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REVIEW OF REDOX PLANT HEAD-END TREATMENT

by

G. R. Kiel

Redox Process Technology, Plant Processes Unit
Separations Technology Sub-Section
Technical Section

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I. INTRODUCTION

Oxidation of the dissolver solution is required before processing through the Redox Plant. Two different Head-End treatment procedures have been used in the plant since start-up, the original one employing sodium dichromate as the oxidant and the current one (initiated in May of 1953) employing potassium permanganate. In addition to oxidizing the plutonium, the permanganate Head-End procedure removes substantial quantities of radio-ruthenium (the fission product most difficult to remove by solvent extraction) from the IAF and, thus, benefits the overall decontamination of the uranium and plutonium products markedly.

II. OBJECTIVES

The purposes of this paper are:

- (1) to describe briefly the dichromate and permanganate Head-End procedures and conditions of oxidation;
- (2) to present and discuss the advantages of the permanganate procedure as compared with the dichromate procedure; and
- (3) to present and discuss the disadvantages of the permanganate procedure and the difficulties associated with equipment maintenance when this process is utilized.

III. SUMMARY

- A. Insufficient decontamination of uranium and plutonium product solutions from the Redox process was achieved when dissolver solution was oxidized by the dichromate Head-End procedure. Adequate decontamination is achieved when dissolver solution is oxidized with the permanganate Head-End procedure, which removes substantial amounts of ruthenium from the solution prior to solvent extraction.
- B. Additional benefits of the permanganate Head-End procedure (compared with the dichromate procedure) include:
 - (1) increased overall plutonium recovery (approximately 99.3 vice 98.8 per cent);
 - (2) improved clarity of IAF by scavenging with manganese dioxide which results in increased IA Column stability (less frequent column flushing) and reduced entrainment of active solids in hexone product solutions;

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- (3) elimination of the process difficulties associated with "extractable" fission products during off-standard conditions (e.g., waste rework);
 - (4) larger margin of safety in decontamination performance for assuring success of waste back-cycling; and
 - (5) simplified subsequent processing of plutonium product solutions in 231 Building because of the low fission product content.
- C. Two major difficulties have become apparent since the permanganate Head-End procedure was initiated in the Redox Plant in May of 1953:
- (1) emission of radio-ruthenium in significant quantities from the ventilation stack into the environs, and
 - (2) gross contamination of the Redox Plant canyon and crane, primarily as a result of the escape of particulate ruthenium dioxide from equipment during maintenance work.
- D. Present data show that adequate control of this ruthenium contamination is possible and that expected equipment and process modifications will reduce the ruthenium problem further.

IV. DISCUSSION

A. Description of Procedures

The Redox process decontaminates and separates uranium and plutonium comprising the metal slugs discharged from the Hanford piles. Greater than 99.9 per cent of the fission products associated with these products are removed in the IA Column operating under acid-deficient flowsheet conditions. Recovery of the plutonium from this column requires that it be oxidized to the hexavalent state. This oxidized state can be attained by two processes, one employing sodium dichromate as the oxidant and the other employing potassium permanganate. The potassium permanganate procedure also accomplishes a removal by volatilization from the IAF of approximately 90 per cent of the radio-ruthenium contained in dissolver solution. The dichromate procedure was used in the plant from start-up (with the exception of short test periods of the permanganate procedure in March and July of 1952) until May of 1953 when the permanganate procedure was adopted because of the need for additional decontamination. The two procedures are briefly described below:

1. Sodium Dichromate Head-End Procedure

- a. Transfer 1900 gallons of dissolver solution from H-7 Sampler Tank to H-4 Oxidizer.
- b. Adjust the acidity to 0.2 ± 0.1 M HNO_3 -deficient.

- c. Adjust the dichromate concentration to 0.15 M $\text{Na}_2\text{Cr}_2\text{O}_7$.
- d. Heat the solution to greater than 95°C ., agitate, and hold for four hours.
- e. Cool to 50°C ., and centrifuge the solution through H-2 Centrifuge (operating at 1740 r.p.m.) at 90 to 100 pounds per minute.
- f. Pump the IAF from H-1 to F-7 tank for processing through the IA Column.

2. Potassium Permanganate Head-End Procedure

The procedures tested during March and July of 1952 had too long time cycles for throughputs required by production. In addition, the ruthenium decontamination factors were lower than expected, and it was believed (but subsequently disproved) that the process may have been contributing to the emulsion problems plaguing column operation at the time. Thus, the permanganate procedure was piloted in the Process Chemistry Laboratory and Hot Semi-Works until it was incorporated in the Redox Plant in May of 1953. Since then several modifications based on plant tests have been made to improve the procedure and decrease time cycles. The following procedure can be modified to include no manganese dioxide scavenging if desired (e.g., when the H-2 Centrifuge was out of service during February of 1954).

- a. Transfer 1900 gallons of dissolver solution from H-7 Sampler Tank to the H-4 Oxidizer.
- b. Adjust the acidity to 0.1 ± 0.05 M HNO_3 .
- c. Concentrate solution to a 1.60 specific gravity at boiling.
- d. Add permanganate to make the solution 0.02 M KMnO_4 . This addition is considered as a "sacrificial kill" to oxidize any reducing agents present and oxidizes a significant portion of the ruthenium to the volatile tetroxide. Heat the metal solution to $95-100^\circ\text{C}$., air sparge, and hold for one hour.
- e. Add a quantity of permanganate equivalent to that required to increase the solution composition by 0.02 M KMnO_4 . This addition accomplishes oxidation of the remaining ruthenium and the plutonium. Hold at 95 to 100°C . for two hours and air sparge.
- f. Add a quantity of chromic nitrate equivalent to that required to equal ± 0.002 M $\text{Cr}(\text{NO}_3)_3$ solution. This "catalytic kill" addition serves to reduce some residual permanganate and accelerate the heat reduction of the remaining permanganate to manganese dioxide. Hold at 95 to 100°C . for one hour and air sparge.

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- g. Add a quantity of chromic nitrate equivalent to that required to equal a 0.021 M $\text{Cr}(\text{NO}_3)_3$ solution to reduce and dissolve solid manganese dioxide, leaving approximately 0.008 M MnO_2 to be used for scavenging. Hold at 95 to 100°C. for one hour and air sparge.
- h. Cool to 50°C. During the cooling period, add a quantity of sodium dichromate (holding oxidant) equivalent to that required to increase the dichromate concentration by 0.089 M. With the dichromate formed by oxidation of the chromic nitrate, the total dichromate ion concentration is 0.10 M.
- i. Centrifuge the cooled oxidized metal solution through H-2 Centrifuge (operating at 1740 r.p.m.) at 90 to 100 pounds per minute.
- j. Sample the centrifuge effluent in H-1 tank for acidity and clarity.
- k. Adjust the acidity of the centrifuge effluent to 0.2 ± 0.1 M HNO_3 -deficient. If necessary, dissolve manganese dioxide fines with additional chromic nitrate solution.
- l. Pump the 'IAF', from H-1 to F-7 tank for processing through the IA Column.

B. Advantages of the Permanganate Head-End Process

1. Final Product Decontamination

Table I gives a comparison of decontamination factors obtained with sodium dichromate and permanganate Head-End treatments under similar solvent extraction conditions and production rates;

TABLE I

Gamma dF's of $\text{Na}_2\text{Cr}_2\text{O}_7$ and KMnO_4
Head-Ended IAF

	Uranium		Plutonium	
	$\text{Na}_2\text{Cr}_2\text{O}_7$	KMnO_4	$\text{Na}_2\text{Cr}_2\text{O}_7$	KMnO_4
Head-End	0.0	0.2	0.0	0.2
1st Cycle	3.5	3.9	4.0	4.2
2nd Cycle	2.1	1.8	1.7	2.2
3rd Cycle	0.8	1.0	1.0	0.8
Total	6.4	6.9	6.7	7.4

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The overall difference between the decontamination performance of IAF prepared by the two procedures is due to ruthenium. The plutonium product from the permanganate process meets 231 Building specifications well. However, the 5-fold higher activity of the product from the dichromate process makes additional processing in 231 Building necessary. This additional processing of the final plutonium stream increases the 231 Building time cycle by a factor of 2, plus increasing the personnel radiation exposure rates. It is doubtful if the high activity material could be processed in Task I 234-5 Building. The activity of the uranium product from the dichromate process is at least 3-fold higher than that from the permanganate process. This higher activity causes operating difficulties during processing in the UO₃ Plant, particularly since the 224-U Building is operated and repaired by "contact" means.

2. Cost Comparison

Economically, the permanganate Head-End process is attractive. Although the chemical costs of the permanganate process are higher, the savings resulting from the lower plutonium losses from the I₁ Column waste stream (as a result of more complete oxidation of plutonium to the hexavalent state) more than compensate for this higher chemical cost. Table II gives a comparison of costs for the two types of Head-End treatment.

TABLE II

Comparison of Costs for KMnO₄ and Na₂Cr₂O₇
Head-End Treatments

<u>Cost Item</u>	<u>KMnO₄</u> ^(a)	<u>Na₂Cr₂O₇</u>
a. Overall Pu Loss - % of Feed	0.72% ^(b)	1.28% ^(c)
b. Cost of chemicals per ton of U		
c. Value of Pu savings per ton ^(d)		
d. Overall Savings (item c - item b)	\$160	- \$24
e. KMnO ₄ saving per ton over Na ₂ Cr ₂ O ₇		\$184

Notes:

- Based on the current 0.02-0.02 M KMnO₄ sacrificial and oxidation concentrations respectively.
- Based on period January 1 through April 23, 1951.
- Based on period January 1 through May 1, 1953.
- Based on cost of plutonium

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3. Time Cycle Comparison

A comparison of the time cycles and capacities of the Head-End treatment operating under the two procedures is given in Table III:

TABLE III

Head-End Time Cycles for $KMnO_4$ and $Na_2Cr_2O_7$ Procedures

Process Step	Time in Minutes in Head-End Vessel							
	$KMnO_4$				$Na_2Cr_2O_7$			
	H-4	G-5	H-2	H-1	H-4	G-5	H-2	H-1
1. Transfer H-7 and E-22 (Recycle) to H-4	45				45			
2. Preconcentration	30				-			
3. Acidity Adjustment	10				30			
4. Oxidation	200				240			
5. $KMnO_4$ reduction and MnO_2 dissolution	125				-			
6. Cool H-4 to 50°C.	45				45			
7. Jet H-4 to G-5	60	60			60	60		
8. Centrifuge G-5 to H-1		330	330	330		330	330	330
9. Adjust acidity in H-1				60				-
10. Centrifuge cleanout perforated over 3 batches			90				90	
Total time per tank	515	390	420	390	420	390	420	330
Maximum processing Rate, tons per day*	10.7	14.0	13.0	14.0	13.0	14.0	13.0	16.6

* Basis 3.8 tons uranium per Head-End batch.

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The foregoing comparison indicates an advantage for the dichromate Head-End procedure. However, the capacity of the equipment operating under the permanganate Head-End procedure is adequate for plant processing rates. If higher capacities are needed, slight increases can be achieved by additional process modifications, and larger increases could be attained by equipment changes.

4. Removal of Solids by Scavenging

Scavenging of the metal feed solution (IAF) with manganese dioxide is easily achieved with the permanganate Head-End procedure. Perhaps a similar scavenging could be developed for use with the dichromate Head-End procedure, but the relative effectiveness is not known. There have been indications of improvement in IAF clarification (by centrifugation) even without manganese dioxide scavenging when the permanganate procedure is used; perhaps there is a coalescence of the siliceous materials in dissolver solution as a result of coformation and complete dissolution of manganese dioxide. It is known that manganese dioxide scavenging has three beneficial effects:

- a. decreases the frequency of IA Column flushes (required because of flooding) by approximately a factor of two;
- b. significantly reduces the entrainment of active solids (4 to 100-fold higher activity than solution) in the hexone overflowing the decontamination columns with resultant improvement in overall decontamination factors; and
- c. removes greater than 50 per cent of the zirconium-niobium present in dissolver solution.

5. Corrosion Rates

Redox dissolver solution with sodium dichromate present is quite corrosive at elevated temperatures. With the use of permanganate as the oxidizing agent, lower concentrations of dichromate, the holding oxidant, are necessary and may be added at lower temperatures (50°C.). This factor tends to reduce corrosion in the Head-End tanks (H-1, H-2, H-4, G-5 and F-7), in the in-concrete lines, and in the D-12 Waste Concentrator. Laboratory evaluations of the relative corrosion rates are currently in progress in the Metallurgical Laboratories.

6. Extractable Fission Products

Extractable fission products (apparently certain species of zirconium, niobium, and ruthenium) are those which have a distribution ratio of the same order of magnitude as uranium and, therefore, will follow uranium into the final product solution. From observation of plant performance, it is difficult to differentiate between extractable fission products in the solutions and the effect of entrainment of active solids in hexone overflowing the decontamination columns. However, special analyses and treatments of plant solutions in the laboratory are useful in defining the condition.

Reworking of uranium solutions containing extractable fission products through the solvent extraction battery does not efficiently remove the activity. During plant operation with the dichromate Head-End procedure, extractable fission products were apparently encountered in the uranium stream on several occasions with resulting poor decontamination, and expensive rework operation was required. Laboratory tests on some of these solutions indicated that the rework difficulties could be overcome by a permanganate oxidation of the solution prior to rework through solvent extraction cycles. Since the start of the permanganate Head-End procedure in May of 1953, no extractable fission products have been experienced in the plant operation. In addition, it has been possible to blend waste rework (previously a source of extractable fission products) with dissolver solution, prior to the Head-End step, and process it through the plant without a loss of production or decontamination. For example, during April of 1954, the addition of waste rework solution (containing aluminum nitrate) to the IAF allowed a reduction in the aluminum nitrate scrub flow rate (IAS) to the IA Column with an accompanying savings of approximately \$40 per ton of uranium processed.

7. Back-Cycle

Back-cycle is the return of the aluminum nitrate salt wastes from one decontamination column to a preceding decontamination column as the salting solution (e.g., the return of 3DW after concentration, to the 2D Column as 2DS). The use of the permanganate Head-End process increases the decontamination of the final product solutions and thus gives additional safety factor to assure the back-cycle of the salt waste streams. The savings for total back-cycle of the salt waste (except 1AW) will be appreciable (greater than \$1,000,000 per year).

8. 231 Building Recycle Material

The low activity of the final plutonium product solution produced from IAF oxidized by the permanganate process has allowed processing of Redox plutonium through 231 Building with only one oxalate strike. When higher activities are encountered, it is necessary to precede the oxalate strike with a peroxide strike, and this decreases the 231 Building production capacity by a factor of two and increases the recycle by a factor of two. Thus, to maintain adequate production capacity in 231 Building with dual-strike operation, an increase in the work force to provide three-shift, seven-days-a-week coverage would be required. When Task I is started, it is doubtful if the facilities will be available to make a peroxide strike.

C. Disadvantages of the Permanganate Head-End Process

Two major operating problems have become apparent since the adoption of the permanganate Head-End treatment procedure:

- (1) emission of radio-ruthenium in significant quantities from the ventilation stack and into the environs, and
- (2) gross contamination of the Redox Plant canyon and crane, primarily as a result of the escape of particulate ruthenium dioxide (formed by reduction of the gaseous tetroxide) from equipment during maintenance work.

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Both of these difficulties are the direct result of the presence of particulate ruthenium in equipment, but each one can be minimized with adequate equipment and procedures. The following discussion presents pertinent data relative to each of these problems.

1. Stack Emission

The emission of radioactive ruthenium from the 291-S Redox stack increased significantly when the permanganate Head-End procedure was adopted. Table IV shows the effect of this volatilization procedure on ventilation stack emissions from January 1953 through April 1954.

TABLE IV

Emission of Ruthenium from the Redox Stack

Period	Type Head-End	Avg. (a) Production Rate-Tons U/Day	Avg. Ru Emission Curies/Day	Avg. Ru Emission, Curies Tons U/Day
January to April, 1953	Na ₂ Cr ₂ O ₇	4.0	< 0.04	< 0.01
May, 1953	KMnO ₄ -scavenging	3.8	0.27	0.071
June	KMnO ₄ -scavenging	4.9	0.33	0.067
July	KMnO ₄ -complete dissolution	5.5	0.72	0.131
August	KMnO ₄ -scavenging	4.8	0.82 (c)	0.171
September	KMnO ₄ -scavenging	4.9	0.84	0.375
October	KMnO ₄ -complete dissolution	6.2	0.85	0.137
November				
December	KMnO ₄ (b)	6.5	0.96 (d)	0.147
January 1954	KMnO ₄ -scavenging	2.5	1.08	0.430
February	KMnO ₄ -scavenging	4.5	0.67	0.149
March	KMnO ₄ -scavenging	5.5	1.4	0.255
April	KMnO ₄ -scavenging	6.4	0.81	0.126
May	KMnO ₄ -scavenging	5.3	0.51	0.094

- Notes:
- (a) These averages do not include weeks in which less than 10 tons were produced.
 - (b) HE-1 through 4, November, and HE-1 through 9, December were complete dissolution runs. HE-10 through 44 were scavenging runs.
 - (c) On September 5 and 6, 1953, 113 curies of ruthenium were emitted from the Redox stack which are not included in the average.
 - (d) On January 2, 1954, 230 curies of ruthenium were emitted from the Redox stack which are not included in the average.

In addition to these average emissions, indicated in Table IV, there have been two instances (notes "c" and "d" of Table IV) when large quantities of ruthenium were emitted during a relatively short period of time. These were as follows:

On September 5 - 6, 1953, approximately 113 curies of ruthenium were emitted from the 291-S stack. During the period August 30, 1953, to September 10, 1953, the permanganate oxidation was carried out at a temperature of 65-75°C. (vice 95-100°C.) because of complete failure of the H-4 Oxidizer steam coil. The procedure for this "cold" oxidation was as follows:

- a. Receive solution in H-4 Oxidizer at approximately 80°C.
- b. Adjust acidity to 0 to 0.1 M HNO_3 by the addition of sodium hydroxide.
- c. Adjust the solution to 0.01 M KMnO_4 , 0.025 M $\text{Na}_2\text{Cr}_2\text{O}_7$, and air sparge for three hours. On the first six batches a sample was taken at this point for permanganate analysis; total "kill" was observed.
- d. Increase the dichromate concentration by 0.1 M $\text{Na}_2\text{Cr}_2\text{O}_7$, and air sparge one hour. Final temperature was about 50°C.
- e. Centrifuge at approximately 90 to 100 lbs./min. with 0.01 M MnO_2 scavenging.
- f. Adjust acidity to 0.1 M HNO_3 -deficient by the addition of sodium hydroxide.

However, on two specific batches (September HE-7 and HE-8) the oxidation temperature was only 55 to 60°C. whereas temperatures during preceding oxidations were about 10 to 15°C. higher. The result was incomplete "kill" of permanganate and/or incomplete removal of the volatile ruthenium tetroxide from the H-4 Oxidizer. Thus, during centrifugation, RuO_4 was volatilized from the H-2 Centrifuge into the Vessel Vent System and was discharged in large quantities from the stack. This discharge was the inadvertent result of an expedient method of operation devised in order to maintain production while a replacement H-4 Oxidizer was fabricated. No such recurrence should be expected because of the experience obtained from this incident.

The second instance took place on January 2, 1954, when approximately 230 curies of ruthenium were emitted from the stack. The basic cause was the failure of the H-5 Scrubber recirculating pump. However, the total number of curies of ruthenium emitted could have been minimized if the Counting Rate Meter (CRM), monitoring the stack off-gas, had been interpreted properly. The CRM instrument started up the scale at 2330 on January 2, 1954, but shortly thereafter returned to a lower reading. This return was interpreted as a reduction in activity when, in reality it was the result of the CRM automatically switching to a higher scale. The misinterpretation was discovered at 0230 on January 3. Not until shortly afterwards was the emergency

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addition of 15 percent caustic solution started (via the top pressure tap connection) into the H-5 Ruthenium Scrubber tower. The possibility of a recurrence of this incident is minimized by several improvements in the stack monitoring system and by the planned installation of a second ruthenium scrubber in series with the H-5 Ruthenium Scrubber.

Another emission of 70 curies of ruthenium was reported for January 6, 1954. The validity of the stack-gas sample on which this emission was based was questioned since the sampler had been running during a water flush of the stack. Also, the Redox plant had been shut-down for the preceding two days with no dissolving, and several curies of radioiodine were also reported.

In an attempt to understand better the mechanism by which ruthenium travels from the H-4 Oxidizer to the 291-3 Stack, studies were initiated by Redox Process Technology personnel in November 1953:

- a. to determine the distribution, types, and forms of fission product activities in the off-gases,
- b. to evaluate methods for removing the contaminants from the off-gases and,
- c. to serve as a monitoring device for proposed process changes.

In addition the Process Chemistry group performed laboratory work to determine the type of ruthenium that might be expected in various locations of the H-4 Oxidizer off-gas system. Sampling of the off-gas systems was done by Radiation Monitoring Unit personnel.

A study of the H-5 Ruthenium Scrubber revealed that a very small amount of the ruthenium removed from metal solution during a permanganate Head-End treatment was to be found dissolved in the H-5 caustic solution. Therefore, since the bulk of the ruthenium removed from the metal feed solution was not in solution in H-5, it was postulated with the aid of laboratory data, that the ruthenium was removed by three mechanisms:

- a. deposition in the H-4 De-entrainment Tower and Pot;
- b. scavenged by manganese dioxide during centrifugation; and
- c. slurried in the H-5 solution.

The postulated mechanisms by which these occur are outlined below:

- a. the ruthenium in the dissolver solution is oxidized at 95-100°C. by the permanganate to the tetroxide, a gas, which is purged from the solution by boiling action and air sparging.

- b. The volatilized tetroxide is reduced in the H-4 Tower to the dioxide, a solid, as very small (sub-micron) particles. Laboratory data indicate that tetroxide reduction occurs at high temperatures (80-100°C.) and in contact with stainless steel.
- c. A fraction of the dioxide is plated out on the H-4 Tower packing and walls and some is washed back into the metal solution by tower reflux. The dioxide washed into the metal solution is not affected by the permanganate and is removed by manganese dioxide scavenging during the centrifugation step.
- d. A small amount of the total ruthenium as both dioxide and tetroxide passes out the top of the H-4 Tower into the H-5 Ruthenium Scrubber, a fraction of this being removed by the caustic. That which leaves H-5 is partially removed by condensate from H-6 Condenser and the J-1 Fiberglass Filter, the remainder being evolved from the ventilation stack.

Laboratory data indicate that tetroxide gas is very soluble in 20 percent sodium hydroxide. Calculations of the H-5 Ruthenium Scrubber efficiency indicated that at least 99.94 percent of the entering tetroxide gas would be removed and that an increase in the caustic scrub rate would increase the efficiency to 99.99 percent (or an arithmetic decontamination factor of 1×10^4). The dioxide in the H-4 off-gas is insoluble in caustic, and particles of sub-micron size would pass through the scrubber while larger ones would be scrubbed out. The amount and the particle size of the dioxide entering the H-5 Ruthenium Scrubber are controlling factors in the amount omitted from the 291-S Stack.

The postulation that all ruthenium entering and leaving J-1 and J-5 Fiberglass Filters is particulate dioxide was borne out by making tests on the various gas samples. These tests consisted of passing the gas over various agents which will selectively absorb tetroxide and not dioxide and then measuring the radioactivity of the absorbent. In all cases there were no indications of tetroxide being present in the gas samples. The fact that all ruthenium leaving the J-1 Filter is particulate means that either the particle size is on the order of 0.5 micron or less in diameter or that the filter is channeling. A single determination of the size of particles passing the filter (obtained by the use of a cascade impactor followed by a molecular filter paper) indicates that the mean particle size is approximately 0.5 micron. Thus, it is believed that the filter is not channeling. In addition, results of other tests show that:

- a. ruthenium evolution from the stack takes place mainly during the "sacrificial kill" step at the start of the Head-End oxidation period;
- b. G-Sand layer (40 mesh) in the Sand Filter should remove most of the radioactive particulate matter, but occasionally a breakthrough may occur as a result of the presence of extremely small (e.g., 0.01 micron) particles. The seriousness of such breakthroughs and the resultant increase in activity to be expected on the ventilation Fans has not been determined.

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- c. Small amounts of ruthenium are sometimes liberated during centrifugation via the J-5 Vessel Vent system. Since this is apparently particulate ruthenium (except for that discharged on September 5 and 6, 1953) replacement of the J-5 Filter which is thought to have failed should minimize this problem.

From the foregoing data, it was concluded that the ruthenium reaching the environs was formed in the H-4 Oxidizer as finely divided particles. Therefore, efforts have been devoted to changing the Head-End procedure in an attempt to minimize the formation and emission of this fine particulate matter. Table V shows the changes made and the results obtained.

TABLE V

Changes Made to Minimize Ruthenium Emission from the 291-S Stack

Date	Change	Results
December 1953	Counting Rate Meter (CRM) recorder installed in dispatcher's office. This CRM monitors a caustic solution and therefore is more sensitive to iodine than to ruthenium. Used to control H-4 oxidation after January 3, 1954.	This instrument showed upward trends during Head-End oxidation, but was not quantitative. It did indicate the large emission on January 2-3, 1953. (See previous section).
January 6-15, 1954	Installed new H-5 Ruthenium Scrubber recirculating pump, new G-5 Centrifuge Feed Tank, and new flow control jet from G-5 to H-2 Centrifuge.	New H-5 pump provided recirculation after period with possibly negligible flow. G-5 increased the Head-End capacity and the new jet gave much better control of the centrifugation rates.
February 1	Air leak noted in H-4, H-5 system believed to be due to H-5 pump installation.	Increase in air in-leakage would decrease the H-5 scrubbing efficiency.
February 3-16	The strip filter was installed on the stack gas sampler line.	The survey of the individual samples revealed that the ruthenium evolution was during the "sacrificial kill" addition of permanganate.
February 18	Started operating with maximum water reflux in the H-4 Tower during the "sacrificial kill" and oxidation periods.	Some reduction observed in the ruthenium stack emission.

Changes Made to Minimize Ruthenium Emission from the 291-S Stack

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TABLE V

Changes Made to Minimize Ruthenium Emission from the 291-S Stack

Date	Change	Results
April 1-30	e. Heat the sacrificial KMnO_4 solution to 170-185°F. before adding to the boiling H-4 solution.	
	f. Add the sacrificial KMnO_4 solution at 50 pounds per minute vice 100 pounds per minute.	
	g. If the stack gas strip-filter monitor exceeds a counting rate that indicates a ruthenium emission from the stack of 20 millicuries per minute or greater, H-4 is to be cooled to 40°C. and the oxidation held until the counting rates fall below the 20 millicuries per minute.	

Further refinement of the permanganate Head-End procedure should be possible when a new strip filter (now on order) is available for monitoring of the inlet and outlet gas streams on either the J-1 or J-5 Filters. This new strip filter will sample two gas streams simultaneously for preset time intervals such that the evolution of ruthenium during the Head-End treatment steps can be defined closely. In addition, the new strip filter will give a comparison of the ruthenium content of the stack-gas as recorded by the 291-S Stack strip filter and the off-gas from the J-1 and J-5 systems.

2. Canyon and Crane Contamination

The Redox canyon and crane are presently contaminated (primarily with ruthenium) to such an extent that access to the canyon proper is very limited, and routine maintenance of the 60-ton crane is very difficult. Prior to July, 1953, the canyon contamination was widespread with spot radiation levels of approximately 23 Rads./hour, and the crane radiation levels were approximately 65 to 200 mrads/hour with spots to 1 Rad./hour. Although these radiation levels were higher than desirable, they were not prohibitive from an operating stand point. Subsequent to July, 1953, the Redox canyon and crane radiation levels increased quite rapidly. The data show that the increases were sporadic with the individual instances occurring during August and September, 1953, and January, 1954.

From August 1 to September 1, 1953, an increased effort was necessary to maintain the radiation levels on the canyon crane within reasonable limits. During the months of May, June, and July, 1953, many instances of pressurizing

of the H-4 Oxidizer were recorded, and these brief periods of positive pressure resulted in contamination of the outer surfaces of equipment (vessels and jumpers) adjacent to H-4. Thus, subsequent removal of the cell cover blocks without prior cooling of the vessels, resulted in thermal up drafts carrying contamination to all parts of the canyon. Placing of jumpers on the unpapered canyon deck also contributed to the overall contamination level. The large number of entrances into H-Cell during this period (including the H-2 Centrifuge replacement), while the cell was thermally hot, permitted increased contamination of the canyon and crane, to occur, thus, necessitating the increased decontamination efforts.

The period during which there was a large increase in the Redox canyon and crane radiation levels was the first part of September, 1953. At this time the H-4 Oxidizer was replaced (because of a failed coil). During the replacement operation, the H-4 Tower and many jumpers were placed on the canyon deck. After the time that the H-4 Tower was set on the deck, a white powder was observed to have fallen from the tower to the deck. The amount of powder released was unknown, but enough radioactive ruthenium was certainly liberated to contaminate the canyon and crane. Subsequent smears of the canyon walls were found to be 100 percent ruthenium and the radiation level on the crane jumped to a general field reading of 1 to 2 Rads./hour. Fresh air was piped to the crane cab to permit the use of a fresh air mask (vice Chemox) by the operator. It is visualized that during the subsequent weeks of operation, radioactive particles floating in the canyon would tend to settle on any flat surface, such as the crane bridge. When the crane moved, it would agitate the dust on the canyon walls, runway, and rafters which would then resettle. Thus, maintaining low radiation levels on the crane was next to impossible by local decontamination effort. The month of November was set aside to decontaminate the canyon and crane and repair the crane.

The second incident of gross canyon and crane contamination occurred on January 10 and 11, 1954 when an attempt was made to route the J-1 Filter off-gas to the stack via the Sand Filter. A steam jet was installed on the outlet nozzle of the J-1 Filter which discharged into a plenum chamber supposedly aligned with four outlet ports from the cell to the air tunnel. The plenum chamber was held against the cell wall by means of a wedge between it and the dunnage of the J-1 Filter. When the jet steam was turned on and no vacuum was obtained in the H-4 Oxidizer, the misalignment of the plenum chamber and air ports was suspected, and the wedge was loosened momentarily. Steam was seen to issue from the plenum chamber before the wedge was replaced. The crane operator and the supervisor with him at the time of the above incident were found to have extensive personal contamination. Later, surveys of the canyon crane indicated that the crane activity level had increased by a factor of 10. From this time to the present, continued decontamination efforts have resulted in average contamination levels of 300 mrad./hour on the crane.

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A review of the causes of the two main difficulties resulting indirectly from the use of the permanganate Head-End procedure indicates that it should be possible to operate with the permanganate Head-End procedure and prevent excessive contamination of the environs or recontamination of the canyon and crane. Continued use of strip filters for monitoring of off-gases should afford adequate control of ruthenium emission from the 291-S Stack. In addition, use of such techniques should permit development of improved Head-End procedures in which ruthenium emission is significantly reduced. Careful planning and performance of future canyon cell work should make it possible to prevent gross recontamination of the canyon and crane. Procedures for adequate control would include thermally cold cells (< 40 to $50^{\circ}\text{C}.$); water spraying before removal of the cell blocks; and proper boxing of vessels and jumpers when they are removed from the cell.

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