

DECLASSIFIED

JW 36112

RECORD CENTER FILE

Distribution List:

RESTRICTED DATA

This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmittal or the disclosure in any manner to an unauthorized person is prohibited.

DECLASSIFIED

NY 100-361049

- Copy # 1 - CR Anderson
2 - GE Backman
3 - OF Beaulieu
4 - RS Bell
5 - WG Browne
6 - LW Finch
7 - CB Foster
8 - CT Groszwith
9 - TW Hauff
10 - OF Hill
11 - LM Knights
12 - JE Maider
13 - HW Murray
14 - PEL Nussbaum
15 - EG Pierick
16 - WC Schmidt
17 - 300 File
18 - Yellow File

Richland, Washington
April 6, 1955

This document consists of
6 pages. ~~Copy 18 of~~

TO: C. T. Grosz, Superintendent
T Plant Sub-Section
Separations Section

RECEIVED

JUL 10 1956

**300 AREA
CLASSIFIED FILES**

- I 131 EMISSION PROBLEM - BISMUTH PHOSPHATE PLANT

In order to control the ^{135}I emission from the T Plant ventilation stack to a maximum of 1.0 curie per day with the present processing equipment, the uranium metal processed must be cooled a minimum of 90 days with 100 days desirable. To process uranium metal with shorter cooling times will require silver reactor design improvements, revised product reduction procedures, and the adoption of dissolver operating techniques which will insure a controlled rate of gas evolution during metal dissolving.

Of the eight iodine isotopes produced in the irradiation of uranium, either as fission products or as a result of the decay of fission products, only three of these (I^{127} , I^{129} , I^{131}) are of importance at the time the uranium is actually processed, since the remainder are of very short half-life and decay to non-iodine isotopes. I^{127} and I^{129} isotopes account for the major portion of the iodine present in the dissolver solution. The I^{131} is a very small part of the

DECLASSIFIED

THIS DOCUMENT IS PUBLICLY
AVAILABLE

DECLASSIFIED

HW-36112

total iodine present in dissolver solutions but, being of short half-life (8.14 days), it is responsible for most of the radioactivity due to iodine isotopes.

In 70 day cooled uranium from Piles 100 DR, B, and C there are 230 curies of I131 per ton. This is equivalent to 0.0015 g of I131/Ton. ($0.0000066 \text{ g I131/curie} \times 230$). Total iodine produced is 0.3 to 0.4 g/Ton. Thus for each atom of I131 present in the uranium metal there are 200 atoms of "cold" iodine. Based on an average of 5 tons of uranium metal processed per day 0.0075 g of I131 would be released by the dissolver operation each day. 85% of this amount or 0.0064 g. are evolved in the dissolver off-gases and with the silver reactors operating at 99.9% efficiency this means that 0.0000064 g. of I131 or approximately 1.0 curie would be emitted from the T Plant stack. To attain an I131 emission of 0.5 curies (0.0000032 g. of I131) or less per day from the dissolver, the silver reactors must operate at an efficiency of 99.95% or greater. Since it is highly improbable that the present silver reactors can be operated at an efficiency of 99.95%, uranium metal with a longer cooling period should be used for processing, if a maximum I131 emission of 1.0 curie is to be maintained.

Peak iodine emissions can occur at T Plant, either during the nitric acid dissolution of the irradiated uranium metal or during the subsequent processing of the uranium nitrate solution through the uranium extraction cycle. During the uranium metal dissolving, approximately 85% of the original I131 present is evolved by the sparging action of gases released during dissolution and passes with these gases through the silver reactor. Since the present reactors under the best conditions, are only 99.9% efficient, this allows approximately 0.1% of the original I131 present to escape through the T Plant stack. The remaining 15% of the original I131 is transferred in the uranium nitrate solution through the uranium extraction process. Of this 15% residual I131 approximately two thirds would be evolved in subsequent processing and the remaining third would be carried out in waste solutions. Present procedures require that the uranium nitrate solution be stabilized with mercuric nitrate salt, and only approximately 0.15% of the original I131 present in the dissolver will then escape via the sand filter to the T Plant stack. On the basis of 70 day cooled uranium metal, containing 230 curies of I131 per ton, and a dissolving rate of 5 tons per day a minimum of 2.8 curies of I131 should be emitted from the T Plant stack via the dissolver off-gas and canyon air with all equipment operating at maximum efficiency. Since the maximum limit of 1.0 curie of I131 is exceeded, it is apparent that either longer cooled uranium metal must be processed or equipment design and processing procedures must be revised such that the limiting I131 emission can be attained.

Iodine emissions may occur in the dissolvers when the aluminum jackets are removed from the uranium slugs, when the uranium slugs are being dissolved in nitric acid, and when the uranium nitrate solutions are transferred, agitated or air sparged. When emission occurs, the silver reactor design, operation, condition, and state of saturation, can significantly affect the efficiency of I131 removal from the gas streams.

Following the uranium metal dissolving, iodine emissions may occur during the subsequent transfer of the uranium nitrate solution through the metal storage tanks, batch make-up tanks, and the uranium extraction tanks. Iodine I131 emission during these operations is undesirable because it increases the hazards to personnel working in the Canyon Building and because it contributes a major portion of the iodine discharged to the stack.

DECLASSIFIED

DECLASSIFIED

HW-36112

In the coating removal step in the dissolvers, a caustic solution is used to dissolve the aluminum jackets on the uranium slugs, and though caustic solutions will normally dissolve iodine, it might be advantageous to add sodium iodide to the caustic solution before heating it to boiling. This should guarantee the rapid dissolution of iodine in the caustic solution, and prevent any appreciable I¹³¹ emission during coating removal. At the end of the coating removal procedure, the caustic solution is air sparged prior to jetting the solution to the 15-7 coating waste tank. If air sparging were responsible for evolving dissolved I¹³¹, this air sparging step could be eliminated, since the water flush which follows transfer of the coating waste to 15-7 is normally air sparged also.

During the uranium metal dissolution in the dissolvers, the majority (85%) of the I¹³¹ is released and carried out of the dissolver solution by the evolution of nitrous oxide gases. The problem at this point, is either to prevent the solution from evolving I¹³¹ or to scrub all of the I¹³¹ from the dissolver off-gases, and the latter method has been adopted in the form of a silver nitrate reactor scrubber. However, if it is desirable to prevent I¹³¹ emission during dissolving, some ion such as mercury, silver, potassium, sodium, etc., might be added to the dissolver to chemically combine with the I¹³¹ and keep it in solution. Since even then, some of the I¹³¹ might escape the solution, a spray of dissolver solution could be used to wash the gases above the dissolver solution and further remove the I¹³¹ from the dissolver off-gases.

If little or no attempt is made to prevent the I¹³¹ emission from the dissolver solution, the gases must be scrubbed to remove all traces of I¹³¹ before it is discharged to the atmosphere. Certain variables must be controlled to maintain the maximum efficiency of the silver nitrate reactor scrubber, the most important ones being, rate of evolution, contact time, degree of saturation, and condition of the equipment. The uniform evolution of I¹³¹ would give maximum efficiency for operating the silver reactor, and although maximum emissions do occur under present conditions, every effort should be made to keep the emissions as uniform as possible. At the start of dissolving a new batch of metal, the I¹³¹ emission seems to be greatest, probably because the maximum surface area of uranium is presented to fresh nitric acid. As the acid is heated to boiling, the reaction rate increases and the I¹³¹ evolution probably becomes appreciable as the solution boils and all dissolved gases, including iodine are purged from the solution. Since refluxing doesn't start until after the solution has boiled for several minutes, the gases evolved as the solution comes to the boiling point, are not scrubbed by the returning reflux solution as they pass through the reflux condenser on their way to the silver reactor. It might be advantageous to introduce steam into the top of the dissolver to start the refluxing before the solution in the dissolver begins to boil. This would insure the start of refluxing as the first gases are evolved, and give the maximum washing of evolved I¹³¹ as the solution is brought to the boiling point.

To control the rate of I¹³¹ evolution during dissolving, certain changes in dissolving procedure might be initiated. These changes could include reducing the concentration or the amount of nitric acid charged at the beginning of dissolving, reducing the uranium metal heel, air sparging the dissolver solution during the period prior to boiling, or slowing down the rate of the initial reaction. Any or all of these dissolving procedure changes should insure a constant rate of I¹³¹ evolution, and allow the off gases to have maximum contact with the silver nitrate in the silver reactor.

As noted previously 15% of the original iodine present in the dissolver is transferred in the uranium nitrate solution through the uranium extraction process. Of this 15% residual iodine, approximately two thirds would normally be evolved during the

DECLASSIFIED

DECLASSIFIED

HW-36112

pre-reduction and uranium extraction steps.

The addition of 5×10^{-4} molar mercuric nitrate to the completed dissolver solution results in an 80% suppression of the iodine which could be evolved. By increasing the mercuric nitrate concentration to 1.0×10^{-3} molar, an iodine suppression of 90% might be obtained which would effectively reduce the iodine evolution in these steps by 50%.

Since most of the residual iodine is evolved during the reduction step prior to uranium extraction, it may be possible to make the reduction in the dissolvers after dissolution of the uranium slugs. The iodine evolved would thus be scrubbed by the silver reactor and be so effectively removed by the reactor that subsequent emissions during processing would be negligible. Consideration might also be given to vigorous sparging of the metal solution in the dissolver prior to transfer, so that any iodine which could be removed would be trapped by the silver reactor.

Since 85% of the original iodine present in the uranium metal is removed during dissolution in the dissolvers, it is very important that the design of the silver reactor scrubbers be of sufficient capacity and efficiency to remove the I¹³¹ evolved. The present silver reactors are 99.9% efficient in removing the iodine from the dissolver off-gases. However, on short cooled uranium and with the present operating procedures this is not sufficient to control the I¹³¹ emission rate to a maximum of 1 curie per day.

A silver reactor design study has been started to explore the possibility of processing shorter cooled uranium metal at T Plant. Present silver reactors were designed on the basis of space available in the canyon cells, and the processing of longer cooled uranium. Efforts in the new design study will probably be directed towards improving the reactor preheaters, decreasing the possibility of plugging and channeling of the present silver reactor columns, and increasing the gas-silver contact time through increased reactor column volume.

Tests on the former Berl saddles used for packing the silver reactors as compared to the new type interlocks has revealed that the interlocks by design are capable of greater packing efficiency per unit volume than the Berl saddles. On the basis of a random packed column (50 berl saddles per 110 ml. versus 50 interlocks per 68 ml.) 39% more surface area is available using the interlocks than would be available using an equal volume of Berl saddles. Tests by Purax personnel have also revealed that the absorption of silver nitrate by the interlocks was 1 1/2 to 2 times greater than for the former Berl saddles. Both of these tests indicate that packing of the silver reactors with interlocks rather than Berl saddles would probably increase the reactor absorption efficiency. However, it has been noted that the interlocks are more fragile and have a greater tendency to chip or break. This condition would have a negative effect on reactor efficiency since the probability of plugging or channeling in the silver reactor column would be significantly increased. To decrease interlock breakage and prevent any tendency to plug or channel, the use of spacer grids in the silver reactor has been suggested.

In controlling the I¹³¹ emission problem, adequate sampling techniques and control points are necessary to provide valid analytical data. Specifically, sampling equipment should be provided which will provide data on the contributions of the dissolver off-gases and the building ventilation system to the total iodine emission through the T Plant ventilation stack. From this data, the major source of any

DECLASSIFIED

DECLASSIFIED

HW-36112

iodine emissions may be more easily associated with specific processing conditions and appropriate corrective action can be taken.

At the present time the data necessary for calculating the total I131 emitted from the T Plant stack, are collected from sampling equipment located in the 292-T Building. A sample of the stack gas is drawn into the 292-T Building through a sample line about 150 feet long at a flow rate of about 0.3 cu. ft./min. After filtering the stack gas sample, the gas is introduced into a caustic scrubber, and the scrubbed solution monitored for radioactivity. This radiation measurement is recorded on a roll recorder and because of long sample lines and relatively large columns of liquid hold up in the sampling equipment, a time lag of 30 to 60 minutes elapses between dissolver upsets and corresponding radiation recordings. After the scrubbed solution is monitored, it goes to a trap which in turn overflows to a sample accumulation bottle which accumulates the total amount of scrubbed solution and absorbed I131 collected over a 24 hour period, 48 hour period, or such period as is convenient for sample collection and transportation to the laboratory. If the scrubber solution collects for two days, the total I131 is divided by two and is reported as the average accumulation of I131 per day.

From the above description, it is apparent that the data reported by the daily sample, or that taken from the recorder, indicates only how much total I131 has been emitted. It does not identify the specific contributor to the total emission, such as the building ventilation system, or the individual dissolver off-gases. It is also apparent that once the equipment has become contaminated with a concentrated I131 solution, the dilution rate is so slow that it may take several days before the new solutions wash out the strong solutions and return the equipment levels to their former background.

For control purposes additional sampling points must be established and the flushing of equipment and subsequent sampling must be made at more frequent intervals. Individual samplers should be provided for each dissolver off-gas line and for the building ventilation which passes through the sand filter (installation of some equipment has already started). The equipment basically should consist of caustic scrubber columns and associated flow and radiation monitors. By establishing these additional sampling points, process movements can be more thoroughly reviewed and the source of excessive iodine emission can be more readily corrected.

Processing of special 300 MWD/T uranium metal test material has just been completed (Production Test 200-2, Supplement A) boiling time on this material averaged 276 days and the average I131 emission per day was 2.6 curies. Stack monitoring during processing has indicated a defective silver reactor on the 3-5R dissolver so this unit was replaced on 3-30-55. Following the reactor replacement one dissolver will be charged with 200 MWD material (presently 73 day cooled) and processing will be checked carefully step by step to make sure that the emission of I131 does not occur in any significant quantities. Very slow dissolving rates can be used to control the I131 release and at any time the reaction can be stopped by removing the acid from the uranium slugs and then holding the slugs in water until they decay properly or until appropriate equipment changes can be made. On the basis of this special processing for 200 MWD uranium metal as outlined above, the processing of shorter cooled uranium with present processing equipment should be well established.

DECLASSIFIED

DECLASSIFIED

HW-30112

At the present time the recommended cooling period for 200 MWD uranium to emit 0.3 curies of I131 per day or less under optimum operating conditions is 90 days. To process uranium metal with shorter cooling times and still maintain the I131 emission to a maximum of 1.0 curies per day, silver reactor design improvements and revised processing procedures will in all probability be necessary.

W. G. Browne

W. G. Browne, Superintendent
Process & Plant Services Unit
T Plant Sub Section

WGB:rr

DECLASSIFIED