# NNWSI WASTE FORM PERFORMANCE TEST DEVELOPMENT

CONF-841157--17

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CONF-841157--17

DE85 002745

## ABSTRACT

A test method has been developed to measure the release of radionuclides from the waste package under simulated NNWSI repository conditions, and to provide information concerning materials interactions that may occur in the repository. Data from 13 weeks of unsaturated testing are discussed and compared to that from a 13 week analog test. The data indicate that the waste form test is capable of producing consistent, reproducible results that will be useful in evaluating the role of the waste package in the long-term performance of the repository.

## INTRODUCTION

The Nevada Nuclear Waste Storage Investigations Project (NNWSI) is investigating the volcanic tuff beds of Yucca Mountain, Nevada, as a potential location for a high-level radioactive waste repository. One of the topics to be addressed during this investigation is the performance of waste package components in the repository at the termination of the containment period, i.e., following the 300-1000 year period during which containment of high level waste within the waste package will be substantially complete [1].



The containment period is followed by the isolation period during which the potential for canister breach and subsequent groundwater/waste form contact exists. Radionuclide release from the waste package would then be possible, although in accord with Nuclear Regulatory Commission regulations [1] the total release rate must be less than one part in $10^5$ per year of the total repository inventory of a particular radionuclide after the 1000 year period.

To measure this radionuclide release, a test method is required that incorporates the interactions between the waste package components and the groundwater under realistic repository conditions. Release results obtained in this fashion could then be used as source term data in modeling the long-term behavior of the repository. NNWSI is developing such materials interaction tests and using them to produce waste form release data.

The first test is a rock cup, total submersion test [2] while the second test, termed Unsaturated, is a more realistic simulation of conditions expected in the unsaturated zone in tuff. This report summarizes the Unsaturated waste form test procedure, and provides some results from 13 weeks of testing. Also presented are the results of analog testing which relates the Unsaturated test to repository conditions.

## NNWSI WASTE FORM TEST DEVELOPMENT FOR THE UNSATURATED ZONE

The guiding principle behind the development of the Unsaturated test is to provide reliable data using a test matrix and procedure that are simple enough to be performed and interpreted by different laboratories, and that can produce results within a useful time period. Considerable emphasis is placed on reliability, which implies that the data must be reproducible, site-relevant, and of good enough quality to be used in further applications.

The NNWSI repository site is located in the unsaturated zone in tuff. This introduces a degree of variability to establishing an experimental method for which there is limited experience to use as reference. It is recognized that the effect of any variable could affect the behavior of the waste package in an unanticipated manner. Yet, to study the effect of each variable in the test method would not be practical. The best approach was believed to require identification of important variables and physical processes, assignment of reasonable values, and performance of the test.

Under the restricted set of experimental conditions only radionuclide release from the waste package make up reportable data that can be used directly in repository modeling. The experimenter is given freedom to study other effects, but the use of this information is solely to guide or interpret other experiments or to suggest modifications to the Unsaturated test procedure.

The utility of the data depends on the selection and restriction of the repository conditions and on the materials interactions that are incorporated into the test. The rationale used for selecting test conditions and variables was to address those materials interactions that may exist in a repository during the isolation period. The materials consist of the waste form and the canister overpack. No packing material is included because it is not part of the reference waste package [3]. The interactions are promoted by contact between water and air and the waste package components. The test provides for several interactions to occur and allows the experimenter to assess the importance of each. During actual repository disposal each waste package may not be subjected to all possible materials interactions. The experimental design simulates interactions, but does not attempt to model the current waste package conceptual design.

The anticipated repository conditions impose constraints on several parameters that could affect release from the waste package. The test conditions were chosen to simulate conditions that may exist in the repository after 300/1000 years of burial, attempting to anticipate worst-case, but realistic bounds. The test conditions are:

1) temperature is 90°C;
2) water contacting the waste package is actual J-13 well water that has been reacted with tuff at 90°C;
3) the amount of water that contacts the waste package is a function of the type of waste being tested and the associated package design. A contact rate is given for defense and commercial glass, and spent fuel;
4) canister material is Type 304 L stainless steel, aged as required;
5) contact mode is dripping water with a drop volume of ∿0.1 mL per drop, based on laboratory observations of saturated tuff samples;
6) rock is Topapah Spring tuff (the candidate repository horizon);
7) pressure is set at 1 atm (100 kPa) by repository conditions; air is assumed saturated with water vapor; and
8) temperature differential between the waste package and the test vessel is based on the thermal equilibration of test components.

Additional conditions have been incorporated into the test procedure to provide the experimental simplicity necessary to obtain reproducibility. These constraints are mentioned and more detail is given elsewhere [4].

1) waste form shape, dimension, and physical description;
2) waste form/canister contact; and
3) degree of component aging.

The parameters described above are limitations placed on the test to provide a reference scenario and to ensure data reliability.

## NNWSI UNSATURATED TEST DESCRIPTION AND PROCEDURE

During the isolation period it is assumed that the canister will be breached and that air/water/waste form/metal interactions will occur. These interactions may, in part, consist of the waste form being contacted by either water or water saturated air. The contact could be via either standing or flowing water and could be at a metal/waste form interface or isolated on the waste form. The metal could contain weld affected and nonaffected regions, and the waste form (glass) will likely be stressed. All the components will have undergone aging during the containment period and will undergo further changes due to reaction during the isolation period. The test procedures and the design of the test apparatus and associated solid materials create opportunities for these types of interactions to occur, but are specifically not designed to be a miniature model of the waste package.

The test apparatus is shown diagramatically in Fig. 1. The components are the test vessel, which provides for collection and containment of liquid and support of the waste package; the waste package which consists of the waste form and metallic components representing the canister; the tuff cup, which acts to collect the solution that drips directly from the waste package and which interacts with vapor; the tuff cup supporting ring which separates the tuff cup from the test vessel; and a solution feed system to inject test water.

Specimens representing the anticipated NNWSI waste package components (waste form and canister) are contacted intermittently by dripping repository water. The nature and degree of radionuclide release from the waste

Fig. 1. Test Apparatus Used for NNWSI Unsaturated Testing

package is determined by collection and analysis of the water that has contacted the package and by surface analysis of the waste package components. Materials interactions are noted.

The test schedule incorporates batch and continuous testing. In the batch mode, tests are terminated at selected 13 week time intervals. The test apparatus is disassembled, and analyses of both the solution and components are performed. In the continuous mode the waste package (including liquid associated with the waste package) is transferred to a new test vessel, and the test is continued. Analyses can be done on the solution in the old vessel. Using the continuous testing matrix, replication of solution analysis can be achieved, investigation of the test components is possible at the termination points, yet the test can continue indefinitely or until information most useful to repository evaluation is obtained. A detailed description of the apparatus and test procedure is provided by Bates [4].

## INTERIM UNSATURATED TEST RESULTS

A series of tests using the Unsaturated procedure are in progress. These tests are being done with SRL 165 frit borosilicate glass that is doped with uranium, cesium, and strontium [5]. The tests have been completed through the initial 13 week period using the batch testing mode and through two 6.5 week sampling periods using the continuous testing mode. At this point no trends or positive conclusions can be made regarding the results, however, several pertinent observations can be made.

1. A priori it can be judged that the extent of the water/glass contact will greatly affect the amount of release that occurs. Any aspect of the test design that influences this contact is, therefore, a critical test parameter. The appearance of the test components at the termination of the 13 week test provides an indication as to how and where interactions occur. At this time the top surface of the test assembly is covered by a thin layer of water which evaporates within 30 seconds of opening the test vessel. The sides of the glass are watermarked (Fig. 2) and there is a considerable amount of standing water around the bottom of the assembly. From these observations the method of contact between the water and the waste form can be ascertained. After initial contact with the test assembly, the water spreads rapidly over the top surface and down the sides of the glass. Little standing water remains on the top surface because flow is promoted by the tight fit that exists between the perforated metal and the glass. However, at the bottom interface (see Fig. 2) more water collects and some interaction occurs. Thus, to some degree the test incorporates water reaction with the test components via both thin film and standing water interactions. These types of interactions are expected to exist during the isolation period.

The type and degree of water/package component interaction is important and the effect of varying this parameter is being studied in parametric testing [5]. Tests are being done with no metal present, with metal of varying degrees of perforation and flow retarding design, and with waste forms with differing ratios of cut to as-cast surfaces. Details of these experiments are given elsewhere [5], but of interest is that when no metal is present the waste form actually gains weight during the testing periods due to the formation of calcium-containing species.

2. There is considerable reaction between the glass and the bottom part of the canister as evidenced by discoloration of the glass and

Fig. 2. A Photograph of NNWSI Unsaturated Test Glass Waste Form after 13 Weeks of Testing. The glass is located on a metal stub. Watermarked areas where reaction has occurred are evident on the sides of the form, especially around the bottom, and on the top cut surface where the holes in the perforated metal existed.

the canister. The same type of reaction was also seen in earlier tests. This reaction is focused mainly, but not exclusively, around the weld affected area of the canister. A considerable amount of rust colored flakes are present in the solution. Examination of these reacted areas in earlier testing indicated the reacted areas consist of iron and chromium silicates [6].

3. Weight loss measurements were made for the waste package components. For the waste form the normalized weight loss for both samples was 0.25 g/m$^2$. As was observed in previous tests [6] weight loss measurements are consistent between samples and offer a good method of monitoring the gross reaction of the waste form. The perforated metal pieces, in most cases, actually gained weight during the test period, due to the formation of alteration products on the surfaces.

4. When tuff is present in the test, the degree of waste form reaction can be measured by the amount of Li, B, and U in solution. Lithium provides the most consistent results, probably because it does not interact with any of the test components. Li release from the 13 week tests gave a normalized elemental loss of $\sim$0.2 gm/m$^2$ based on the total surface area of the waste form. Boron release, as had been observed previously [5], was more erratic, but still the $(NL)_B$ values, 0.14 and 0.22 gm/m$^2$ are not too different than $(NL)_{Li}$, which would be expected. U release, as based on solution analysis, was quite low, and varied between $(NL)_U$ of 0.008 and 0.022 g/m$^2$. Uranium is expected to interact with both tuff and stainless steel and an analysis of these components must be done to fully describe the uranium behavior.

Based on the above observations, preliminary conclusions of the Unsaturated test method are that reproducible materials interactions have been achieved for the terminated tests. For these tests, waste form degradation is similar, based on the overall appearance of the waste package components, normalized mass loss from the waste form, and normalized elemental losses for those elements representative of the waste form.

## ANALOG EXPERIMENT

In order to establish the relationship between the unsaturated test and the repository, an analog test is being performed. The analog test attempts to more closely simulate anticipated repository conditions than the Unsaturated test and is necessary because some of the constraints required in a controlled Unsaturated test procedure may not exist in a repository. If these test constraints cause a significant deviation between the analog and Unsaturated test results, then the data obtained by use of the Unsaturated test may not be a reasonable repository simulation and should be questioned if used in repository modeling.

The analog test utilizes a tuff rock core the shape of a right circular cylinder, 5" in length and 2-1/2" in diameter, as a reaction vessel (Fig. 3). Each core is cut diametrically to give two sections. A cavity is machined in the larger section (Fig. 3) to accommodate a test assembly similar to that used in the Unsaturated test. The dimensions of the cavity are similar to the inside of the Unsaturated test vessel, except that the upper section of tuff, which acts as the vessel lid, had a flat lapped surface.

Fig. 3. Diagram of Analog Test Apparatus

The test was initiated by placing the waste package in the cavity and placing both sections of J-13 saturated tuff into a Teflon™ sleeve. The mating surfaces of both tuff sections had lapped faces which produced a good seal. The teflon sleeve was placed in a stainless steel holder and end caps were secured over the top and bottom of the tuff core. The end caps were tapered so they only contacted the tuff along the outside edges. The end caps were connected to inlet and outlet tubing. The Teflon™ containment was sealed by water which pressurized the Teflon™ jacket to 1600 psi. This provided for flow through the tuff core and not at the Teflon™/tuff interface.

The input of water to the tuff core was supplied by a storage reservoir of water that was heated to ~140°C. The inlet line was also heated. The goal was to supply the tuff core with an evenly distributed supply of water vapor. The rate of flow through the tuff core could be regulated by the temperature (pressure) of the storage reservoir. Water, after passing through the tuff core, was collected in a vented bottle for analysis of radionuclides, cations, and anions.

The first analog test was initiated with a projected flow of ~0.2 mL/day. This is roughly the maximum flow that would be expected through a bore hole containing DWPF waste. The initial water temperature was set at 140°C. DWPF glass spiked with with $^{133}$Ba, $^{137}$Cs, and $^{152}$Eu was used as the waste form. $^{137}$Cs was used to represent highly mobile, easily leached elements, but is not expected to be a significant radionuclide during the isolation period. $^{133}$Ba was used to represent the alkaline earth group of elements. Again few of these elements will be of concern during the isolation period. $^{152}$Eu was used to represent fission products and actinide elements that are slowly removed from the glass and will be important during the isolation period.

The test was terminated after ~3 months of constant flow. The core was carefully disassembled and observations were made of all components. The test assembly was rinsed with ~10 mL of high purity water which was analyzed for cations and radionuclides. The tuff sections were γ-counted and the bottom section was cut diametrically just above the bottom of the cavity for further counting. Of interest was whether the radionuclides were located at the bottom of the cavity or spread over the walls, bottom, or top of the cavity. The test assembly holder was also γ-counted.

Several observations can be made:

1. Upon disassembly, the test assembly was visually dry on the top and wet on the bottom. The sides of the glass had watermarks similar to those observed in the final version of the unsaturated test. Overall, the waste package had an appearance identical to one from the Unsaturated test.

2. The weight loss from the glass was 0.14 mg after ~90 days of testing. This corresponds to a normalized weight loss of 0.1 g/m$^2$. In Unsaturated testing the weight loss after ~90 days of testing is 0.35 mg or $(NL)_{wt}$ of 0.25 g/m$^2$. These values are in remarkable agreement.

3. The elemental releases for B, Li, and U as measured by what was rinsed from the test assembly, are also similar to values for test assembly rinses reported in earlier testing [5]. The total amount of each of these elements that is released from the waste package cannot be directly determined because each is a minor constituent of the tuff. However, the waste package rinse provides a means of measuring the amount of these elements that is present in the standing water in contact with the waste package and is an indication as to the extent of the glass/water interaction.

4. Release of $^{152}Eu$, $^{133}Ba$, and $^{137}Cs$ was found to occur. These radionuclides were found either in the test assembly rinse, on the bottom of the collection cavity, or on the waste package holder. No radioactivity was found on the top of the cavity or on the walls of the cavity. This would indicate the radionuclides were transferred from the test assembly to the tuff by dripping from the waste package. Normalized release values for these elements are $(NL)_{^{152}Eu} = 0.03$, $(NL)_{^{137}Cs} = 0.2$, and $(NL)_{^{133}Ba} = 0.09$ g/m$^2$. These values are below the 1 part in $10^5$ required by the NRC, and are in the range calculated from the Unsaturated test solution analyses.

5. The canister sections, particularly the bottom section, show signs of corrosion. Each section shows a weight gain which is due to reaction with components of the glass and the J-13 water and occur at the glass/metal interface. This type of corrosion was also noted in unsaturated testing.

The results of the 90 day analog test are very similar to unsaturated test results for similar time periods. However, they are the results of only one test and may represent only a portion of possible material interactions. Analog tests that will run for six months and one year duration are in progress. The results of these tests will be compared to unsaturated test results, and if the analog test can be shown to be a reasonable simulation of the repository, then it may be possible to judge the relevance of the Unsaturated test to the repository environment.

## CONCLUSIONS

Preliminary results of tests done using the NNWSI unsaturated test method indicate that consistent reproducible results can be achieved. A close relationship between the laboratory environment of the Unsaturated method and a more realistic repository environment, as simulated in the analog tests, is also indicated. These observations provide confidence that data acquired in longer term Unsaturated testing will establish trends that will be applicable in modeling long-term NNWSI waste package behavior.

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fig 1a

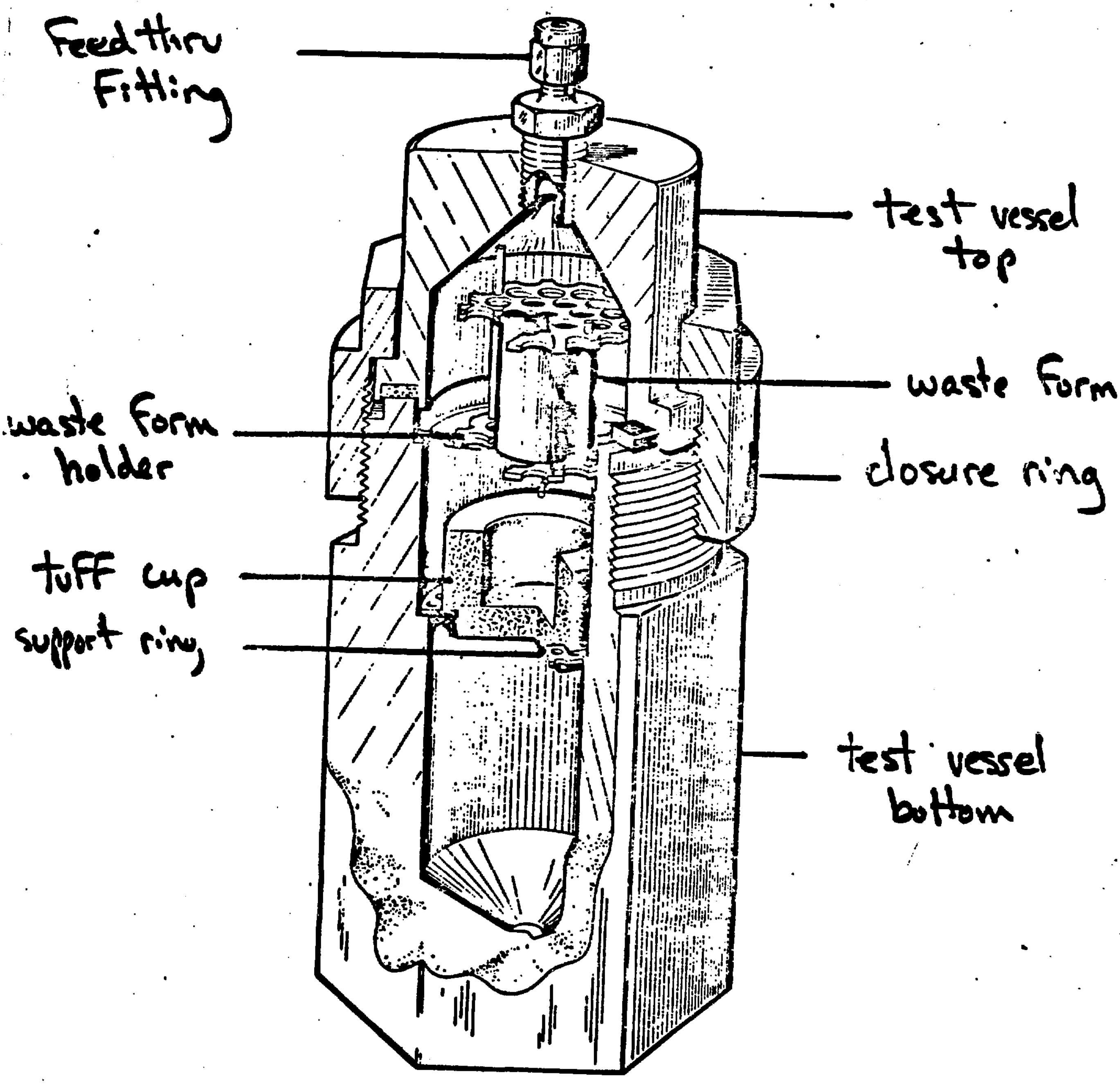

Feed thru Fitting
test vessel top
waste form
waste form holder
closure ring
tuff cup
support ring
test vessel bottom

fig 2

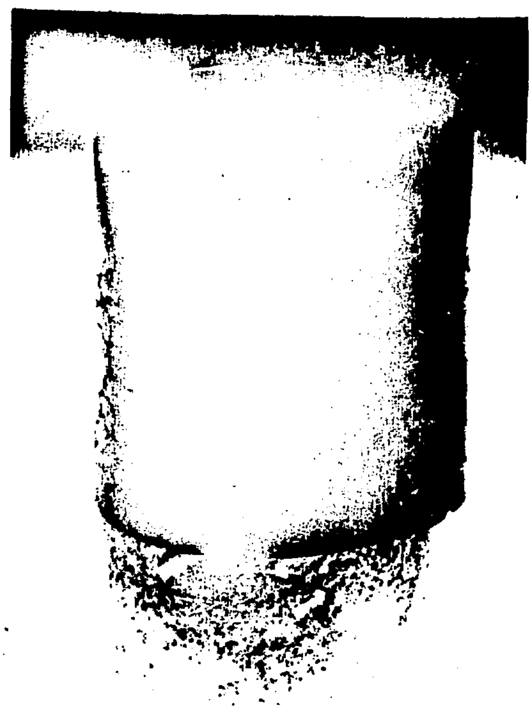
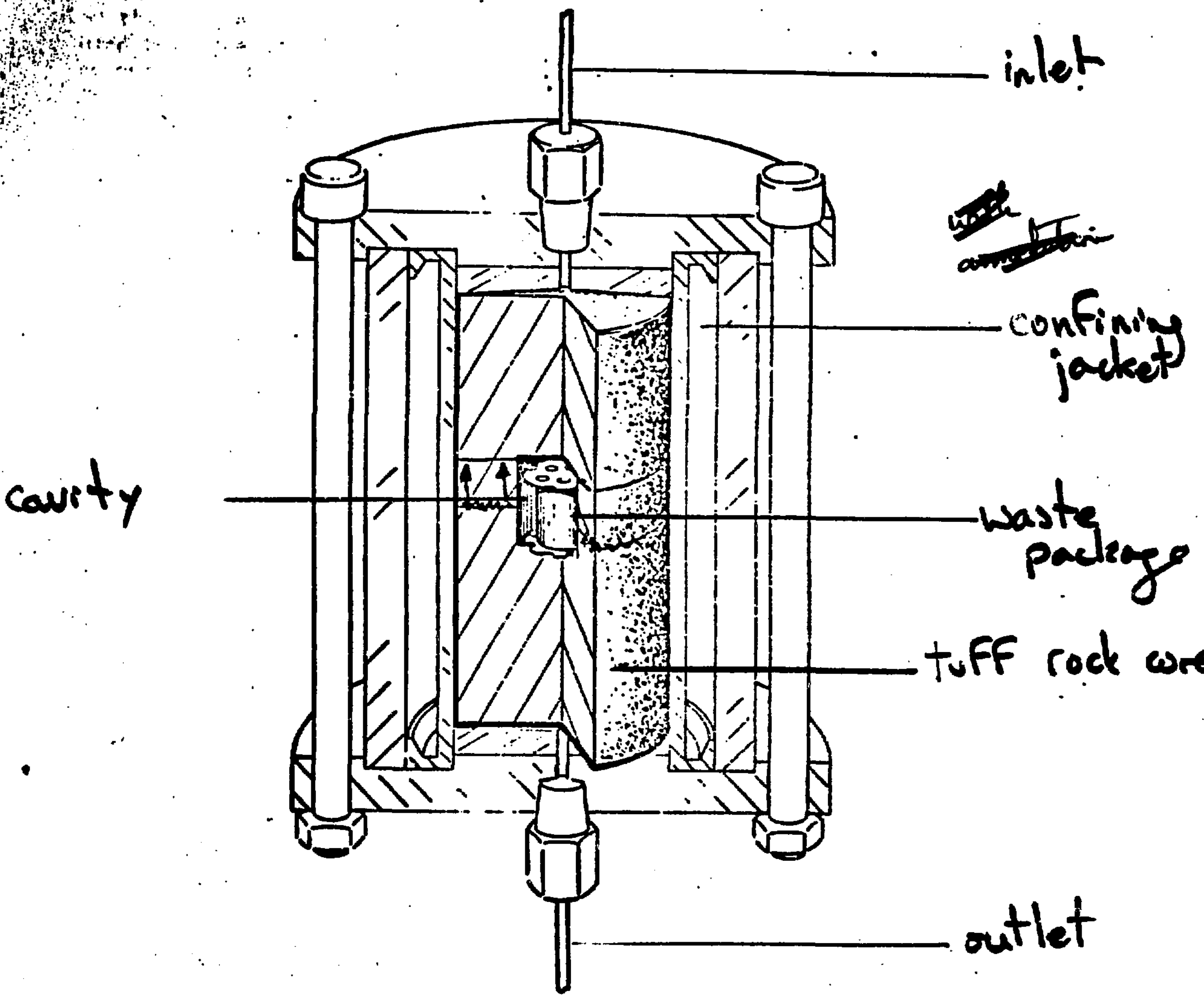


fig 3




~~Fig. 10. Diagram of Analog Test Apparatus and Rock Core.~~