficult to control in cave. The solution was to have a solid pipe connection and to move the crates.

The furnace crate is lowered onto a base frame, which included rails on which the collection crate rolls. Each crate has a 'hole' which are aligned to approach each other with a double ended 'spike' used to connect the crates together as the collection crate is pushed up and held by a lever clamp. The 'holes' are standard vacuum fittings, which are used for connecting onto a plain pipe via a compression O-ring. The 'spike', made from vacuum weld fittings, holds the O-ring and compresses it into the female fitting Figure 4.

We have found that this connection method to be almost perfect with a total leak rate of 0.023 mPa/s for the collection volume which would relate to 140 years to return to atmospheric pressure. The O-rings can also be easily replaced in cave if they become contaminated by dust picked up from the cave floor.

3.2.3 Pressure transducers

The pressures within the collection volume are measured using two Edwards Baracell capacitance gauges covering the ranges 0–15Pa and 0–1500Pa respectively. The two transducers were fitted to cover such a large range since the amount of fission gas that would be released from active fuel samples was unknown. The experience obtained shows that a 250Pa range would have been adequate. These transducers, which contain amplifier electronics, are mounted within a 25mm thick lead castle to extend their operational life.

3.3 RIG CONTROL

The rig is controlled by a computer, which interfaces with a Solartron data logger to provide a number of functions.

- To operate the rig's air actuated valves via electric solenoids.
- To switch On and Off the pumps and RF generator.
- To measure a number of parameters.

The controlling program was written at Windscale using Microsoft's Visual basic to provide the user with an on screen mimic panel which reacts to the users mouse inputs. The software either immediately carries out a single action, i.e. a valve is moved or a complete sequence of programmed actions can be performed.

The use of such a computer program allowed for

- Verification that certain conditions are met before continuing with the test sequence i.e. that the pressure is low before switching on the RF heating, this limits the risk of damage through human error or equipment malfunction.
- The pre-programmed nature of the sequences made sure that the procedure for each test was identical, i.e. the crucible and sample were always heated for the same length of time.

The program is run using a mimic screen (Figure 3) which depicts the process flow diagram. By selecting the appropriate screen button, sub-programs are run for starting pumps, hydrogen injection, heating the sample, measuring the hydrogen content of the collection volume and regenerating the palladium finger.

3.4 RESULT PROCESSING

A typical pressure trace for the collection volume recorded during a test is shown Figure 5. A computer program was used to automatically examine the trace and determine the pressure of hydrogen removed by the palladium finger. A correction is applied for the average blank level obtained during the current work programme and then this pressure is used together with the collection volume and in cave air temperature to determine the mass of hydrogen removed from the sample. The sample was weighed beforehand, and thus the sample's mean hydrogen concentration can be determined.

4 Development Experience

4.1 MASS SPECTROMETER

During the commissioning phase a quadrupole mass spectrometer was attached to both the collection volume and furnace section, in order to identify air leaks and the source of extraneous gases originating from cracked hydrocarbons and other contaminants.

A 0-300 atomic mass unit quadrupole detector was fitted in the collection volume when the rig was installed in cave. This has not been used for the study of fission gases liberated from fuel since the electronic amplifier would have a limited life in-cave. Until a programme of work warrants its use, the amplifier has not been posted into the cave.

4.2 BLANK LEVEL HYDROGEN

Owing to the presence of water vapour from outgassing and diffusion through O-ring seals, the high crucible temperature, and the catalytic properties of the tantalum crucible, hydrogen will be produced to some extent even with no sample present. Since this is the largest source of error in determining the hydrogen quantity this blank level should be as low as possible and as constant as possible. During the initial non-active commissioning it became apparent that blank levels were unacceptably high and variable. The variability of the results was largely caused by the practice of allowing the crucible to cool immediately after the hydrogen extraction process, so that hydrogen backstreamed from the turbopump and was re-adsorbed by the crucible and sample. The variability could be much reduced by keeping the crucible at temperature throughout the extraction process until the hydrogen measurement was complete and the system could be completely evacuated.

4.2.1 Different O Ring Seals

High blank levels were traced to diffusion of water vapour through the silicone O-ring seals isolating the water coolant from the vacuum system. The substitution of the O-rings with a type that have low moisture permeability produced a large reduction in the blank level and its variability Figure 7.

4.2.2 Hydrocarbon contamination

When a new crucible is used, larger than expected quantities of hydrogen are liberated during the first few blank measurements. Use of the mass spectrometer confirmed that this was due to the breakdown components of hydrocarbons, which may come from the use of cutting fluids used during the manufacture of the crucibles, not all of which can be removed by washing in solvents and some of which are also a source of hydrocarbons.

4.2.3 Water absorption

During a programme of tests the furnace and collection volumes are continuously maintained at the zero pressure regime. When a blank test is carried out in the morning a significantly larger quantity of hydrogen is liberated than in further blank tests. This first reading is therefore rejected as being part of a daily degas

programme. It is possible that the water leaking past the furnace O-rings is adsorbed onto the tantalum crucible giving a large hydrogen evolution when heated up for the first time during the day.

4.3 STANDARDS

The principle of the HVE method of hydrogen measurements does not require a calibration with known amounts of hydrogen. The amount of hydrogen is measured directly with only pressure and volume measurements needed. To confirm that all the hydrogen in a metallic sample is extracted, and that all the hydrogen is removed from the rig via the palladium finger, hydrogen in titanium standards were used. These standards were obtained from international organisations who have used a number of laboratories to measure the hydrogen levels in production material.

A large number of 'Standard' measurements have been carried out whilst the rig has been in cave. Typically a measurement of the hydrogen concentration in 0.4g of titanium is done between each actual sample measurement. Also a large number of 'Blank' measurements are carried out to confirm that conditions within the rig are not varying Figure 6.

The program of measurements using the standards showed that:

- Using these standards the rig appeared to give slightly high values, by approximately 3% higher for the 49ppm hydrogen standards.
- The variability in measured hydrogen concentration originated in the samples and not the rig. The standard deviation did not reduce when multiple samples were used.
- No hydrogen released from the samples was 'lost' to absorption or reaction with the materials of the rig or to fission products deposited within the rig. The values obtained for 'standards' remained constant during the analysis programme of samples with fuel.

4.4 LIQUID NITROGEN

The rig contains two liquid nitrogen cold traps to limit the spread of fission products. The collection volume cold trap can condense a large proportion of the xenon fission gas released from the heated sample, so possibly allowing the higher resolution pressure transducer to be used. It was found that most of the fission products condensed on the furnace glasses and that the xenon condensation temperature was too close to the liquid nitrogen temperature for reliable extraction to occur. Therefore the operation of these cold traps was not advantageous.

4.5 TEST OPERATION

Before the rig could be used the whole system needed to be maintained under vacuum for 24h to outgas the system after first starting up or after returning to atmosphere for modifications or maintenance. Subsequently after introducing the sample for analysis via the Parker airlock, a few minutes further evacuation is

necessary to ensure removal of all the air introduced with the sample. The automatic test programme can then be started via the computer display, which carries out the following sequence:

- 1 minute is allowed to record the cold outgassing rate.
- The furnace is switched on and a crucible temperature of 1200°C is maintained for 13 minutes to ensure that all the hydrogen has been removed from the sample and collected.
- Valve V0 is closed to separate the furnace and collection crates, and isolate the extracted gasses.
- The system is allowed to stabilise for 3 minutes.
- Valve V8 is opened to allow the hydrogen to diffuse out through the palladium finger, which is maintained at a temperature of 400°C.
- After 20 minutes to allow all the hydrogen to be extracted, the whole rig is evacuated for 5 minutes before switching off the RF heating.
- After the crucible is cold, 200Pa of air is introduced to the Palladium finger for 5 minutes to regenerate the reaction sites on its surface.
- After this air is removed the rig is ready for another test.

4.6 ACCURACY OF MEASUREMENT

The accuracy of an analysis may be affected by errors in collection volume, pressure reading, and variability of the blank hydrogen level. The volume was measured by introducing an extra volume into the collection volume and using pressure ratios, that new volume being previously measured by filling with distilled water and weighing. The readings from the two pressure transducers were continually compared for scaling inconsistencies and linearity was checked by assuming that over these pressure ranges, outgassing rates were constant. The use of standards containing known levels of hydrogen also confirmed the accuracy of the measuring system.

Standard	Declared H ₂	Measured H ₂
BCR - H ₂ in Ti	12.2 ±0.8 µg/g	13.8 ±1.4 µg/g (10 Samples)
NIST - H ₂ in Ti	49.0 ±0.9 µg/g	50.9 ±2.6 µg/g (69 Samples)
NIST - H ₂ in Zr	107 ±3 µg/g	108.1 ±0.3 µg/g (3 Samples)

The results of the blank determinations made in cave are shown in Figure 6 in chronological order. There are no trends apparent in the results, which appear to be normally distributed. As discussed above, the blank levels in the first determination of the day tended to be high, due to water vapour adsorption by the crucible. Therefore a blank run was carried out at the start of each day to drive off the accumulated water vapour, and its result rejected. The mean blank level of the Figure 6 data is 0.91 µg with a standard deviation of 0.22 µg. Thus for a sample size of 1g the resolution will be ±0.22 µg/g (1σ). As the required resolution is ±0.5 µg/g (1σ), a sample size of 0.5g is sufficient.

5 Conclusions

- A facility for the measurement of the concentration of hydrogen in material containing irradiated nuclear fuel has been successfully built and operated at the AEA Technology Windscale laboratory.
- Detailed engineering has enabled a high vacuum rig to be remotely operated within a standard cave facility.
- Hydrogen released from a sample can be measured with a repeatability that enables a $\pm 0.5 \mu\text{g/g}$ (2σ) determination from small 0.5g samples.

6 Acknowledgements

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Mr G Farran

Mr J Cooke

Dr J G Gravenor

Mr I E Wilson

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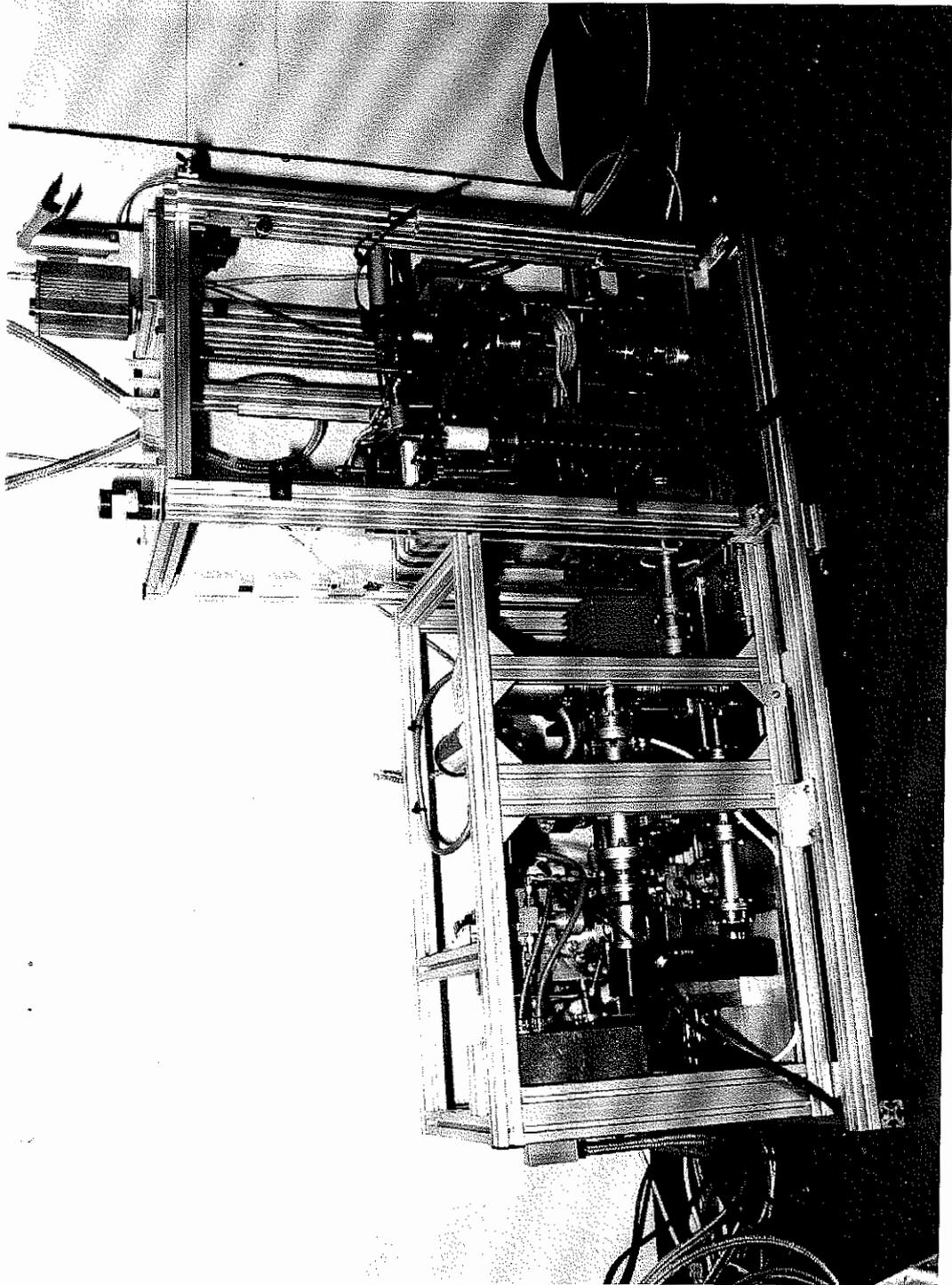


Figure 1 The Hot Vacuum Extraction Rig

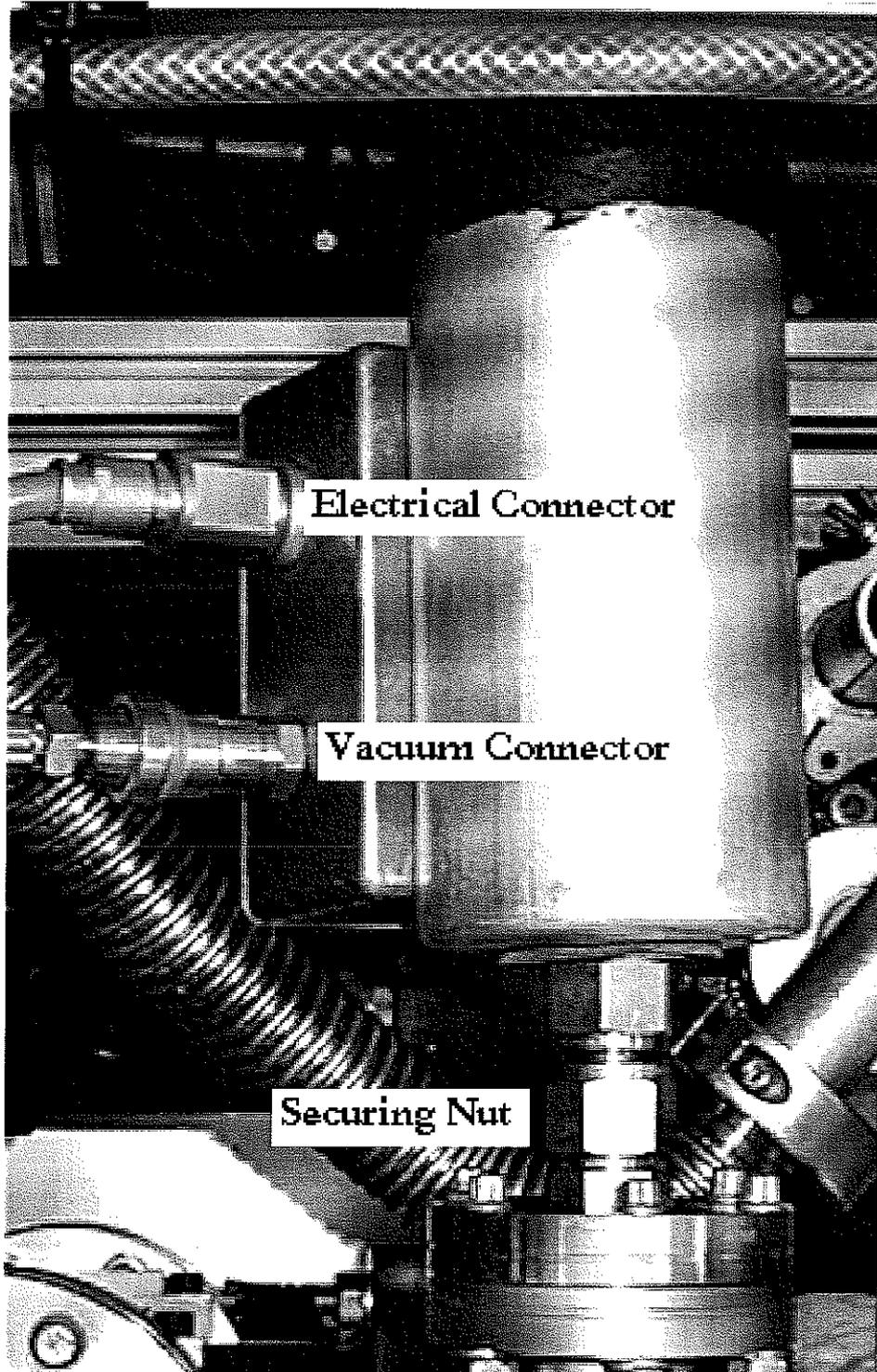


Figure 2 Palladium Finger Module

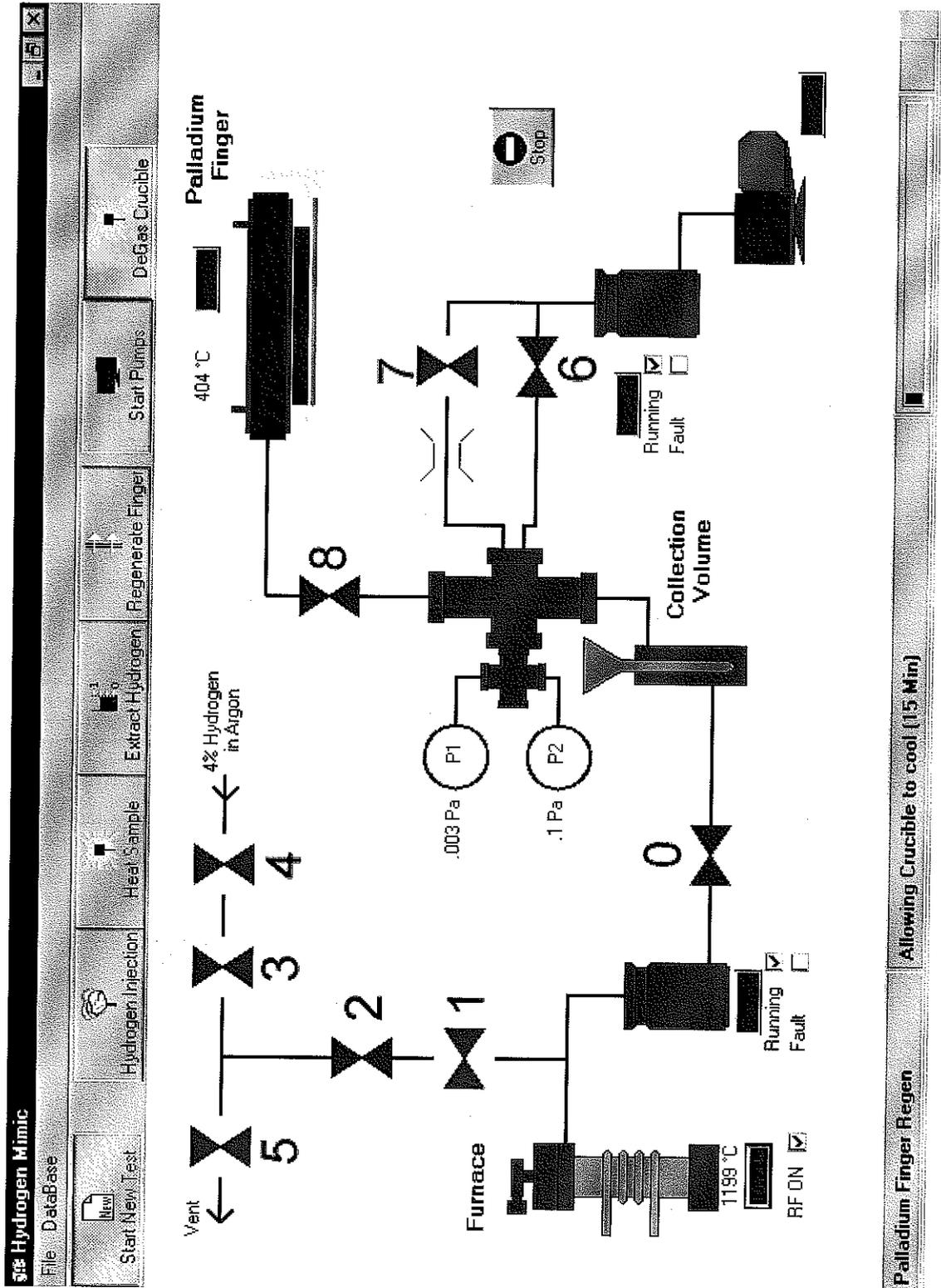


Figure 3 Computer Mimic Diagram

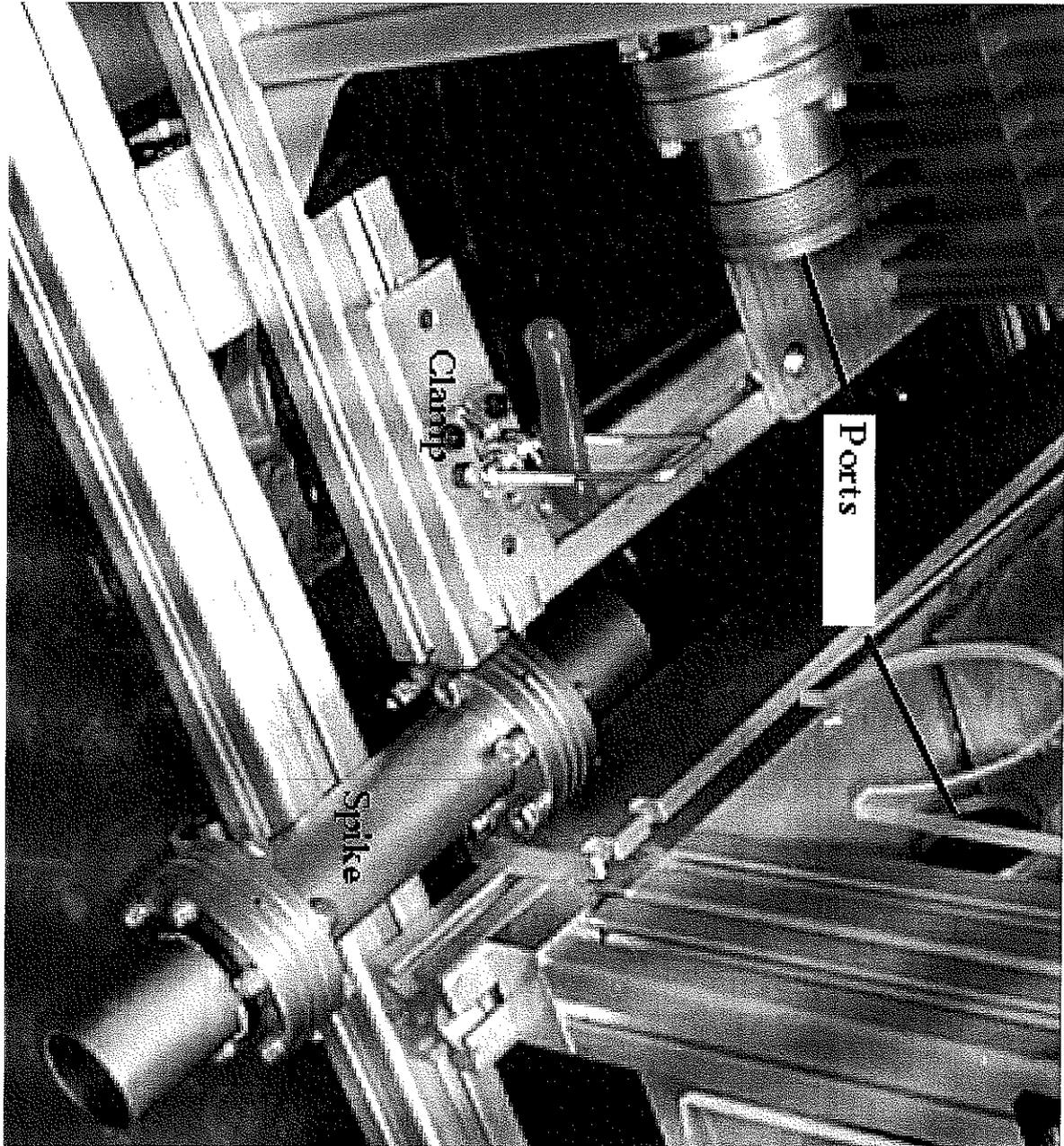


Figure 4 Interconnection 'Spike'

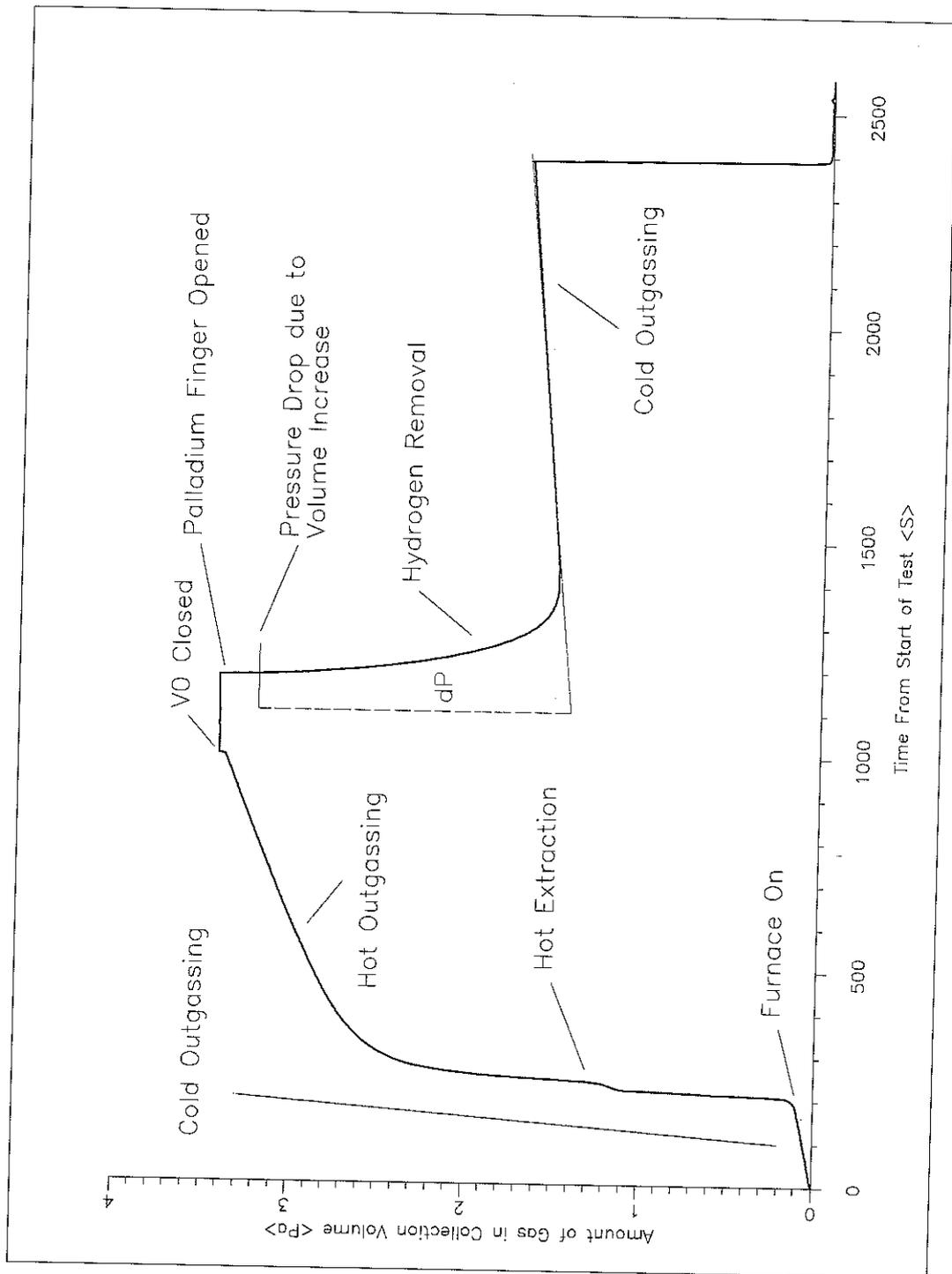


Figure 5 Collection Volume Pressure Record

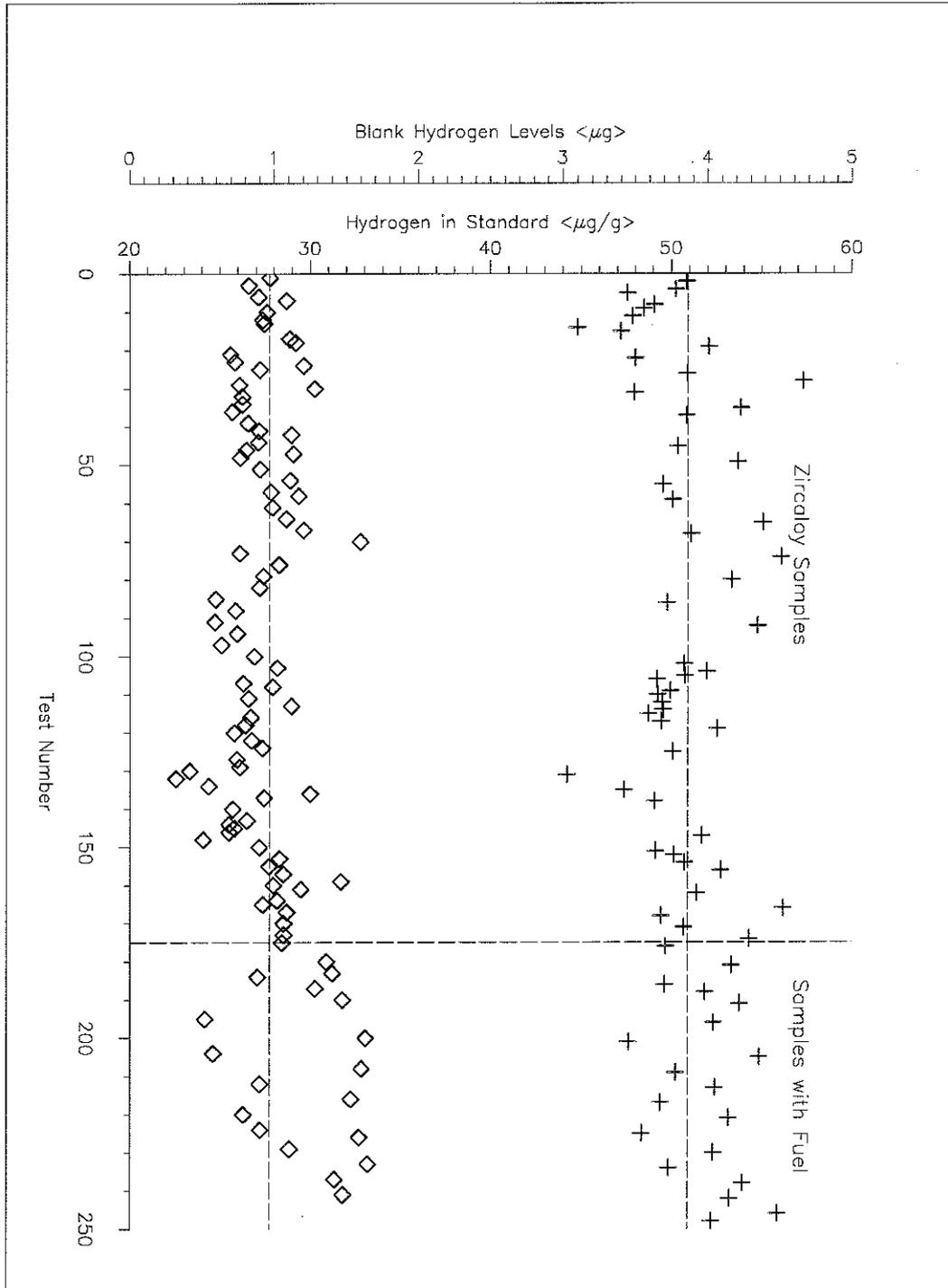


Figure 6 In-Cave Results ('Blanks' and 'Standards')

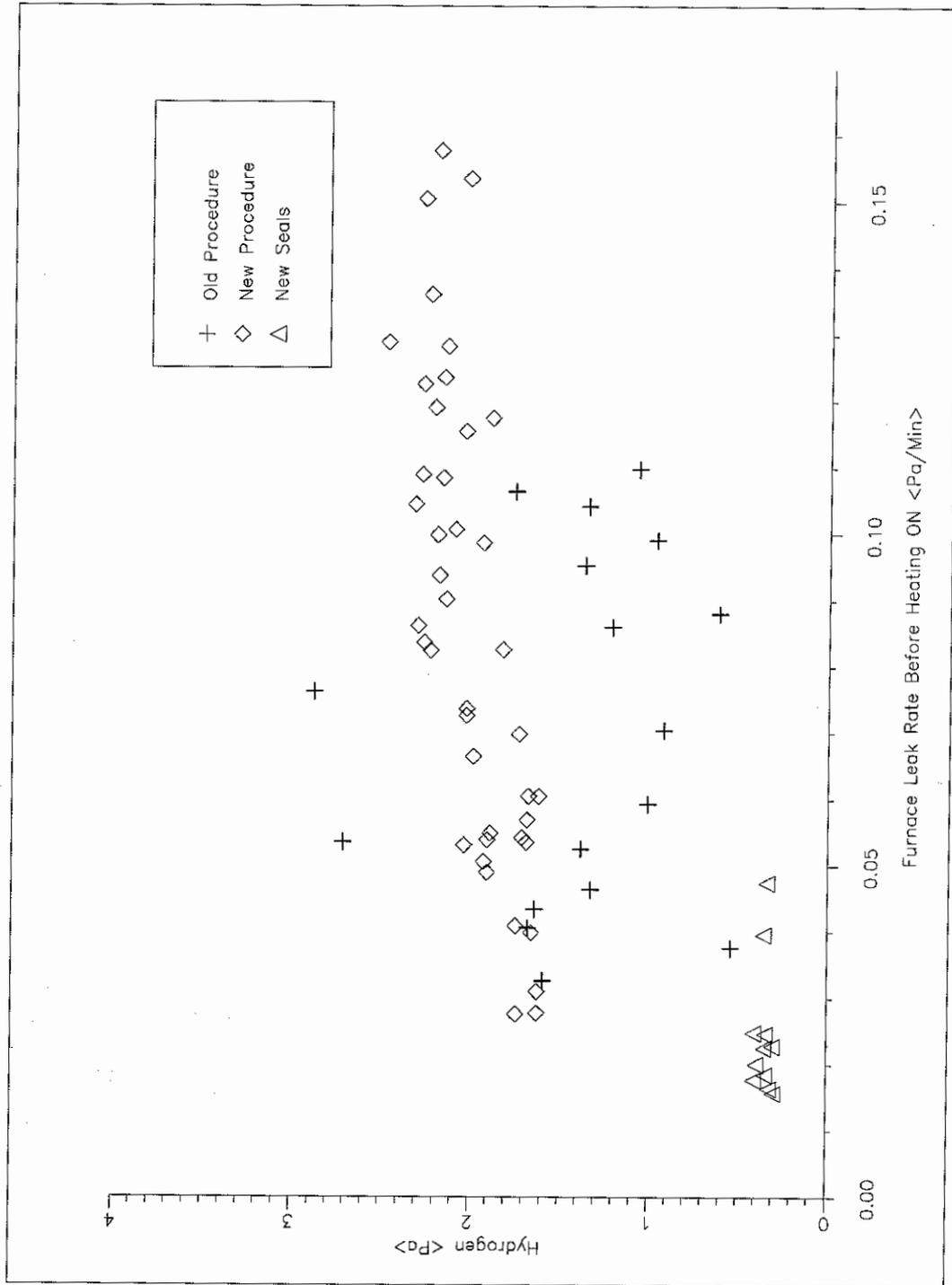


Figure 7 Effect of Furnace Glass Seals

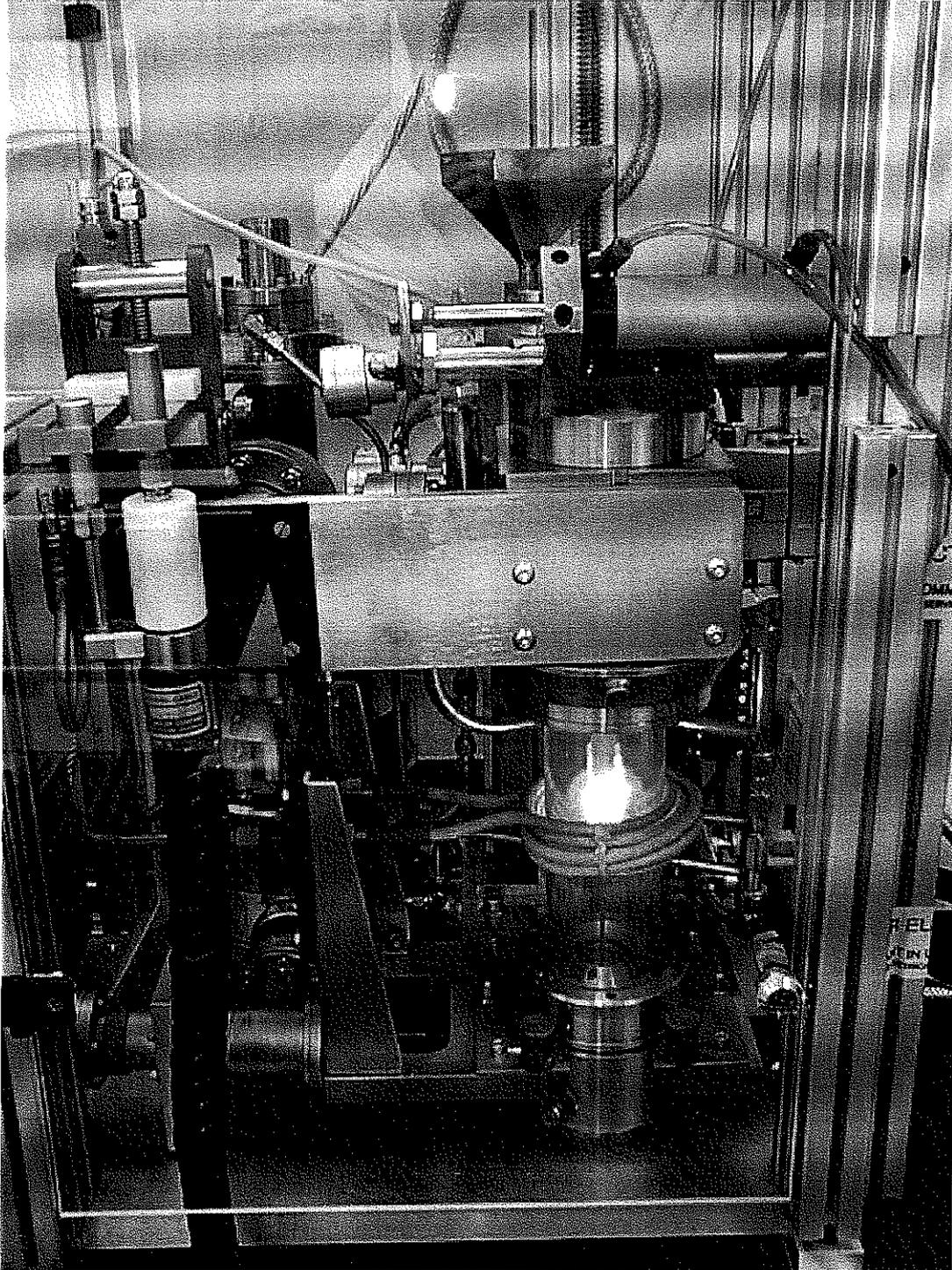


Figure 8 Testing of Furnace

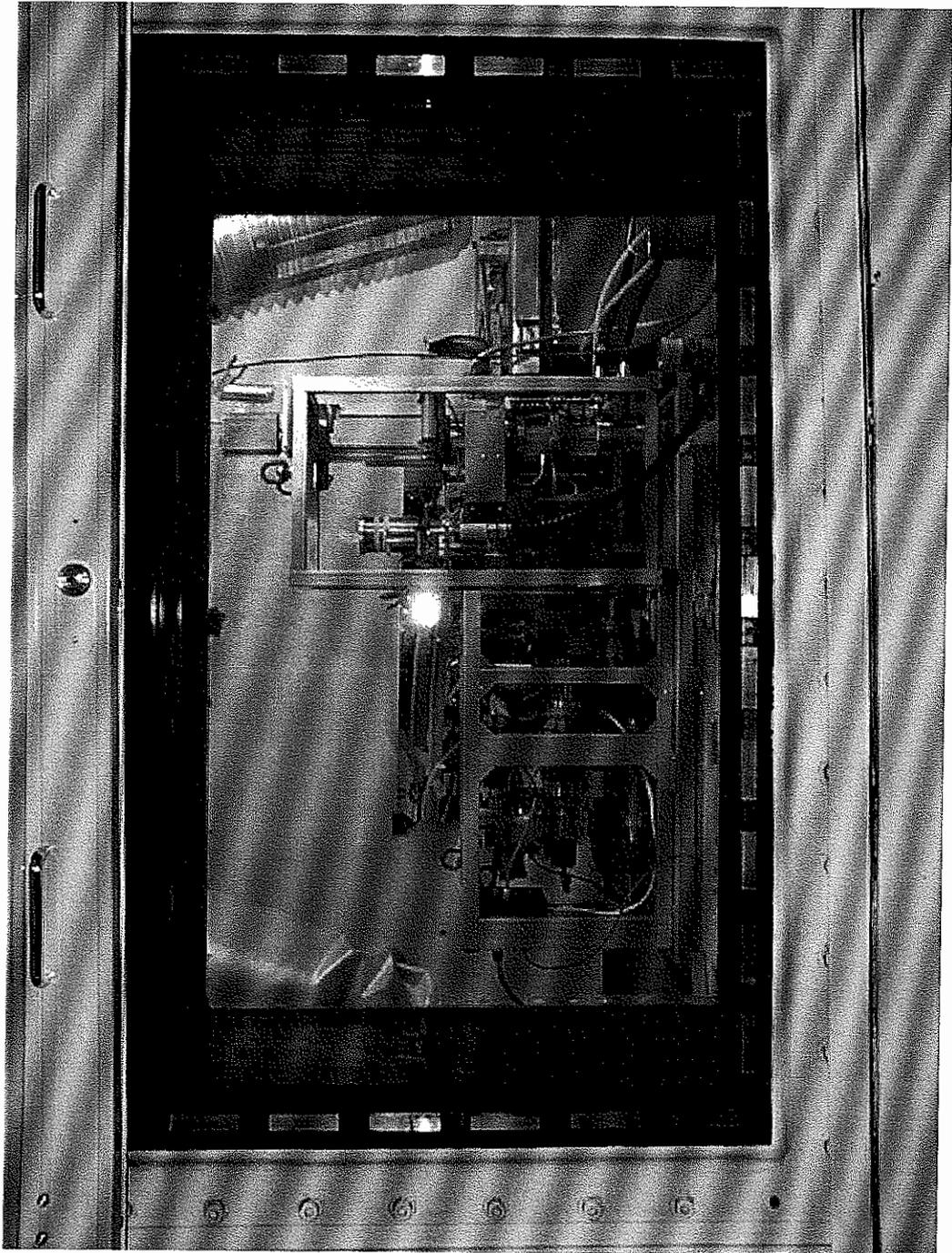


Figure 9 HVE in Cave

