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Route List

1. ~~F. J. Laitz~~ 7/10
2. ~~G. F. Hill~~
3. ~~R. E. Burns~~
4. ~~S. H. G. [unclear]~~
5. ~~[unclear]~~

~~H. H. Van [unclear]~~
~~H. H. [unclear]~~ 62997

DATE 7/3/50

SUBJECT Feasibility Survey - Krypton

Removal at Hanford

TO HOO-AEC - Attn. D.F. Shaw

FROM O. H. Greager

COPY NO. 9 A

APR 22 1957

BEFORE READING THIS DOCUMENT, SIGN AND DATE BELOW:

FR	7/10/50
McHale	7/13/50
L. E. Burns	7-14-50
CR	1/17/51
JWA	5/10/52
GS	6/15/52
W. H. [unclear]	11/16/53
E. J. M.	8/28/57
H. H. [unclear]	12-26-58

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GENERAL ELECTRIC COMPANY
Hanford Works
Richland, Washington

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Sc. Snyder 12/8/93

M. Krueger 12/3/93

- #1,2,3. AEC - HCO
Attn. D.F. Shaw
4. G.R. Prout
5. A.B. Groninger -
O.R. Greager
6. R.H. Benton
7. B. Weidenbaum
8. V.R. Cooper
9. F.J. Lutz
10. 700
11. Pink
12. Yellow

July 3, 1950

Atomic Energy Commission
Hanford Operations Office
Richland, Washington

COPY 1 OF 1, SERIES MA

This document consists of
10 pages. The 9th of
12 pages is a

Attention: Mr. D. F. Shaw, Manager

Gentlemen:

FEASIBILITY SURVEY - KRYPTON REMOVAL AT HANFORD

- Ref: (1) Letter, FC Schlemmer to GR Prout, 5/10/50 - Doc. GSH-16,757
(2) Letter, OH Greager to FC Schlemmer, 5/22/50 - Doc. LH-17871

Reference (1) above requested the General Electric Company to make a preliminary evaluation of the cost, effort, and interference with other programs for providing facilities for the routine removal of krypton during operation of both the present canyons and Redox. Reference (2) acknowledged receipt of this request and promised an answer on or before July 14, 1950.

A committee was appointed in the Separations Technology Division to undertake a feasibility survey of the problem and has prepared a summary report, a copy of which is attached to this letter. In brief outline, the results of this survey may be summarized as follows:

1. Prevention of the release of krypton during irradiated metal dissolution by the so-called "fumeless" dissolving used by the British at Harwell, as quoted by Professor Warren C. Johnson in an attachment to Reference (1), does not appear to be feasible. Solubility data for krypton would indicate that this should be very nearly scientifically impossible under practical conditions.

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2. Personal contacts with the Argonne, Brookhaven, and Oak Ridge National Laboratories, as well as the Knolls Atomic Power Laboratory, all of which are also familiar with and interested in fumeloss dissolving, have revealed no knowledge of this claim for fumeloss dissolving. Dr. S. G. English, of the Atomic Energy Commission Division of Research, also knows of no other reports of this claim.
3. Fumeloss dissolving, however, would be the first step in the most promising direction of achieving krypton removal, because of the extremely desirable decrease in off-gas volume for subsequent treatment that should be obtained.
4. Low-temperature adsorption, on the basis of limited data presently available, would appear to be the most promising method of krypton removal from low-volume off-gases from fumeloss dissolving.
5. At least one man-year (two men for six months) of additional scouting effort in literature search, direct discussion with Harwell personnel, and limited laboratory research should be carried out before a decision is made on the proper approach to follow for a development and design program.
6. An additional five to ten man-years of technical effort is roughly estimated to be required to develop a krypton removal method for readiness for engineering design scoping.

In view of the general lack of required information described above and as enlarged upon in the attached memorandum report, it is not felt that the over-all effect of the installation of krypton removal facilities upon Harford operations can be realistically evaluated at this time. If desired, the more extensive preliminary studies referred to in paragraph (5) above can be carried out with no serious effect on existing programs. The subsequent development program referred to in paragraph (6), however, if attempted on anything less than a two-year schedule, would be of significant effect.

We should be pleased to hear if you wish this matter pursued further.

Very truly yours,

O. H. Greager
Assistant Manager,
Technical Divisions

OGG:KREB/jw

Attachment

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June 29, 1950

TO: R. H. Beaton
FROM: V. B. Cooper, F. J. Leltz, and B. Weidenbaum
SUBJECT: Preliminary Survey - Methods and Feasibility of Krypton-85 Removal.

A. INTRODUCTION

Fission-production of krypton-85 in natural uranium piles is substantial and in direct proportion to plutonium production. The known chemical and nuclear properties of krypton are such as to permit its determination in air samples taken at considerable distance from its source and to allow correlation of such measurements with plutonium production.

This preliminary feasibility study suggests the direction and magnitude of the effort required to develop a method of krypton removal applicable to current and contemplated processes. This estimation of developmental effort may in turn serve as a basis for evaluation of the cost of such effort and of the interference with other programs at Hanford Works. (1,2)

B. CONCLUSIONS

1. The choice of methods for separating krypton from other gases is very limited, the most promising involving adsorption on activated charcoal at $-90 \pm 30^\circ\text{C}$.
2. In current canyon operation, krypton is evolved in the uranium dissolver off-gases which have an awkwardly large volume for application of any krypton separation method.
3. Concurrent development of fumeless dissolving of uranium is recommended to minimize the volume of gas from which krypton must be removed.
4. If dissolving be achieved so fumeless as to leave krypton in the dissolver solution, purging with a carrier gas should be provided at this point to avoid subsequent complications.
5. Non-fission production of large quantities of krypton-85 to obscure the amount generated during plutonium production is not feasible.
6. Laboratory studies of fumeless dissolving in progress at Harwell and ANL should be followed closely if interest in this problem continues at Hanford Works.

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7. Similarly, work on krypton separations; e.g., at ORNL and the Bureau of Mines (Amarillo), as well as ANL studies specifically related to this problem should be investigated further.
8. A scouting program involving two men working for about six months on literature and laboratory research and off-site consultation would provide a much sounder basis than this survey for judging the feasibility of krypton removal.
9. An additional 5-10 man-years of technical effort is tentatively estimated to be required to develop a krypton removal method to the point of engineering scoping.

C. DISCUSSION

For convenience in presentation, the considerations on which the foregoing conclusions are based are grouped under the following headings:

1. Nuclear Properties of Krypton-85
2. Non-Fission Production of Krypton-85
3. Solubility of Krypton
4. Off-gas Dissolving of Uranium
5. Low-Temperature Adsorption of Krypton
6. Alternate Methods of Separating Krypton from Other Gases
7. Integration with I¹³¹ Waste Disposal
8. Proposed Attack on Krypton Removal Problem
9. Tentative Flowchart for Krypton Removal

1. Nuclear Properties of Krypton-85

Pertinent nuclear properties of krypton-85 include⁽³⁾

Fission yield	ca. 0.24%
Half-life	9.4 years
Radiation	0.74 Mev beta; no gamma
Parent's half-life	< 3.0 min.
Daughter's half-life	Stable Rb ⁸⁵
Total fission yield, stable krypton	ca. 1.2% (1.0 - 3.0)
Total fission yield, stable xenon	ca. 12.3% (19.1)

This fission yield and half-life correspond to pile production of krypton-85 at the rate of ca. 0.4 curies per megawatt-day. The short half-life of parent activities rapidly brings the krypton activity to equilibrium with the plutonium produced; viz., ca. 0.4 curies per gram plutonium. The high rate of production, long half-life, and appreciable beta energy appear to make radiochemical gas analysis of air samples practicable. Decay to a stable daughter requires that analysis be made for krypton-85 itself.

The total fission yield of noble gases corresponds to a production rate of 5.5×10^{-4} moles of xenon and 5.4×10^{-5} moles of krypton per megawatt-day. For a 250 megawatt pile this is equivalent to a daily generation of 100 curies of krypton-85 associated with but 12 cc. of xenon and 1.2 cc. of krypton (STP). From a waste disposal standpoint, this is an encouragingly small volume. However, from a health physics standpoint, escape of even a small fraction of such concentrated gaseous activity would require considerable dilution to reduce atmospheric contamination to the tolerance level of 3.3×10^{-5} microcuries/cc. for external radiation. (4) Error
31. Xe
0.31. Kr

2. Non-Fission Production of Krypton-85

No known radioactive gas has chemical, physical and nuclear properties sufficiently similar to krypton-85 to serve as an indistinguishable stand-in. Hence, only non-fission produced krypton-85 could be used to obscure its fission production and, thus, the related plutonium production. The only available method for producing the kilocurie quantities required would be by pile irradiation of natural krypton to produce the $\text{Kr}^{84}(n, \gamma)\text{Kr}^{85}$ reaction. Even if conditions for this reaction were favorable, it would seem unpromising from a neutron consumption standpoint if the 0.24% fission yield of krypton-85 were to be exceeded by any appreciable factor. Further, conditions for the n, γ reaction are not favorable; these include (1) the total capture cross-section for krypton is low, (2) there are competing nuclear reactions with other krypton isotopes having relatively high yields, and (3) krypton's chemical properties make it an awkward target material.

3. Solubility of Krypton

As a gas krypton obeys Henry's Law; i.e., its solubility cannot be expressed in absolute units but only as a distribution between the gas and liquid phase. Its absorption coefficient, expressed in terms of cc. of gas (STP) dissolved in 1 gram of water in equilibrium with 1 atmosphere of gas, ranges from 0.11 at 0°C to 0.04 at 60°C. (5) In other words, the ratio of the amount of krypton in the gas phase to that in the aqueous phase is equal to the ratio of the phase volumes in equilibrium with each other times a factor varying from 10 to 25 over this temperature range. The temperature coefficient in the 50-100°C range is very small. Thus, in this range if water were in equilibrium with but an equal volume of gas phase, 96% of the krypton would be in the gas phase.

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The presence of high concentrations of salts, as in dissolver solution, would be expected to reduce this very low solubility still further. Accordingly, krypton-85 must certainly be quantitatively removed from dissolver solution into the off-gases in current canyon operation. The claim that no krypton is evolved in certain laboratory dissolving operations at Harwell seems remarkable, and must mean that such dissolving is fumeless. Indeed.

The solubility of noble gases in some organic liquids is greater than that for water by an order of magnitude. However, the solubility would have to be greater by several orders of magnitude for this to afford an attractive means of scrubbing krypton-85 from a gas stream of any appreciable volume.

4. Fumeless Dissolving of Uranium

Currently the uranium dissolver off-gases consist of large volumes of nitrogen oxides and air in addition to the gaseous fission products. Removal of krypton-85 from this gas stream would be greatly facilitated if its volume were much reduced. So-called fumeless dissolving, according to the equation

shows most promise of accomplishing this result.

In this procedure, the nitrogen oxides normally evolved on dissolution are reoxidized to nitrate by a countercurrent flow of oxygen. Application to column and "pot" operation has received laboratory investigation at Harwell.⁽⁶⁾ In most of these studies a 20% excess of oxygen was used to achieve useful dissolution rates. Difficulty in obtaining stoichiometric oxygen consumption and thus off-gasless dissolving was tentatively ascribed to the presence of traces of inert gas; e.g., nitrogen or carbon dioxide, in the oxygen supply. Subsequently, W. C. Johnson of ANL has reported⁽¹⁾ "...this process prevents the liberation of any fission product gases, such as krypton, from the dissolver solution." S. G. English, head of the Chemical Section of the Division of Research in the Washington, D.C. A.E.C. office, indicated in a telephone conversation that nothing further is now known in the U.S. concerning British development of fumeless dissolving.

ANL initiated laboratory investigation of fumeless dissolving in the last quarter of 1949.⁽⁷⁾ Presumably, the immediate objective of such investigation was to reduce nitric acid consumption and also to reduce the dissolver off-gas volume for convenience in waste disposal. It is worth noting that the cost of fumeless dissolving development may be justified by potential nitric acid savings alone. However, S. Lawroski stated in a telephone conversation that ANL is aware of the specific interest in krypton removal and has this subject on their agenda for future investigation.

Electrolytic dissolution of metallic uranium as investigated at K-25 may be an alternative method of achieving off-gasless dissolving.⁽⁸⁾ In this case, uranium is anodically oxidized using nitric acid as the electrolyte. Cathodic gas evolution might be provided for by the use of a porous membrane.

⑥
Radiation decomposition of dissolver solution should not be overlooked as a possible small source of off-gas; viz., hydrogen. If off-gasless dissolving can be obtained in plant operation, provision should be made for purging krypton-85 from dissolver solution. Undesirable complications are certain to result from dependence on continued solubility of krypton in the various liquid waste streams, aqueous and organic, of any anticipated solvent extraction processes. This purging should probably be done with a small volume of some carrier gas; e.g., helium, nitrogen, oxygen, etc., to provide throughput to the krypton separation system. If quantitative purging of krypton unexpectedly requires a larger volume of gas, the bulk of the carrier gas might be of a type readily chemically absorbable; e.g., carbon dioxide, steam, etc., so that the krypton separation system itself would not be over-burdened. ⑥

5. Low-Temperature Adsorption of Krypton

Low-temperature adsorption appears to be the most promising method of separating noble gases from other gases.^(9,10,11) Adsorbents which have been used include activated charcoal (best), silica gel, granular magnesia, Magnesols, etc. Percentage of adsorption increases with decreasing temperature, of course; $-90 \pm 30^\circ\text{C}$ is estimated to be required for quantitative adsorption of krypton. As the temperature required for noble gas adsorption increases with increasing atomic weight, xenon will be adsorbed along with krypton. Provision should be made for prior removal of any chemically absorbable gases which would otherwise freeze or adsorb out and thus bulk-up the krypton separation system.

In the absence of information on the capacity of adsorbents, it is judged that regeneration of the adsorbent by desorption would lead to most convenient disposal of krypton-85. This desorption can apparently be achieved simply by heating the adsorbent to $50 \pm 50^\circ\text{C}$. The krypton-85 along with stable krypton, xenon and possible small amounts of carrier gas could be pumped into storage containers.

6. Alternate Methods of Separating Krypton from Other Gases

These include liquefaction, rectification, thermal diffusion, gaseous diffusion, centrifugation, etc., and are generally unattractive because of low efficiency and/or involved engineering design.⁽¹²⁾ Liquefaction and rectification have received most attention in connection with production of noble gases. However, they involve operation at even lower temperatures, ca. -190°C , than adsorption.

The Air Reduction Company has suggested the possibility of freezing out noble gas hydrates at low temperatures as a possible means of avoiding use of a solid adsorbent.⁽¹³⁾ No laboratory investigation of this approach has been made.

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7. Integration with Iodine-131 Waste Removal

The iodine-131 waste disposal problem will obviously be influenced by any modification of the dissolving procedure. Removal of iodine from waste gas streams would presumably continue to be by means of a silver reactor. However, the scale of such operation would be substantially reduced. Further, a method for transferring iodine-131 from dissolver solution to an appropriate gas stream following krypton removal would have to be developed. The alternative of leaving the iodine-131 in solution does not appear attractive; e.g., the extraction of iodine left in Redox IAF into IAP would probably be objectionable.

8. Proposed Attack on the Krypton Removal Problem

It appears that an at-any-cost solution to this problem could probably be developed, but that no sound basis exists now for estimating the magnitude and cost of such an effort. A scouting program; e.g., occupying two men for a period of about six months, directed as suggested in the foregoing should provide a basis for a reasonably firm estimate. Such a scouting program should initially involve literature research and detailed inquiry into the work done elsewhere on fumeless dissolving and krypton adsorption. The amount of exploratory experimental research to be undertaken should be based on this literature survey and the availability of such laboratory effort at the other project sites already doing related work.

Five to ten man-years of technically trained effort is very tentatively estimated required for development of a krypton removal method to the point of engineering scoping.

9. Tentative Flowsheet for Krypton Removal

See Figure 1, attached.

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BLOCK FLOW DIAGRAM
FUMELESS DISSOLVING
WITH I_2 AND Kr REMOVAL

FIGURE 1

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