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HW-32467

CHEMISTRY-SEPARATION PROCESSES
FOR PLUTONIUM AND URANIUM

AEC RESEARCH AND DEVELOPMENT REPORT

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July 13, 1954

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TERMINAL STATUS REPORT - REDOX CONTAMINATION

The Redox ruthenium contamination problem has two distinct phases; the environs contamination as a result of stack emissions, and the in-canyon contamination which controls time and cost factors for plant maintenance. On stack emissions, the probability of serious environs contamination exists so long as the batch-type, permanganate headend ruthenium volatilization process is used. Knowledge of the characteristics of volatilized ruthenium is not adequate today to give complete assurance that the off-gas treatment facilities will satisfactorily remove the particulate and gaseous forms of ruthenium on every headend batch. Until the required knowledge of ruthenium reaction rates is developed, the filtering and scrubbing efficiencies are determined, and the requirements to guarantee 100 percent reliability of equipment operation are solved, the prediction of frequency and amounts of ruthenium emission must be based on the experience factor gained in actual plant operation. (1) The environs contamination problem would seem to require more absolute assurance than this, that significant stack emission of ruthenium will not occur.

On in-canyon contamination, the knowledge and technique required to prevent ruthenium migration during replacement of the oxidizer system is similar to the knowledge of ruthenium process chemistry, i.e. it is inadequate at the present time. In replace-

-2-

ment of any major equipment item in the oxidizer system, it is to be expected that crane deposition and canyon air activity will increase markedly. On two known occasions, in February 1954 and June 28, 1954 black sooty deposits of ruthenium oxide were observed on the canyon deck. Improvements in equipment handling and crane maintenance (2,3) continue to be made and the current joint effort on crane improvements by the Design Section and Redox personnel will improve the maintenance control of the vital crane operation. However, to contain ruthenium oxide deposits completely during every equipment outage does not appear possible.

Experience in the plant is the only current test on methods for handling equipment which contains the friable ruthenium oxide deposits. If one part in 10^7 parts (3) potentially present in the H-4 tower and pot in June 1954 were spread into the canyon, Redox would have a recurrence of crane contamination equivalent to that experienced in September and again in February.

During the current Redox outage, the in-canyon control on activity was excellent from June 10 through June 23 with several major replacements being made on equipment. On June 24, replacement of major equipment items in the oxidizer system was begun. Concurrently, there was a one thousand fold increase in canyon activity, equalling that experienced in September and again in February. This very high level of in-canyon activity requires only 30 micrograms of radioactive ruthenium oxide or about 1 milligram of the ruthenium oxide mixture (about 4 percent is radioactive).

It might be postulated that equipment handling techniques can be improved to eliminate this contamination spread during equipment replacement. This would appear reasonable only if most of the oxidizer equipment is redesigned. It is required that ruthenium contaminated equipment be thoroughly decontaminated prior to replacement if spread of contamination is to be controlled. The H-4 tower and the H-4 and H-5 vapor line illustrate the limitations of the present equipment in regard to accomplishing this decontamination. There is no apparent way to decontaminate the H-4 to H-5 vapor line, and the means for decontaminating the H-4 tower are so inadequate that, on the current replacement, it was concluded that the risk attendant with decontamination was greater than is the known risk of handling the contaminated tower.

In-canyon contamination and potential break through to the environs during equipment replacement appear to be in themselves of such magnitude, both from the engineering and the economic standpoint, as to justify an alternate process for Redox.

An alternate process, ozone tailend, (4) shows every promise of satisfactory performance, and an accelerated program of pilotscale, design and construction work could make ozone tailend available for operation within a few months. This process alternate would remove the permanganate headend process from its current "must" status (i.e. today there is no process alternate for the Redox operation) and thus allow considered judgment on future plant operation. Full expedition of the entire program for ozone tailend is an imperative part of the Redox contamination work. The successful plant operation of this alternate will place the present permanganate headend ruthenium volatilization process in the position that the

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environs contamination risk be justified on the basis of improved plant performance.

It is the writer's opinion that once a process alternate is available, continuing ruthenium studies will further support a decision to not use headend ruthenium volatilization.

STACK FLUSH

The stack flush was started on June 29, 1954 but was discontinued soon after flushing started because of a rapid activity buildup in the Redox Plant operating zones. Improvements were then made in sealing-off the canyon and, on July 2, the planned stack flush was done. About 1 curie was removed from the stack and about $1\frac{1}{2}$ curies from the breeching.

These $2\frac{1}{2}$ curies are small compared to the 70,000 curies of ruthenium in each head-end batch, but it is significant in light of what is required for serious environs contamination. J. W. Healy of the Radiological Sciences Department has calculated the activity of a particle as a function of size where the ratio of 10^3 to 10^6 ruthenium is 0.8. These activities, which are the maximum possible for a spherical particle, converted to particle numbers equivalent to the $2\frac{1}{2}$ curies removed during the flush show the following:

4.0×10^9 particles 1 μ diameter or
 4.0×10^6 particles 10 μ diameter or
 3.3×10^4 particles 50 μ diameter or
 4.0×10^3 particles 100 μ diameter

For comparison, the particle density found during the July 3, 4, and 5 cleanup of the environs was:

Purex area 200-E - 1 particle per 1000 Sq. Ft.
Power House area 200 E - 1 particle per 600 Sq. Ft.
Batch plant - 1 particle per 600 Sq. Ft.
Shops 200 W - 1 particle per 75 Sq. Ft.
Badge House 200 W - 1 particle per 25 Sq. Ft.

The stack flush effluent activity was more than 90 percent ruthenium with about 1 percent cesium, 1 percent zirconium and niobium, 1 percent strontium and about 3 percent rare earths. There was a trace of ammonium nitrate on only the first wash effluent with none being detectable after the initial few minutes of the flush period. A separate, detailed report, covering the entire flushing operation, is being prepared by W. C. Schmidt and W. H. Koontz.

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STACK SAMPLING

The existing samplers do not furnish a representative aliquot of the stack effluent. L. C. Schwendiman, Radiological Sciences Department, has designed a probe system for installation at the top of the stack. W. C. Schmidt is working with him in a modification to the proposed sampler to assure isokinetic flow at all times. This modification is required because of the varying gas flows and will consist of a pitot tube installation at the 50 foot level with automatic control take off on the sampling probe system.

SOURCE OF ENVIRONS CONTAMINANT

The plot survey results obtained by Radiological Sciences personnel show a marked increase between June 25 and June 28. Redox Stack emissions during this period were less than 0.1 curie per day which introduces the possibility of sources other than Redox. Resurveys are being made of T, U, and UC₃ Plant operations but the primary source of these plot increases appears to be migration of the particles already in the environs.

The migration of particles is also indicated by the plot surveys after June 28. Six of the plots show the following:

Radiation levels mrad/hr.

<u>Plot Number</u>	<u>June 21-25</u>	<u>June 28</u>	<u>June 29</u>	<u>July 6</u>
4	500	5000	5000	1500
9	20	2500	no reading	1200
10	150	1000	1800	800
20	30	3000	500	300
22	20	300	900	105
52	20	900	10	110

Of special interest is the change in these plot survey results. This type of continually changing levels of activity or particle migration is also evidenced by the continuously recording plot survey instrument at the meteorological tower. The normal background level is at a chart reading of 15. Periodically, the chart reading will move vertically to as high as 60 where it may remain only momentarily or again it may remain at a high reading for two hours. The chart decline to the background reading is often rapid as was the increase. This rate of change has been postulated to be the result of particles moving across the monitored plot of ground.

The particulate nature of the ruthenium environs contaminant, combined with its relatively long half life, will pose a continuing problem long after the emission source is removed. Physical removal of this particulate matter from all plant working areas is planned. The changing plot surveys indicate that these area cleanups may have to be repeated several times before the problem is resolved. Fixing this activity near Redox, to prevent further migration to other areas, may prove less costly than this physical removal program.

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PROCESS VESSEL INSULATION

The new H-4 pot and tower were insulated with two inches of 85% magnesia and covered with stainless steel sheathing. Currently these are the only insulated vessels in Redox, but all future replacements for process boilup units will be insulated.

FUTURE PROGRAM

The most important single phase of the current effort centers in the work on the alternate process of ozone tailend. This process alternate, however, is not considered a panacea for the Redox contamination problem. Aside from the longer range development of other process alternates and potential improvements or modifications to the permanganate headend, such as continuous intercycle oxidation, the Redox plant has problems related to equipment and to the physical building structure. It is known that pressurizing of the canyon is common when the railroad tunnel door is open and a northerly wind is blowing. Recent observations have shown canyon pressurizing to occur even at wind velocities of only 5 m.p.h. Considerable information was also gained on canyon in-leakage during the complete ventilation outage for the Stack flush and it now appears that a systematic, step-wise program of investigation and design by the Redox plant and Design Section personnel may resolve the ventilation problem without major plant additions for supply and exhaust systems. The most apparent indicated improvement would be a workable airlock arrangement on the railroad tunnel entrance. The original airlock system, installed during plant construction, did not prove to be workable and has been scrapped.

Pressurizing of the vessel vent header system is also a common occurrence. This potential source of in-canyon contamination has not been resolved and will require a thorough analysis of plant operating conditions after plant startup to define the limitations of the system both from the operating standpoint and from the physical limitations of the equipment. It is recommended that this study be conducted initially by Redox plant personnel to define the inadequacy of the present vessel vent header system.

The gas sampling program being conducted by W. C. Schmidt is covered in detail in his letter of May 20, 1954. The sampling equipment has been installed and, following plant startup, the planned sampling program on all gas streams will be resumed. This gas sampling study includes particle size measurements, filtering and scrubbing efficiencies determinations on existing plant equipment, stack sampling studies, and resolution of the question of ruthenium emission during dissolving or concentrating operations.

The equipment required for the cell air thermal studies is on hand and the installation will be made in the 200 W shops following completion of the work associated with the present Redox shutdown. W. H. Koontz is coordinating this work in the shops for the Design Section.

It is believed that the short term objectives for the Redox plant are defined and are attainable. These objectives are (1) a definition of the ruthenium problem, (2) a design and plant program to improve the physical plant structure such as ventilation and crane equipment, and (3) selection of an alternate process for the current headend process. The long range program will be developed as results are

obtained from the work now in progress by the various groups. It is recommended that a research and development review be held jointly by these various groups on a regular basis so that the thinking of everyone is made available for the long range program.

The "task force" approach to the Redox contamination problem was instigated April 15, 1954. The status reports up through June 21, 1954, along with a summation of the advantages and the design and process problems of Intercycle Oxidation by R. G. Barnes, have been combined for record purposes in document HW 32468. A similar summation was prepared on ozone tailend by E. R. Irish⁽⁵⁾ and was issued as HW 32037. The process review of ruthenium chemistry, (status report April 30, 1954) has been completed by Technical Section personnel and is documented in HW-32331, "Ruthenium Process Chemistry Considerations Redox Process" by M. K. Harmon, C. G. McCormack, R. L. Moore, and A. S. Wilson.

References:

- (1) HW-32331 Pages 4, 5, and 11 "Ruthenium Process Chemistry Considerations Redox Process" by M.K. Harmon, C.G. McCormack, R.L. Moore, and A.S. Wilson June 10, 1954
- (2) HW-32468 April 29, 1954 letter C.R. Anderson to E. Doud.
- (3) HW-32468 May 17, 1954 letter C.R. Anderson to E. Doud.
- (4) HW-32468 May 27, 1954 letter C.R. Anderson to R.S. Bell.
- (5) HW-32037 "Ruthenium Removal from Redox Product Solutions by Tail-End Ozonization" - E.R. Irish May 28, 1954.

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