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SEPARATION PLANT EFFLUENT GAS MEASUREMENTS FOR DETERMINING
PLUTONIUM PRODUCTION RATE

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APPENDIX II - F

SEPARATION PLANT EFFLUENT GAS MEASUREMENTS FOR DETERMINING
PLUTONIUM PRODUCTION RATE

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SUMMARY

The use of ion chambers or proportional beta counters is recommended for the measurement of Kr^{85} in separations plant gaseous effluent. It will be necessary to evaluate the Xe^{133} present if short cooling times (less than about 90 days) since irradiation are used. This can be accomplished through calibration and decay measurements. It is concluded that the Kr^{85} evolution could be determined to about $\pm 5\%$ with careful measurements.

DISCUSSIONNoble Radioactive Gases Produced in Fission

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Several krypton isotopes are produced either directly in fission or as the descendants of other fission products. Of these isotopes, which range from Kr⁸³ to Kr⁹², only one, Kr⁸⁵, has a half-life long enough to be of practical use

The half-life of Kr⁸⁵ is ^{10.57 ± 0.14} ~~10.57 ± 0.14~~ years, after an isomeric transition of half-life ^{4.4} ~~4.4~~ hour(1). The fission yield of ~~0.260 %~~ Kr⁸⁵ is ^{0.260 %} ~~0.260 %~~ for U²³⁵, ^{0.15 %} ~~0.15 %~~ for U²³⁸, and ^{0.094 %} ~~0.094 %~~ for Pu²³⁹ (2). The decay of Kr⁸⁵ is 99+% by beta emission of maximum energy 0.695 Mev., which precludes use of gamma detection instrumentation for its measurement(3).

In the heavier group of isotopes formed from fission are the xenons of mass numbers 131 through 145. The longest-lived of these is Xe¹³³, descendant of Sb¹³³. The half-life of Xe¹³³ is 5.27 days, after passing through a metastable transition of 2.3 day half-life. Decay is by beta emission of maximum energy 0.34^{Mev.} followed by a gamma transition of 0.08 Mev.(4). The chain fission yield leading to Xe¹³³ is 0.0662 ± 0.0015 for U²³⁵ fission(2).

Evolution Of Noble Gases Upon Uranium Dissolving

As indicated by Hanford production dissolver operation, the evolution of the noble radioactive gases occurs almost, if not entirely, during metal dissolution, and none is retained in the solution. The initial release is slow, but rises rapidly as solution of the metal progresses, then decreases rapidly when the temperature in the dissolver is lowered. It can be assumed that virtually all the krypton and xenon present will be carried in the dissolver off-gas stream.

Sampling The Stream

Sampling the dissolver off-gas stream directly would be less conducive to errors than sampling in a plant stack, and would permit improved sensitivity when needed. Sampling in dissolver off-gas piping may, however, require several

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sampling probe installations, one for each off-gas line, whereas in the stack only one entry point would be needed.

It will not be of importance to provide isokinetic probes, since problems ordinarily faced in particle sampling will not be of consequence here. A probe of corrosion-resistant material of any convenient dimension will suffice. Provision should be made for sampling simultaneously from several points on the diameter of the duct with the positions chosen to represent equal annular areas, to avoid errors from channeling and incomplete mixing. If the sample can be drawn from the dissolver off-gas line, this requirement will not be critical, since, in general, a small diameter pipe will be used. However, if a ventilation stack is sampled, the off-gas line outlets into the stack may cause channeling at the point of sampling and the sample may not be representative of the total flow. It is recommended that a minimum of two probe inlets per foot of duct diameter or maximum duct breadth be provided, and these be located to sample from points representing equal areas of the duct. Grease should be avoided since noble gases have a measurable solubility in some oils and fats. The sampling point should be placed ten or more duct diameter downstream from entrant lines and elbows to assure homogeneity of the gas. The sampling rate should be as high as the detector and associated equipment will permit, since delays resulting from volumes in delivery lines will be minimized. Response time of the instrument must be considered; it should in general be considerably shorter than the time between significant changes in emission rate.

It will, of course, be necessary to know the total flow through the duct sampled. This can be determined by standard techniques. The duct rate can be determined with a calibrated pitot tube, taking care to traverse the duct making velocity measurements at points representative of equal annular areas⁽⁹⁾. After making the velocity traverse it will be necessary to permanently locate a velocity sensing element at the point of average velocity and to record the velocity on a

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chart recorder. With proper selection of instruments the volume rate through the duct can be measured to about 3% to 5%. An integrating-type flow recorder could be used to give the total gas flow during the sampling period. These components are on-the-shelf items requiring little additional development. It should be possible with a carefully designed and calibrated installation to record the integrated volume with an error of 5% or less.

Sample Preparation

It must be assumed that the dissolver off-gas will contain interfering radioisotopes such as I^{131} , and isotopes carried in fine mist or droplets and particles carried through the stream. Elimination of these interferences can be accomplished by filters, traps, and chemical scrubbers of various kinds. Filtering is mandatory, and this can be made effective by using a Chemical Warfare Service or other type of high efficiency filter. A sodium hydroxide solution makes an effective I^{133} and $Ru^{103-106}$ trap, however, the scrubber will require sizing to insure adequate capacity to absorb any acid constituents in the sample stream and still remain sufficiently basic to remove iodine and ruthenium. This will require testing in the individual case. A de-entrainment section should follow the scrubber to reduce to a minimum entrained droplets. Drying of the sample may be required, depending upon the detection system selected.

Detection And Measurement Of Noble Gases

Two primary beta particle detection systems may be used for measuring the quantity of Kr^{85} in the sample. These are ionization chambers and particle counters. Each has its own particular merits, however, the particle counter can generally be more easily designed to be the more sensitive. In the situations envisioned sensitivity should pose no particular problems, hence each may prove equally useful.

1. Ion Chamber

The ionization chamber must be sized to give an adequate signal to background response for the particular conditions under which it will be employed. In applications foreseen, sensitivity should not pose a particular problem. It will be most practical to have the sampled gas flow through the chamber, although not absolutely necessary if thin chamber walls are used.

In using the ion chamber it will be necessary to maintain the temperature of the gas well above the dew point at all points in the system to avoid condensing water in the chamber. This can be accomplished by preheating the gas adequately to preclude condensation in the chamber which may be insulated. Cooling the gas before entry to the chamber in a cold trap to condense moisture and subsequent warming will also be effective.

An electrometer of the vibrating reed type is recommended to measure continuously the potential developed across a resistor by the ion current produced. A standard strip chart recorder may be used.

Calibration of the chamber and recorder must be accomplished through the use of known Kr^{85} standard gas mixtures. It will be necessary also to calibrate the chamber similarly for Xe^{133} , since it is anticipated that significant ion current contribution from Xe^{133} will be recorded in most cases. This will be discussed later, since it applies to both ionization and particle counting techniques. The Kr^{85} and Xe^{133} gas mixtures may be calibrated to within $\pm 2\%$ using absolute beta-counting techniques⁽²⁾.

The ion chamber calibrations should be accomplished under conditions as nearly identical to those anticipated in the actual field use as possible to avoid errors. A range of gas concentrations comparable to those anticipated should be used to establish the full calibration curve, thus avoiding the uncertainty of extrapolations.

Background must be determined in the absence of radioactive noble gases. Shielding may be effectively used around the chamber to reduce background. The background response is anticipated to make a small fractional contribution to the average ion current during periods of metal dissolving provided an adequate volume is chosen for the chamber.

If care is used in the calibration of the ion chamber and high quality components selected, it will be possible to achieve an accuracy of about $\pm 5\%$ on the absolute quantity of Kr^{85} present in the absence of Xe^{133} . Since the final accuracy of the Kr^{85} concentration will depend upon the quantity of Xe^{133} present, no unqualified statement of accuracy for Kr^{85} can be made without knowing the relative amounts of Kr^{85} and Xe^{133} present. This point will be discussed later in the report.

2. Particle-Counting Measurements

A second type of detector which could be effectively used for the Kr^{85} measurement is a particle counter with walls or window thin enough to give adequate counter efficiency. A thin window gas flow proportional counter would be preferred over a Geiger-Mueller counter because of its unlimited life, low resolving time losses, and excellent voltage plateau. The counter would consist of a hemispherical or cylindrical chamber with a gas tight aluminized window of about 1 mg/cm^2 thick. The window of the counter would form the end of a cell through which the metered sample gas would flow. Cell volume could be selected to permit adequate counting rates at the levels of krypton anticipated. Shielding may be required to reduce background counts. The counter pulses would be amplified in a pre-amplifier, fed to a scaler, then to a printer, which would be set to read out the scaler-accumulated counts during repetitive intervals. A carefully calibrated count-rate meter and strip recorder could be used, however,

the digital counter would be preferred.

Like the ion chamber, the particle counter would require calibrating with absolutely standardized Kr^{85} , and Xe^{133} samples, under identical conditions to those employed in the sample measurement. An occasional background determination will be required, and could be taken automatically through a programming cycle. For samples not containing Xe^{133} the Kr^{85} concentrations in the sample stream should be measured to within 5% of the absolute quantity present.

Corrections For Xe^{133} Present

The ratio of $Xe^{133}:Kr^{85}$ activity will be high at cooling times less than about 50 days. This results from the short half-life of Xe^{133} and its high fission yield. In Table I is tabulated the

$$\frac{\text{curies } Xe^{133}}{\text{curies } Kr^{85}}$$

ratio for 500 MWD/ton, 100 days metal irradiation and various decay times. Kr^{85} was calculated from the equation applicable to Hanford reactors,

The Xe^{133} was calculated assuming that irradiation was long (100 days), all heat was from U^{235} fissions (200 Mev/fission), and that the fission yield of $Xe^{133} = 0.0665$ for U^{235} .

TABLE I

<u>Decay Time</u> <u>Days</u>	<u>$Xe^{133}:Kr^{85}$ (Activity)</u>
0	1500
10	405
20	110
30	22
40	7.6
50	2.1
60	.57
70	.15
80	.041
90	.011
100	.003

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The above ratios could not be used in the general case, since for much shorter irradiation times the ratio will change materially and the calculation for Xe^{133} would require considerable refinement for dependability. The data are presented to show the need for evaluating the Xe^{133} contribution to the total ion current reading or counting rate.

It will be necessary to determine the ratio of $\text{Xe}^{133}:\text{Kr}^{85}$ in the dissolver off-gas experimentally to correct for the Xe^{133} contribution. This can be done through decay measurements for intermediate ratios of Xe^{133} to Kr^{85} , say from 40 days cooling time to 70 days cooling time. At shorter times it will be difficult to identify and measure accurately the Kr^{85} except after long waiting periods, which are believed not practical in the case anticipated. As cooling times approach 90 - 100 days the error from Xe^{133} will be negligible.

An estimate of the error in the fraction of Kr^{85} in the mixture may be determined by assuming a reasonable procedure for a decay measurement and calculating the resulting uncertainty of Kr^{85} taking into account the errors faced in the initial counting and at some later time. Assume that a count of the unknown mixture of the two gases is made initially and found to be N_0 . Two-half-lives later, 10.54 days, a second count is made. It will be equal to $(1 - f_{\text{Xe}})N_0 + 0.250 f_{\text{Xe}}N_0$, where f_{Xe} is the fraction of count initially contributed by Xe^{133} . The ratio of decayed count to initial count, K , will be $1 - 0.75 f_{\text{Xe}}$, or in terms of Kr^{85} , $K = 0.25(1 + 3f_{\text{Kr}})$

$$\text{or } f_{\text{Kr}} = \frac{K - 0.25}{0.75}$$

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Since K is the ratio of two counts, the error in K will be equal to

$$\approx \sqrt{\left(\frac{\text{Error in c/m at 10.54d}}{\text{c/m at 10.54d}}\right)^2 + \left(\frac{\text{Error in c/m at 0 d}}{\text{c/m at 0 d}}\right)^2}$$

The standard error in the counting rate of the individual counts is $\sigma = \sqrt{N/t}$, in which N = total counts during interval "t". Other confidence levels can be

used by multiplying by the appropriate factor. At high fractions of Xe^{133} , say 95% corresponding to decay of about 30 days, K is small and subject to the greatest fractional error for a given absolute error. Assuming that each measurement can be made to accumulate 10,000 counts, and assuming an initial net c/m of 1000 c/m , the first count would have a standard deviation of ± 10 c/m or 1%. The count after 10.54 days will be approximately 230 c/m and would require counting for 42 minutes to accumulate 10,000 counts, again giving a standard error of 1%. The error in K would then be 1.4%. Since f_{Kr} is a linear function of K , f_{Kr} would also have a 1.4% standard error. Shorter cooling periods will require even longer counting times to lower the error in K . The 2 half-life-intervals between counts was chosen merely as an example and could be changed depending upon the need for greater accuracy.

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Calculation Of Curies Of Kr^{85}

The data, then, obtained during monitoring would be the following:

- (a) Average velocity in the main duct as a function of time. Knowing cross-sectional area, the volume through the duct can be determined for any time increment.
- (b) The recorded ion current or counting rate for the detector used as a function of time.
- (c) The c/m or ion current per curie per cc for Xe^{133} and Kr^{85} , through calibration.
- (d) The fraction of count contributed by Kr^{85} .

The counting or ion chamber data would require a background correction then a correction for the Xe^{133} present during the run. Digital data of counting rate

during repeated intervals would require plotting against volume through the duct. The area under the resulting curve during the period of the run would then be measured to give total curies of Kr^{85} during the run. If the record is analog recorded, after a correction for background and Xe^{133} , the area under the chart curve could be measured directly without replotting, provided duct flow rate had been steady during the run and the proper scale was assigned to the time axis of the chart. It would be easily possible to feed the signal from the detector and from the volume rate recorder to a proportional multiplier and integrator whose output would be proportional to curies output.

A detailed analysis of the errors entering into each part of the data would be required for the monitoring system developed to place limits on the Kr^{85} produced. With proper selection and development of components, and with care in their calibration and use it is believed that the quantity of Kr^{85} released in metal dissolving could be measured to $\pm 5\%$.

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Important factors influencing the $\text{Kr}^{85}/\text{Pu}^{239}$ ratio are the exposure time in the reactor, the conversion ratio, and the cooling time out of the reactor.

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