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GAS CHROMATOGRAPHIC SYSTEM
FOR FFTF FAILED FUEL DETECTION AND LOCATION -
STATE-OF-THE-ART REPORT

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GAS CHROMATOGRAPHIC SYSTEM
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INTRODUCTION

A system for rapid detection and location of failed fuel elements will be highly important to successful reduction of the FFTF down time. The usefulness of the system can be extended considerably if it can be made to function both on an operating reactor and on a reactor that has been down for a period of time. In the event of a fuel element failure, rapid location of the failure can potentially make major savings of: a) reactor down time and b) system contamination. Present plans call for the separation of the functions of failure detection and failure location on the FFTF.⁽¹⁾ Delayed neutron and cover gas monitors are the prime contenders for detection of failed fuel in the reactor primary coolant and cover gas. Location of failure--pin hole or massive--could be accomplished by measurement of the fission gas content or radioactivity in the cover gas in individual coolant channels. Maximum use will therefore be made of the strong feature of each of the systems.

The calculations of D. R. Marr⁽²⁾ show that a system based on the gas chromatographic approach would have ample sensitivity. Marr has calculated expected krypton and xenon isotope activity levels in FTR fuel pins as a function of cooling time. The calculations were based on an irradiation time of 115.7 days and the results are summarized in Table I. (Since only Kr^{88} , $\text{Xe}^{131\text{m}}$, $\text{Xe}^{133\text{m}}$ and Xe^{133} have extended half lives the activities given are approximately the equilibrium levels that will be reached within a few days of startup.)

TABLE I

Isotope	Half-Life	Curies Per FTR Fuel Pin		
		Shutdown	24 Hour Cooling	10 Day Cooling
Kr 83m	1.9 hr	180 Ci	.73 Ci	--
Kr 85m	4.4 hr	140	3.2	--
Kr 85	10.6 y	1.3	1.3	1.3 Ci
Kr 87	76 m	290	--	--
Kr 88	2.8 hr	440	1.2	--
Kr 89	3.2 m	510	--	--
Xe 131m	11.8 d	11	10.4	6.2
Xe 133m	2.3 d	105	83	6.2
Xe 133	5.3 d	2200	2090	700
Xe 135m	15.6 m	650	48	--
Xe 135	9.2 hr	2300	830	--
Xe 137	3.9 m	2100	--	--
Xe 138	12 m	1800	--	--
Xe 139	43 s	1400	--	--

From these figures it may be shown that a long-irradiated fuel pin will contain a large enough fission gas inventory for ready detection of a slow leak using a gas chromatographic-based system. For example, if one assumes that only Xe¹³³ is to be measured, that its leak rate is such that 0.01% escapes from the pin during the sampling period, and that 0.01% of that which escapes is collected and isolated for radiation measurement, the final sample will show an activity of 8×10^5 d/s, a readily measured amount.

A recent survey by Thompson⁽³⁾ lists a number of methods which have been used for fuel failure detection. Some of the methods listed are also designed for failure location. The most elaborate of the methods discussed is that on the United Kingdom's PFR⁽⁴⁾ and is based on the measurement of delayed neutrons in the primary coolant. The most widely used failure monitoring system which makes use of measurements on the cover gas is based on an electrostatic precipitation separation. This system has been used on EBR-II⁽⁵⁾ and Fermi⁽⁶⁾ as a failure detector by monitoring the cover gas as a whole. No attempt has been made to apply it to the monitoring of individual fuel channels.

An apparently more promising approach for FFTF application involves the use of a gas chromatographic separation of the fission gases krypton and xenon from the other radionuclides present in the gas sample (primarily Ar⁴¹) followed by gamma or beta counting of the separated rare gases. Gas chromatographic separation occurs when a mixture of gases is passed through a column packed or coated with a substance that has a different affinity for each of the various components of the mixture. The specific separation of interest for fuel failure

detection is that of xenon and krypton from all other gases. In this separation strongly absorbing materials such as the molecular sieves or activated charcoal have been shown to produce the best results.

DISCUSSION

Gas Chromatographic Separation of Krypton and Xenon

The separation of krypton and xenon from other gases by gas chromatographic means has been studied by a number of workers. The earliest pertinent reports are those of W. R. Kritz⁽⁷⁾ of the Savannah River Plant of I. E. duPont. His reports describe an automatic system for monitoring a stream of helium after bubbling through the reactor coolant. The helium stream is sampled periodically and the krypton and xenon in the sample separated on a chromatographic column packed with 5A molecular sieve. The output of the column is passed through a thin walled chamber in contact with an anthracene crystal which functions as a beta radiation detector. Calibration with Kr⁸⁵ showed the system to have a sensitivity of 4 μ Ci/liter. Under the operating conditions used the column had the following retention times: oxygen and argon, 120 seconds; nitrogen, 200 seconds; krypton, 300 seconds; and xenon, 1250 seconds. A cycle time of ten minutes was used and therefore the krypton of one sample rode through the xenon of the previous sample. This did not interfere with the detection and measurement of the krypton. The system described was still operating satisfactorily in October 1967⁽⁸⁾ after almost 10 years of service.

Ockenden and Tomlinson⁽⁹⁾ used a gas chromatographic method for isolating krypton and xenon during a study of the radiation produced by short lived isotopes. In this investigation a short (15 cm) column packed with fine activated charcoal supported on glass wool was used. Separation was rapid and under the conditions described retention times of four seconds for krypton and twenty-seven seconds for xenon were obtained.

The separation of xenon from argon by gas chromatography was also reported by Havlena and Hutchison⁽¹⁰⁾ at Fermi. They reported data on the effect of temperature on the separation using silica gel, molecular sieve 5A, and charcoal packed columns. Charcoal packing was found to be preferable because it minimized interference by carbon monoxide. Under the flow conditions used the retention time of xenon on the seven foot charcoal column was found to be 9.8 minutes at 150°C and 4.8 minutes at 200°C.

Xenon was concentrated from large volumes of air or argon with a mixed charcoal-molecular sieve trapping column immersed in a dry-ice-alcohol bath. The trapped gas was then transferred to a chromatographic column for isolation of the xenon. The column was not coupled to satisfactory radiation detection equipment at the time of their report, however, they expressed optimism that the method would prove to be satisfactory.

French and Ockenden⁽¹¹⁾ separated krypton and xenon from the Magnox reactor coolant (CO_2) by caustic scrubbing and cold charcoal trapping. They then made gamma energy measurements on the trapped gases. Xe^{133} and Xe^{135} were found to be useful, not only in detecting leaks but also in analyzing the type of fuel failure involved. Detectable activity levels as low as 50 disintegrations per second per gram of coolant were reported.

Comparison of Gas Chromatographic and Electrostatic Precipitation Systems

A system to be effective as a fuel failure location device must meet the following requirements:

1. It must have great maximum sensitivity to permit the detection of leaks at the earliest possible time and to permit the location of small leaks.
2. It must have great selectivity to permit the measurement of low levels of fission gases in the presence of the other radionuclides which are likely to be present in the reactor cover gas - notably Ar^{41} and Na^{24} .
3. It must be capable of rapidly scanning a large number of sampling points because of the large number of driver fuel elements.
4. It should function on both an operating and a shut down or "scrammed" reactor.
5. It must be simple and capable of reliable sustained remote operation.

Only two systems appear capable of meeting these demands. They are both based on radiochemical counting of the rare gas fission product isotopes of xenon and krypton (or their daughters) after separation from the cover gas. One system is based on a gas chromatographic separation and the other is based on an electrostatic precipitation separation.

The electrostatic separation system depends upon the fact that, at the time of generation, the daughter atoms from argon, krypton and xenon are positively charged alkali metal ions. This permits efficient collection by the application of an electrostatic field. High selectivity is obtained because of the absence of any interfering radioactive charged particles. The potassium daughter of Ar^{41} is, fortunately, stable.

A comparison of the inherent advantages and disadvantages of the two separation techniques reveals that the gas chromatographic system more nearly meets the requirements set forth for a satisfactory fuel failure location system.

a) Sensitivity

The gas chromatographic system is inherently more sensitive than the electrostatic system because it makes use of all of the radioactive isotopes of xenon and krypton that are carried in the gas stream whereas the electrostatic system isolates and detects only the daughters of the isotopes Kr^{88} , Kr^{89} and Xe^{138} . The radiation that would be detected in the short (approximately one minute) measuring period would, therefore, be greater not only because all the krypton or xenon isotopes could contribute but also because only those krypton and xenon isotopes that decayed while in the electrostatic collection chamber contribute daughter atoms for collection and subsequent measurement. The magnitude of the inherent advantage is a function of reactor operating conditions and time and will be discussed in more detail in a later paragraph concerning the location of a failed fuel element in a "scrammed" reactor.

b) Selectivity

Both the chromatographic and electrostatic precipitation methods have adequate selectivity. The major potential source of interference is Ar^{41} . A major source of this isotope is potassium impurity in the sodium. A potassium impurity level of 150 ppm in the reactor sodium, exposed to an average fast flux of $4.3 \times 10^{15} \text{ n/cm}^2\text{-sec}$ (if the cross section is 1 mb) is calculated to produce an equilibrium Ar^{41} activity of 30 $\mu\text{Ci/cc}$ of sodium. If this transfers to the helium* cover gas at the same concentration, a 10 cc sample of gas will contain $1.1 \times 10^7 \text{ d/s}$ of Ar^{41} . Xenon activity in a 10 cc sample from a slow leak could be much less than this whereas a full fuel pin rupture would be 100 to 1000 times higher. Additional Ar^{41} will be generated by the activation of any argon impurity in the helium cover gas or from an argon cover gas but the amount cannot be estimated from the data at hand.

The Ar^{41} activity establishes a background that is high enough to interfere with direct measurement of fission gas activity⁽⁵⁾ in the cover

* At the time this document was written, helium was the reference cover gas.

gas. Gamma energy analysis of the activity provides inadequate discrimination for the fission gases because the Ar^{41} gamma energy is high (1.29 Mev) and its Compton tail masks the lower energy gammas of the fission gases when they are present in low abundance. Only a major rupture releases sufficient activity for successful direct gamma energy analysis. Therefore, the separation methods under discussion are necessary to locate small leaks.

The gas chromatographic system has another advantage resulting from its isolation of all the isotopes of krypton or xenon. This is an ability to provide isotopic composition information through gamma energy analysis of the radiation from the separated gases. Since the half lives of isotopes that could conceivably be measured range from 43 seconds to 5.3 days for xenon and 33 seconds to 10.6 years for krypton it is possible to determine the time lag between generation of the gases and their measurement. A slow leak will hold up the gases for a long enough time to permit the short lived isotopes to decay while "fresh" gas will be rich in the short lived isotopes. The British⁽¹¹⁾ report of the use of Xe^{133} and Xe^{135} measurements in analyzing the types of fuel failure involved.

Questions have been raised concerning possible problems resulting from sodium vapor fouling of the chromatographic system. Indications are that sodium vapor concentrations in the sample gas stream can readily be reduced to acceptable levels by simple cold trapping⁽¹²⁾. No loss of krypton or xenon to the trapped sodium is expected because of the inert chemical nature of these gases.

c) Speed of Response

The relative speeds of response of the systems is an important factor in choosing between them if failed fuel location is to be accomplished with a single or minimal number of instruments. In a ninety channel reactor using a system with a cycle time of two minutes, three hours will be required to survey all channels sequentially. This time could be reduced by suitable manifolding (provided the failure is detectable at the manifolding dilution). Available data indicates that an instrument based on a gas chromatographic separation can attain cycle times as short as two minutes. Lag times associated with flushing the gas from the precipitation chamber, introducing a fresh sample and changing the stripping liquid in the collector cell may limit the electrostatic precipitation system to cycle times slightly longer than this. The present EBR-II system⁽¹⁵⁾ response time is five minutes.

d) Failure location on a "Down" Reactor

The gas chromatographic system holds much greater promise for fuel failure location on a down or "scrammed" reactor than the electrostatic precipitation system because of its ability to separate and detect all of the isotopes of xenon. The longest lived isotope to which the electrostatic precipitation system responds is Kr^{88} with a 2.8 hour half life while the gas chromatographic system will respond to the 5.3 day Xe^{133} . Thus, assuming a continued escape of fission gases, the chromatographic system is potentially capable of failure location a week or more after reactor shutdown while the electrostatic system cannot be expected to perform satisfactorily for more than one day after reactor shutdown.

e) Simplicity

The two systems will be of about equal over-all complexity. The gas sampling and conditioning equipment will be similar for both systems. Both will require internal sample flow control. The radiation detection and counting equipment will be the same for both systems. Only in the separation portions of the systems will there be significant differences. The electrostatic precipitation unit consists of: a precipitation chamber through which a charged wire is moved, a drive to move the wire, and a power supply to maintain the electrostatic field in the chamber. A scrubbing solution supply, handling lines and discard system are also required. The moving wire passes through mercury seals to prevent escape of the radioactive gases and through the chemical scrubbing solution to remove the alkali metals for counting. The chromatographic system will consist of pneumatically or electrically operated sampling and switching valves, a carrier gas supply, a chromatographic column, oven and temperature controls for the column, a timer to activate the sampling valve and a chromatographic detector with its power supply and measuring circuit. The chromatographic detector is not used as a readout device but merely to activate valving for the isolation of samples for counting. The wire drive and scrubbing solution system of the electrostatic precipitation system requires a number of moving parts whose maintenance will probably about match that of the more complex electronic circuitry of the chromatographic system. Both should be capable of long term, reliable, remote operation and indeed the electrostatic precipitation system has proven reliable in some applications⁽¹³⁾.

A New Approach to Failure Location

Perkins and Thomas⁽¹⁴⁾, as part of an investigation of fuel failures in the PRTR, have reported measurements on the activities in the helium cover gas. Their calculations based on the observed activity increase in the PRTR helium system during bursts indicate that during the first minute of a burst the gas activity from a tube containing a failed element will be about two orders of magnitude greater than normal. This activity differential will drop to about a factor of five in five minutes and to about one percent in thirty minutes. They therefore conclude that, at least in PRTR, almost instantaneous failure location may be necessary if defective fuel element location is to be successful. If conditions in the FFTF are similar a new approach to rupture location will be necessary.

One suggestion for such a system does not involve a chromatographic separation but is based on the adsorption principles used in chromatography. By passing a mixture of gases through an adsorber, such as charcoal, the more strongly adsorbed components will be delayed in their passage thus increasing their relative concentration in the delay volume. Two cases can be considered: First, a continuous low level of a strongly adsorbed component (such as xenon). The concentration of such a component in the adsorber will increase until it becomes saturated and an equilibrium is established. Second, a "slug" of xenon. The "slug" would be held up in the delay bed for a time but would gradually diffuse off into the passing gas stream. In either case the concentration of a strongly adsorbed component, such as xenon, relative to that of a less strongly adsorbed one, such as argon, would increase. By close coupling of a radiation detector to the delay bed, concentrations of the fission gas that were too small to be seen above the background could be measured.

By combining the gas samples from an array of channels so each channel feeds a "row" and a "column" of a matrix the number of detectors needed to locate the channel in which a failure has occurred can be reduced to $2\sqrt{n}$ where n is the perfect square equal to or larger than the number of channels. Thus, a 10 by 10 matrix of twenty detectors could monitor 100 channels. A leak in a given channel is pinpointed by a simultaneous signal in a "row" and "column" detector.

Since the system would operate continuously, it is estimated that the response time could be made of the order of seconds for a step release of sufficient activity to give a ten fold increase in the radiation level at the detector. The time required to deliver the gas to the delay bed is the major

variable. The time constant of the radiation detection system at the activity level being measured is a secondary variable.

CONCLUSIONS

A review of the present state-of-the-art in the areas of gas chromatography, radiochemical counting and inert cover gas sampling reveals that:

1. The chromatographic approach to fuel failure detection and location is technically feasible and holds promise of having distinct advantages over existing methods.
2. Considerable knowledge which is directly applicable to the problem exists and therefore the research and development costs required will be modest.
3. Existing knowledge indicates that there is a high probability that a successful failed fuel locator can be constructed based on gas chromatographic separation of the rare gases followed by radiochemical counting.
4. Sample selection and conditioning will pose a major problem in any failure location system which is based on the measurement of fission gas concentration in individual cover gas channels.

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