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HANFORD ATOMIC PRODUCTS OPERATION

AEC RESEARCH AND DEVELOPMENT REPORT

RUTHENIUM PROCESS CHEMISTRY CONSIDERATIONS REDOX PROCESS

by

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INTRODUCTION

During the first 15 months of operation of the Redox process, it was clearly demonstrated that in the absence of any pre-solvent extraction treatment of the starting metal solution, ruthenium contributed from 75 to 95 per cent of the ~~total~~ remaining fission product activity in both the final uranium and plutonium streams, and that three solvent extraction cycles were able consistently to produce, at best, only marginal quality product. This precarious position was further endangered by a three-fold reduction in the gamma radioactivity specification for recovered uranium shipped from Hanford, and by increased power levels in the reactors, resulting in still higher fission product concentrations in Redox feed solutions.

The permanganate pre-solvent extraction (Head-End) treatment, perfected specifically for Ru removal, was used in the Redox plant with seemingly complete success starting in May, 1953, and for a period of approximately three months thereafter, appeared to be making possible the elimination of the third uranium decontamination cycle.

However, within four months after its inception, this process led indirectly to two very serious, unexpected problems involving ruthenium contamination of the operating canyon and plant environs, and the succeeding months have been spent in a concentrated effort to determine the cause and cure. The difficulties with the present process are under study as are alternative processes, but none of the alternatives can yet be endorsed for plant use.

The schemes considered and/or used to date for Ru removal or control (including the permanganate Head-End) have, in the laboratory, been directed at several process regions, viz., both pre- and post-solvent extraction, between cycles, and during solvent extraction. Further intensive efforts have been directed toward interpretation of ruthenium chemistry, identification of ruthenium species, and behavior of these species under process conditions.

The general problems associated with ruthenium suggest that a review of the process chemistry information relating to this fission product is desirable in orienting the views of the various organizations involved in the current intensive study of the over-all technical, engineering, and manufacturing requirements for its proper control.

OBJECTIVES

The purposes of this review are to summarize briefly:

1. The chemistry of Ru in the Redox process;
2. The permanganate Head-End treatment and its associated problems in plant operation;
3. Alternate possibilities for the elimination or control of Ru, including those which might solve the permanganate process difficulties.

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It is also the purpose of this document to present a selected bibliography on the subject of ruthenium specifically for those points under discussion, herein.

SUMMARY AND CONCLUSIONS

1. Chemistry of Ru in Redox. Several different forms of Ru have been found to exist in dissolver solution, but very little is known regarding their fundamental chemistry. Complexes are formed slowly in solution, but under normal conditions of uranium dissolving in the presence of a high concentration of nitrite ion, ruthenium nitroso species are believed to be formed in significant amounts in addition to the normally expected Ru(IV) species. The various species show markedly different rates of oxidation and degrees of extraction into hexone⁽¹⁾, although variations in dissolver operation, solution acidity, storage time, and temperature, in themselves, have little or no effect on subsequent solvent extraction behavior of Ru as a whole.^(6,9,11) The use of ozone and/or permanganate to oxidize and remove part of the ruthenium before solvent extraction, however, appears to decrease the solubility of the residual ruthenium in hexone, and thus improves extraction decontamination.^(4,5) This is presumably due to the slow destruction of the solvent-soluble nitroso complexes with the corresponding production of less extractable compounds intermediate between this form and the volatile tetroxide. Thus the permanganate Head-End treatment also contributes to a slight increase in the proportion of the entering Ru which accompanies the exit plutonium stream from the U-Pu partition column.

2. The Permanganate Head-End Process. The principles of this treatment of Redox feed solution are based on the oxidation of Ru existing in the metal solution, to the volatile tetroxide (RuO_4) and its removal as a gas prior to solvent extraction. Certain species of Ru, e.g., the nitroso complexes, are oxidized by permanganate slowly and with difficulty, and are thus not completely removed, but are believed to be partially converted to less solvent-soluble forms. The arithmetic Ru decontamination factors across the Head-End step, based on the past year's performance in the Redox plant, have ranged from 5 to 20 with an average of about 6 to 8. This has given overall Ru logarithmic decontamination factors across the Redox process averaging 6.2 for Head-End plus 3 solvent extraction cycles, compared with 5.5 for 3 cycles without the head-end treatment. This has further resulted in a second-cycle product which, if based on Ru decontamination alone, would permit the elimination of the third cycle. The ruthenium content of both uranium and plutonium product streams which averaged from 75 to 95 per cent of the total before this head-end treatment was adopted, has since dropped to 10 to 20 per cent.

Serious, unexpected process difficulties have arisen, however, as a result of this volatilization procedure, principally from the reduction and thermal decomposition of the gaseous tetroxide to a solid - probably a mixture of the lower oxides such as RuO_2 , Ru_2O_3 , etc. - in the oxidizer vessel and its de-entrainment tower, with two important consequences, namely 1) the emission of hazardous amounts of ruthenium from the plant ventilation stack, and 2) the escape of gross quantities of ruthenium into the operating canyon. Ruthenium, in this solid form, is deposited on the surface of all stainless steel process equipment with which the RuO_4 comes in contact after

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leaving the oxidizer solution.⁽¹⁰⁾ This deposit is then easily removed as a powder by the impact to which it may be subjected during, for example, equipment changes in the cell. The tetroxide is also thermally unstable and is decomposed in the gas phase at temperatures existing in the system. The minute particles thus formed pass into the scrubber, but since the lower oxides are not soluble in the caustic solution (as is the RuO_4) the scrubbing efficiency is drastically reduced, thus allowing some of these fine particles to pass on through the off-gas system to be eventually emitted from the ventilation stack.

3. Alternate Processes and Remedial Measures. The list of alternatives to the present head-end process does not contain many attractive possibilities at present. Aside from returning to the procedures in use prior to May, 1953, with a consequent five-fold increase in product contamination, the following main approaches are under careful consideration: 1) intercycle permanganate oxidation of the aqueous solution resulting from a co-decontamination (precycle) solvent extraction flowsheet⁽¹⁴⁾, 2) ozonolysis of product streams⁽¹⁵⁾, and 3) sulfide precipitation and copper sulfide scavenging (both pre- and post-extraction).⁽⁷⁾ Decontamination factors have been determined for all of these in the laboratory and indicate that all are potentially acceptable from the standpoint of Ru removal. Based on a consideration of all factors involved, post-extraction ozonolysis currently appears the most attractive of the three and sulfide the least attractive. The data on process application, however, are inadequate and thus none of these techniques can yet be fully endorsed for plant use. Among other possibilities currently being explored are organic phase complexing, ruthenium iodide precipitation, and manganese dioxide scavenging, but not enough data have been obtained to justify their serious consideration.

Since there is no alternate process immediately available to replace the current Head-End treatment, several modifications of the permanganate procedure are being tested in the plant which show that adequate control of ruthenium is possible. These include 1) the operation of the oxidizer de-entrainment tower as a reflux condenser (thus serving as an additional gas-scrubbing facility and decreasing the air in-leakage), 2) a ten-fold reduction in sparge gas rate through the oxidizer, and 3) variations in temperature and rate of addition of the oxidizing agent. The net result of these changes has been an approximate two- to five-fold decrease in the amount of ruthenium emitted from the stack. Inasmuch as plans are proceeding for the installation of an additional caustic scrubber and new gas filter, the recommendation is made by the Technical Section that Redox operation continue with the current (as of June 1, 1954) modified Head-End procedure until such time as a replacement process is ready for adoption, or until the new scrubber and filter are installed. This installation will then make possible the otherwise inadvisable plant evaluation of other modifications to the present process, e.g., ozone sweep during oxidation, aimed at maximum delivery of RuO_4 to the scrubber and minimum deposition of solid forms of ruthenium in process lines and vessels. Such a combination of reduced ruthenium emission from the stack and reduced deposition within the system, would constitute a substantial improvement over the present scheme for controlling the ruthenium problem, particularly as it relates to emission from the stack. The problem of dislodging the solid compounds of Ru during the conduct of maintenance operations would remain, but the amount of ruthenium released in this manner should be reduced. Recent site surveys indicate that

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the problem is more difficult than first believed, and the attainment of emission rates as low as 0.1 curie per day (the target at the time the intensive study was initiated) may not be adequate.

DISCUSSION

A. Ruthenium in the Redox Process

1. Ruthenium from Fission. Radio-ruthenium appears as a fission product in irradiated uranium principally as two isotopes, Ru^{106} with a half-life of about one year and Ru^{103} with a half-life of about 40 days. After a 90-day cooling period a ton of 600 MWD uranium contains, on the average, 0.4 gram of Ru^{103} representing 14,000 curies (beta plus gamma) and 0.83 gram of Ru^{106} representing 3,600 curies (beta plus gamma). One batch of Redox plant feed solution generally consists of four tons of uranium and thus contains approximately 5 grams (70,000 curies) of radio-ruthenium..

2. Ruthenium Chemistry. Ruthenium is the only platinum metal fission product of importance in the Redox process. Like the other platinum metals, ruthenium ions undergo complexing reactions slowly in solution. However, oxidation and reduction reactions can be, and in general are, quite rapid. All available evidence indicates that ruthenium in nitrite-free nitric acid solution, should exist as the ruthenium(IV) species which undergo polymerization and colloid formation at low acidities, and are rapidly oxidized to ruthenium tetroxide by permanganate ion. However, since ruthenium species are born in dissolver solutions in the presence of a large amount of nitrite ion, ruthenium nitroso species as well as ruthenium(IV) species are undoubtedly present in plant solutions. Ruthenium nitroso species, unlike ruthenium(IV) species, are slow to change, are solvent extractable, and are difficult to oxidize. Thus the permanganate oxidation (Head-End treatment) presumably results in the slow formation of Ru species intermediate between the nitroso complexes and the volatile tetroxide, which are less solvent-soluble and thus more easily removed in the aqueous raffinate from the first solvent extraction cycle.

3. Identification of Ru Species. Chromatography is a powerful tool in the identification of chemical species in solution. This technique can be used to distinguish between colloidal and ionic species, between solvent extractable and non-extractable species, and between rapidly and slowly hydrolyzable species. Chromatography is currently being applied to the study of Redox solutions in order to determine the distribution of ruthenium species in these various classes as a function of conditions of solution preparation and history, and solvent extraction treatment.(12)

4. Uranium Dissolving. The dissolving operation employed in the Redox Process differs very little from that originally used in the Bismuth Phosphate Process but even now very little is known concerning the effect of dissolver operation on the species of ruthenium appearing in the metal solution and the behavior of these species on subsequent extraction. Until recently, experimental techniques have not been available (see above) to investigate this matter. Furthermore, the low concentration of ruthenium in dissolver solution and the intense radio-activity associated with these solutions make this investigation a problem of very formidable difficulty. A comprehensive empirical investigation into the effects of dissolving variables on the

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Redox extraction behavior of ruthenium and other fission products was, however, recently completed in the laboratory.^(6,9,11) The significant finding of this work was that most of the variables investigated had little or no effect on first cycle ruthenium decontamination. Thus it was found that extended dissolving or digestion times, operation of the dissolver at high or low temperature, the method of acid addition, and the presence or absence of a metal heel, did not govern subsequent Ru behavior. Isotopic dilution, by means of co-dissolution of a ruthenium alloy, failed to significantly alter ruthenium decontamination.

Continuous sparging with air also had no effect on Redox fission product behavior but, conversely, sparging with NO_2 during dissolution or saturation of a plant dissolver solution with NO_2 was found to decrease ruthenium decontamination 10-fold through solvent extraction. Two additional and drastically different dissolving operations, both producing markedly poor decontamination on subsequent extraction, were 1) oxidation of uranium to U_{308} followed by its dissolution in nitric acid, and 2) anodic electrolysis of irradiated uranium into dilute nitric acid.

5. Feed Preparation. In addition to the study of effects of dissolver operation, the effects of metal solution storage and feed preparation have been partially evaluated. A sample of plant dissolver solution was digested at 90°C . for a period of one month and the Redox solvent extraction behavior was observed as a function of time. Ruthenium solvent extraction decontamination was not affected by this treatment.⁽⁹⁾

It was found during the early development of the Head-End process and the measurement of the kinetics of ruthenium tetroxide volatilization, that several species of Ru appear in dissolver solution.⁽⁴⁾ These original species give widely differing distribution coefficients in hexone, but it was noted that the form (or forms) of Ru remaining in the aqueous feed solution following oxidation (by ozone) exhibited lower solvent solubility than the initial gross ruthenium activity in the parent solution. This is apparently confirmed by data from the recent Redox Plant operation with permanganate head-end treatment, in which the first solvent extraction cycle decontamination appears to be somewhat greater than that from corresponding operation without head-end. See below.

6. Solvent Extraction. Due to the existence of several different species of Ru in Redox solutions, no broad generalizations are possible regarding its solvent extraction behavior and the effects of flowsheet changes on this behavior. A few specific points which have been covered in earlier work at several sites (K.A.P.L., O.R.N.L., Hanford) can be mentioned, however. These include:

- a. The weighted average distribution coefficient, E_a^0 , for all Ru species in untreated dissolver solution under current Redox IA Column feed point conditions is about 0.008. The Ru remaining after permanganate oxidation of the feed solution exhibits a distribution coefficient smaller by a factor of 2 to 4.⁽⁴⁾ The E_a^0 for RuO_4 is very large, but it is unlikely that significant amounts of this compound reach the solvent extraction columns under plant conditions.

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- b. An increase of acidity from -0.2 M to 0.2 M HNO_3 in the aqueous phase of an aluminum nitrate salted system, may increase the $\text{Ru } E_a^{\text{O}}$ in the extraction and scrub sections by factors as high as 400 and 10, respectively. This is particularly true of the nitroso complex.⁽³⁾
- c. Increasing the extraction temperature decreases $\text{Ru } E_a^{\text{O}}$ slightly.
- d. The E_a^{O} for Ru (primarily the nitroso) tends to increase somewhat as the time of scrubbing contact is increased even under acid-deficient conditions.

Qualitative confirmation of some of the above points (particularly the effects of acidity) has been obtained from time to time during plant operation when changes (either intentional or accidental) have been made in the flowsheet and/or stream compositions. Changes in L/V (aqueous-to-organic flow ratios) in the columns do not significantly change the actual phase hold-up time in the columns, so that item d., above, is of little consequence. Changes in L/V, however, are important from the standpoint of their effects on acidity, this being the condition which most closely regulates ruthenium decontamination in solvent extraction.

Average logarithmic decontamination factors (df) are presented in the table below, showing ruthenium decontamination by cycles for operation both with and without Head-End treatment.

Process	Average Log Decontamination, Operation without Permanganate Head-End Treatment (For 5-month period prior to May, 1953)	Average Log Decontamination, Operation with Permanganate Head-End Treatment (For period of last half of 1953 and first half of 1954)
Head-End	--	0.8
First U Cycle	2.55	2.81
Second U Cycle	2.00	1.84
Third U Cycle	0.90	0.70
First Pu Cycle	3.40	3.45
Second Pu Cycle	1.80	1.80
Third Pu Cycle	0.40	0.67

B. Permanganate Head-End

1. Principles. The original purpose of a "head-end" treatment was the removal of ruthenium from the feed solution prior to solvent extraction. It was decided that the best method was the oxidation of the ruthenium to the volatile tetroxide followed by its removal as a gas which could be collected in a scrubber filled with sodium hydroxide solution. Permanganate ion was selected from a long list of possible oxidants, e.g., in preference to ozone, because in addition to its comparatively moderate cost, it served the secondary function of acting as a scavenger (for Zr-Nb and siliceous materials which could be centrifuged out and sent to waste) after being reduced to MnO_2 in solution.

During Redox plant start-up, considerable difficulty was encountered in maintaining adequate permanganate concentration, due to unknown factors adversely affecting its stability in dissolver solution, and thus greatly reducing its effectiveness as an oxidant. Extensive laboratory and Hot Semiworks studies have since shown that permanganate stability in such a system is a function of temperature, acidity, and an auto-catalytic effect which is still not completely understood. The effects of fission product radiation and the condition of the oxidizer wall surface are of secondary importance (if any) to permanganate stability. It now appears that dissolver solution contains a reducing potential equivalent to 0.01 to 0.02 M Mn^{+2} ion, and that a part of the residual MnO_2 in the oxidizer pot is actually converted to the Mn^{+2} ion at 70° to 95°C. during the period preceding the oxidation. The consequent reduction of permanganate to manganese dioxide, then, seems to involve the production of a catalyst which sharply increases the rate of the first order reaction by which the remaining permanganate decomposes. However, if the permanganate is added in two increments, the first of which is a 0.02 M "sacrifice", and if its decomposition to MnO_2 is allowed to go to completion, a second addition of permanganate then exhibits a much longer half-life. Following the oxidation and removal of ruthenium, the remaining permanganate is then decomposed by applying the same principle in reverse, i.e., a reducing agent (chromic nitrate) is added in a quantity less than sufficient to reduce all the permanganate, and as the reduction starts, an auto-catalytic reaction is produced which completes the decomposition of the remaining permanganate. (17)

At this point, the approximate manganese dioxide concentration is known and a stoichiometric quantity of reducing agent is used to dissolve the desired portion of manganese dioxide, leaving the maximum amount of MnO_2 solids that the centrifuge bowl can accommodate.

Permanganate stability is inversely proportional to the acid concentration in this system and is more than adequate in an acid-deficient solution. However, the manganese dioxide centrifuge cake is an almost completely unmanageable paste in acid-deficient systems, but forms an easily centrifuged, crystalline precipitate in acid systems. Therefore, since ruthenium appears to be oxidized with equal ease between +0.2 M and -0.2 M HNO_3 , the optimum acidity recommended for plant operation is 0.05 to 0.10 M HNO_3 , thus giving a satisfactory combination of permanganate stability, ruthenium decontamination, and MnO_2 centrifuging characteristics.

It should be observed that the gross gamma decontamination on the centrifuge cake is a function of the amount of MnO_2 present in the slurry, and that below 0.06 M MnO_2 the efficiency of zirconium and niobium removal is sharply reduced. (5) In the Redox plant with a 0.01 M MnO_2 slurry, low gross gamma DF's (1 to 4) are obtained, but much of the siliceous material resulting from the slug jacket bonding agent is scavenged and centrifuged from the oxidized metal solution, as mentioned above. This has effected a reduction by a factor of 2 to 3 in the down-time required for cleaning the extraction batteries in the Redox plant.

In addition to the ruthenium decontamination obtained across the oxidation step in the head-end process, a large percentage of the "extractable" ruthenium species are apparently destroyed, thus also increasing slightly the solvent extraction decontamination for this fission product.

2. Ruthenium Decontamination. Ruthenium tetroxide, RuO_4 , is a yellow crystalline solid which melts at about 25°C . and decomposes at 106°C . Recent laboratory experiments, however, have shown that this decomposition temperature is drastically reduced when water vapor is present.⁽¹⁴⁾ It is easily volatilized from aqueous solutions, the rate of removal increasing as the temperature increases. Decontamination factors of 100 or greater are easily obtained in 10 to 15 minutes with Ru^{+3} and Ru^{+4} ions in solution are oxidized with 0.01 M to 0.10 M solutions of permanganate, periodate, perchlorate, bismuthate, or similar oxidants at 90° to 100°C . In dissolver solution, however, ruthenium appears only partially in this cationic form. The anionic complexes, e.g., nitroso, which are also present, are extremely difficult to oxidize. (See A.2., above.) Thus in the Redox plant it is necessary to digest the permanganate-treated dissolver solution for about two hours at 95°C . with a slow air sparge to obtain arithmetic decontamination factors ranging from 5 to 20. However, data from K.A.P.L. indicate that approximately the same decontamination is achieved at a temperature of 80°C . with no sparge required. This is known as the "simmer" technique.⁽²⁾ Almost all (greater than 99%) of the RuO_4 evolved from the solution in the Redox Head-End process is reduced to RuO_2 on the stainless steel surfaces in the presence of water vapor. A significant amount of this is believed to be refluxed into the oxidizer whence it is removed along with the other solids by centrifugation. It appears also that under certain conditions ruthenium is actually scavenged on the manganese dioxide (cf. C.2., below).

3. Disposal of Ruthenium. Off-gases from the Redox oxidizer vessel rise through a 12-foot by 2.5-foot de-entrainment tower, packed with 1-inch stainless steel Raschig rings, mounted atop the oxidizer and thence by way of a 6-inch diameter line into a caustic scrubber which basically resembles the oxidizer and its tower. In the scrubber the gases pass upward counter-currently through a 6 M NaOH solution continuously recirculated to the top of the tower, likewise packed with 1-inch stainless steel Raschig rings. The NaOH solution removes any entering RuO_4 , thus:

In practice, however, it has been seen that less than one per cent of the ruthenium removed from solution in the oxidizer is found in the caustic in the scrubber as the ruthenate ion, RuO_4^- . Laboratory investigations to explain this phenomenon have disclosed that:

- a. When gaseous RuO_4 plus water vapor leaving the oxidizer contacts stainless steel surfaces at 80° to 90°C ., virtually all the RuO_4 is reduced to RuO_2 (or a mixture of the solid lower oxides) mostly on the steel surfaces, but partly by thermal decomposition in the gas phase. This appears to be the situation in the Redox plant.
- b. These solids freshly deposited on the steel surfaces are believed to be largely returned to the oxidizer by refluxing condensate, but some inevitably remains on the rings and tower walls.⁽¹⁰⁾ This deposit, when dry, is readily removed by impact, is a light powder, and is almost chemically inert.

- c. The RuO_2 resulting from the gas phase decomposition probably occurs as sub-micron size particles (and even likely in the molecular range) many of which thus pass through even the most efficient of scrubbers because they are not wetted. Furthermore, such fine particles cannot be efficiently removed by filtration. This probably accounts for the reported emission of 0.5 curie of Ru per day during the month of May, 1954, when approximately 38,000 curies (Ru beta) were being processed daily through the Redox Head-End treatment.
- d. RuO_4 is stable with respect to both beta and gamma radiation, but is unstable in light (presumably ultra-violet). At or below 70°C ., the decomposition of RuO_4 in the absence of light is a complex reaction, which requires the presence of water.⁽¹⁴⁾ Numerous active metals and/or their oxides (including stainless steel) act as the third component, but pyrex glass, platinum, and inert plastics such as fluorothene, will not participate in the reaction, and RuO_4 is stable in their presence. This decomposition occurs to a certain extent even in the presence of ozone, but an ozone sweep or sparge during ruthenium oxidation and volatilization will greatly reduce the amount of RuO_2 ultimately plated on the stainless steel surfaces in the oxidizer vessel, de-entrainment tower, and gas lines. Above 70°C ., RuO_4 becomes increasingly unstable regardless of other conditions.

4. Emission of Ruthenium from the Redox Stack.⁽¹⁶⁾ The emission of Ru from the 291-S stack was reported to have increased from an average of less than 0.04 curie per day during the period from January to May, 1953, to an average of 1 curie per day for the succeeding months (through April, 1954) after the inception of the permanganate Head-End process. These averages do not include major emissions of 113 curies and 230 curies, occurring in September, 1953, and January, 1954, respectively. The September incident was explained on the basis of the failure of the oxidizer steam coil, necessitating permanganate oxidation at reduced temperatures (55 to 60°C .) instead of the normal 95 to 100°C .) which in turn, resulted in an incomplete removal of RuO_4 from the oxidized solution. When this solution was centrifuged, the residual RuO_4 was liberated into the Vessel Vent system and thence into the stack. The January emission was the result of the failure of the recirculation pump in the caustic scrubber, combined with the failure to interpret properly the readings of the meter being used to monitor the stack gas. The latter failure did not, of course, cause the emission, but had the true situation been recognized, steps could have been taken to minimize the emission.

The emission of ruthenium from the stack is accompanied by the emission of solid ammonium nitrate in the form of both macro particles and finely divided "solid fog." Since the NH_4NO_3 crystals frequently carry adhering or occluded particles of RuO_2 , both health hazard and environs contamination could be seriously aggravated when such an emission occurs. The weather conditions at the time of emission are believed to exert a strong influence on the nature of the contamination problem, but as yet this factor has not been correlated. The formation of NH_4NO_3 is the result of the mixing of NH_3 and NO_2 gases which are evolved during aluminum jacket removal and uranium dissolving, respectively, when these operations are simultaneously under way in

separate dissolvers. Since it is impossible to alternate these processing steps and still maintain desired production capacity, the substitution of mercury-catalyzed aluminum dissolving in nitric acid for the presently used sodium hydroxide-sodium nitrate technique, is being studied. Procedures have been tested on a semi-works scale which give adequate dissolving rates and no ammonia. Flowsheets have been tested in the laboratory which incorporate the use of the aluminum nitrate solution from the jacket as salting agent in solvent extraction. Due, however, to the unsolved problem of evolution of hydrogen during the dissolving step, this process cannot yet be recommended for testing in the plant.

The current theories regarding the formation of minute particles of RuO_2 and their passage through the off-gas system are set forth under B., 3, above. For confirmation of the existence of such particulate ruthenium, a program was started in the Redox plant for obtaining samples of the gas from the caustic scrubber through sample lines both upstream and downstream from the Fiberglas filter located downstream from the scrubber. By means of these samples it has been possible to establish the following facts:

- a. The ruthenium getting through the system as far as the filter is RuO_2 (or at least is not RuO_4).
- b. The mean particle size of this material downstream from the filter is currently believed to be about 0.45 microns, i.e., less than the minimum size for which the filter is highly efficient. (The filter is not believed to be channeling.)
- c. Most of the ruthenium is emitted from the stack during the "sacrificial" oxidation.
- d. If the off-gas were routed through the Sand Filter ahead of the stack, the "G" sand layer would effectively decontaminate it for an indefinite period. When and if a breakthrough would occur, however, is not known.

Plans are currently under way for the installation of an additional caustic scrubber and a new Fiberglas filter (J-2, J-3) in series with the present H-5 scrubber. It is believed that these new facilities will give an additional decontamination factor (arithmetic) for RuO_2 of 10 to 100, and that the emission problem will thus be minimized. The canyon and crane problem, however, assuming no change in the Head-End process, will not be lessened by the above modifications to the equipment. See below.

5. Canyon Contamination.(16) Prior to July, 1953, contamination in the canyon was rather widespread, with occasional spots of high intensity, but in general was not prohibitive from an operating standpoint. Subsequent to July, 1953, the contamination levels increased sporadically but rapidly, due largely to previous instances of pressurizing the oxidizer vessel and spreading ruthenium over the interior of the cell and the exterior surfaces of the equipment. Thus, when the cell was opened for centrifuge replacement (plus numerous other entries during this period) it is postulated

that thermal up-drafts carried the dry RuO_2 up into all parts of the canyon proper. In addition, two major incidents occurred which resulted in gross contamination of the canyon and crane. The first, in September, 1953, occurred during the replacement of the oxidizer vessel when the oxidizer de-entrainment tower was removed and set on the unprotected canyon deck. The impact dislodged a powder from the interior of the tower. This is believed to have been largely RuO_2 , and, therefore, the primary source of activity which required a month's shutdown in November, 1953, for decontamination purposes. The second incident occurred in January, 1954, while an attempt was being made to route the gas from the oxidizer to the 291-S stack via the sand filter. The plenum chamber into which the gas was discharged was improperly aligned with the cell outlet port into the air tunnel (apparently due to errors in As-Built drawings of the vents) and as a result permitted the escape of the steam jet discharge carrying the ruthenium from the oxidizer into the canyon. As a consequence, the radiation levels on the crane were increased approximately 10-fold.

It is impossible to obtain an adequate material balance for Ru anywhere in the system and so no quantitative data are available regarding the amount of this fission product in the canyon. It has, however, been possible to show that Ru (as RuO_4) does not escape into the canyon under normal processing conditions. Although samples have been taken which indicate that the contamination is 100% Ru, attempts to determine its "age" by measuring the isotopic ratio ($\text{Ru}^{103}/\text{Ru}^{106}$) have not given conclusive results. The most recent indications, however, are that it is from 5 to 8 months old, thus placing it approximately at the time of the January and September incidents.

This problem thus appears to be mainly one of operating philosophy and with the exercise of due care could seemingly be kept under control until the difficulties with the permanganate Head-End process are worked out or until an alternate procedure is ready for use.

C. Alternate Processes

1. Modifications to Current Process. In view of the unanticipated, almost quantitative, decomposition of RuO_4 to RuO_2 in the oxidizer vessel and tower, with its attendant problems (discussed in P. 4. and 5., above), the first approach was a search for means of delivering all RuO_4 to the scrubber. Possibilities, reviewed in HW-29679(10), included cooling the oxidizer tower, removing the Raschig ring packing, and sweeping (or sparging) with ozone during oxidation. These suggestions were based on what was then known regarding the instability of RuO_4 toward heat and stainless steel surfaces, and, although such steps would undoubtedly provide some measure of improvement, more recent laboratory studies have shown that water vapor causes the decomposition to proceed even at 25°C . Thus, since water cannot be eliminated from the oxidizer tower, lowering its temperature and removing its packing would not prevent the decomposition of RuO_4 . The presence of ozone inhibits this decomposition, but does not completely prevent it and, thus, would provide only a limited benefit.

The second approach was the idea of retaining all of the RuO_2 in the tower and oxidizer, permitting none of it to reach the caustic scrubber. This might conceivably be done in a number of ways, one of which has been successfully used in the

plant for several weeks giving steadily decreasing ruthenium emission from the stack. The average daily level for the second and third weeks of May, 1954, was approximately 0.25 curie. The procedure consists of operating the oxidizer tower under conditions of maximum attainable reflux, thus, in essence, converting it to a scrubber to assist in the removal of the particulate RuO_2 formed by decomposition of RuO_4 . The RuO_2 refluxed to the oxidized solution is insoluble and is removed with other solids in the centrifuge.

Suggestions along the same line include, among others, 1) the introduction of a reducing gas at the base of the oxidizer tower to reduce RuO_4 immediately; 2) the introduction of a heated grid at the base of the tower to accomplish the same results by thermal decomposition, each to be followed by the reflux mentioned above. These have not yet been evaluated in the laboratory.

It was also hoped that variations in rate or method of permanganate addition, temperature, etc., would decrease the peak evolution of RuO_4 occurring at the start of the "sacrificial" oxidation, but those so far tested in the plant have failed to show any significant improvement.

2. Alternate Head-End Processes. One alternative which might be considered is the ozone oxidation process originally developed for the Redox Process.⁽⁴⁾ Some improvement in RuO_4 stability (see above) would result, but the possibility of reoxidizing RuO_4 from NaOH solution in the scrubber would require the destruction of the excess ozone before its entry to the scrubber. Thus, all things considered, including installation costs, etc., the use of ozone for a head-end treatment does not appear to be warranted.

Another process, developed through the laboratory stage, is ruthenium scavenging by co-precipitation with sulfur compounds and was followed through two main approaches.⁽⁷⁾ The first was the precipitation of CuS , a few thousandths molar, by the addition of $\text{Cr}(\text{NO}_3)_2$ followed by saturation of the solution with hydrogen sulfide. The second was the precipitation of silver (or other heavy metals) with organic sulfur compounds such as 2, 3-dimercaptopropanol-1 (British Anti-Lewisite, BAL) and beta-mercaptopropionic acid. Both techniques gave Ru decontamination factors (arithmetic) as high as 500 to 700 in dissolver solution, but both introduced process questions such as the formation (and effects) of free sulfur, sulfate ion, excess H_2S , and corrosion of equipment. Two additional serious disadvantages are 1) the batch character of the sulfide precipitation step and the consequent necessity for filtration or centrifugation of the precipitate, and 2) the high cost (ca. \$70 per pound) of BAL. For these reasons the sulfide precipitation procedures do not appear attractive enough to warrant further serious consideration at this time.

The use of MnO_2 as a scavenger for Ru in dissolver solution is currently being studied and shows definite promise in its early stages.⁽¹³⁾ The precipitation of MnO_2 by reverse strike, i.e., the addition of KMnO_4 to a solution containing $\text{Cr}(\text{NO}_3)_3$, followed by digestion for 2 hours at 95°C ., appears to scavenge up to 90 per cent of the initial ruthenium.

The precipitation of ruthenium iodide and the formation of ruthenium nitroso iodide complexes are also being investigated, but it is too early to tell whether or not these will show a profit.

Data from C.R.N.L. indicate that digestion of Thorex dissolver solutions for 2 to 3 hours at temperatures above 100°C. significantly improved decontamination from Ru in the first solvent extraction column. It was also reported that oxidation by periodate (very rapid), followed by reduction with formic acid, markedly improved solvent extraction decontamination. The applicability of such techniques to the Redox process has not been studied, but at first glance do not appear particularly attractive due to the fact that some RuO_4 is formed and volatilized. Other methods for the pre-conditioning of Ru to make it solvent-inextractable are being considered.

3. Solvent Extraction. In addition to the pre-conditioning mentioned above, another method for altering Ru solvent extraction behavior has been studied intermittently for a long time, so far without notable success. It consists of introducing an agent with the streams (either aqueous or organic) entering the solvent extraction columns that will complex the ruthenium so that it will be removed in either the raffinate or stripped solvent stream.

One of the most promising methods now being studied in the laboratory is intercycle oxidation. By running on a co-decontamination (pre-cycle) flowsheet, both uranium and plutonium can be decontaminated from Ru to the extent of the normal factor of 100 to 500 in the first-cycle solvent extraction. The product stream from this operation can then be continuously oxidized by permanganate during concentration and fed into the partition and subsequent cycles. Initial laboratory data indicate that a Ru decontamination factor (arithmetic) of from 2 to 5 during oxidation is accompanied by an improvement in subsequent solvent extraction decontamination of a factor of 2 to 3.⁽¹⁴⁾ This, however, will raise the same kind of problem (differing only in degree) as that now encountered with Head-End, viz., the collection of radio-ruthenium scale in the tower and lines above the concentrator. On this basis then, perhaps the intercycle oxidation is somewhat less attractive than the ozone oxidation outlined below.

4. Tail-End Processes. It has recently been demonstrated that final uranium product solution (E-12) from the Redox plant can be further decontaminated from ruthenium by oxidation with ozone.⁽¹⁴⁾ An E-12 solution resulting from 3-cycle operation without permanganate head-end treatment was sparged with a 2 per cent ozone-in-air mixture at the rate of one volume of gas per volume of solution per minute. In the absence of a catalyst, an arithmetic decontamination factor of about 6 was obtained after 4 hours. When the gas flow rate was reduced 10-fold, the DF dropped to 3.5 in 7 hours, and an additional 10-fold reduction in gas flow gave no detectable Ru removal after 168 hours. It has not yet been established that this same treatment will be effective for final Redox plutonium product or for Uranium Recovery product, but such tests are under way. A comprehensive discussion of the application and economics of this ozone treatment has recently been issued.⁽¹⁵⁾ Based on the current state of knowledge, this method appears to merit the highest priority of all possible alternatives to the permanganate Head-End process.

The sulfide precipitation processes might also be applied as tail-end treatments. The decontamination factors obtainable would be expected to drop from the 500 to 700 reported for head-end to 20 to 60 in the final solutions. The reduced activity levels would minimize radiation damage to H₂O₂ or H₂S and would permit easier handling of the precipitates and easier equipment maintenance. The other disadvantages would be little affected.

The final uranium processing step, the calcination of uranyl nitrate solution to uranium trioxide, affords an additional average ruthenium decontamination factor of about 5. This could probably be employed in place of the head-end treatment were it not for the problem of radiation exposure of the process operators during the batch-wise filling and emptying of the calcination units as now conducted. This consideration, plus the imminent need for additional increased production capacity, makes the development of a continuous calcination process a high priority alternative. Such studies are currently in progress.

Still another possibility, directly related to the question of the final uranium product, is that of finding either a better method of preparing the trioxide or an entirely different product. Several (e.g., uranyl oxalate, fluoride, peroxide, etc.) have been appraised⁽⁸⁾, and although they are not at present on sound economic footing, many have been found to give both substantial fission product decontamination and more desirable characteristics as intermediates in the final preparation of uranium hexafluoride, with the added advantage of completely eliminating the necessity for calcination. On this basis it is believed that additional development work on some of these alternatives is justified.

No successful use of adsorption techniques for removing ruthenium, e.g., silica gel, resins, alumina, etc., has been reported.

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