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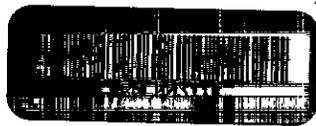
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A HISTORY OF THE REDOX RUTHENIUM PROBLEM

Operation of the Redox separation facility has resulted, almost from the very first, in frequent emission of varying quantities of radioruthenium in excess of desired limits. Although the exact cause of the ruthenium emission has varied, most of the incidents have been characterized by particulate contamination. This report summarizes pertinent information on this problem. Section I is a chronological review of the incidents and operational problems attendant with the emission of ruthenium from the Redox facility. Section II is a brief review of some of the more relevant process operations. Section III discusses the various systems for monitoring the stack effluents and Section IV presents data on the composition and structure of the particulate contamination.

I - Radiation Incidents Associated with Ruthenium Emission

Startup tests were performed in the Redox facility during January of 1952. The first processing of undiluted process material occurred during February, 1952. The first known incident (Class I #199, HW-24123) of uncontrolled release of radioruthenium occurred on March 8, 1952, due to failure of the caustic recirculation system in the H-5 scrubber. (1) No accurate estimate of the quantity of radioruthenium released was possible, as the stack air sampling system was not yet in operation. Air concentrations of ruthenium within the 202-S and 222-S buildings were estimated to be less than 2×10^{-8} $\mu\text{c}/\text{cc}$. However, no data was obtained as to the air concentrations existing at ground level outside the building during the height of the incident. Hand and shoe counters (5-folds) exhibited a high background count during the few hours that the condition existed.

(1) A discussion of this system is presented in Section II of this report.

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That this incident probably involved the first major release of a quantity of ruthenium, is evidenced by the fact that the dose rate in the 292-S jet house pit, through which the ruthenium off gas scrubber (H-5) line passes, increased from 50 mr/hr at approximately 25 feet before the incident to 1 r/hr at the same location after the incident. This increase was believed due to condensation of ruthenium vapors on the inner surface of the ruthenium off gas line.

The second incident (Class I #206, HW-25097) probably indicating the release of ruthenium from the Redox stack was detected on April 8, 1952. A GM survey meter from 202-S was discovered, by Calibration personnel, to have a small but highly radioactive particle adhering to the outside of the meter case. The particle had a dose rate of approximately 40 rads/hr (corrected for source size) and a chemical analysis showed that the activity was due principally to ruthenium. As the instrument had been surveyed and found clean just before pick-up by the Calibration Unit, it was assumed that the particle settled out of the air on to the meter. This assumption was substantiated by the fact that the particle was very easily removed from the case. The station wagon was left parked with its windows open for about an hour on the day in question in an area within the Redox facility that was subsequently found to have many radioruthenium particles. (See next incident description)

The detection of contaminated shoes at Redox on April 29, 1952 (Class I #246, HW-27447) led to the discovery of the third ruthenium emission incident. During the next few days widespread particulate contamination was discovered primarily in the eastern and northern sections of the Redox area. The particles were found to range in activity from 100 c/m at one inch to 800 mrad/hr at surface, all uncorrected for source size. Gross beta activity of the more active particles approached 0.1 μ c/sample. The contamination is believed to have been released from the Redox 1A column by sparging operations performed when the column was empty following routine cleaning of the column. The activity then passed through the vessel vent system (which includes a glass wool filter in series) to the main stack. This process operation had been performed with 100 % "hot" material at least once a month since startup and may, therefore, have caused some emission several weeks previous to this known incident. An examination of Regional Survey air sample data taken southeast of the Redox area revealed a significant increase in the number of particles per unit volume of air for the week ending April 25, 1952. This corresponded to the latest sparging period for the 1A column. A subsequent examination of Regional Survey air sample results taken at this location since the start of the "hot" runs revealed a somewhat similar increase in particle activity per unit volume of air for the week ending 3-28-52 (The 1A column was sparged during this week) and of course for the period covering the known emission of ruthenium occurring on March 8, 1952. It was also noted that there was another period (week ending 2-21-52) which showed an increase in particle concentration. One conclusion to be joined from these data is that some particles were probably emitted for several weeks prior to detection of the incident of April 29, 1952.

Operations other than the sparging of the "dry" 1A column are now believed to have contributed to the emission of ruthenium and, perhaps, to other isotope particles. For example, the transfer of process waste from H-2 to H-3 (centrifuge precipitate to waste solution tank) frequently results in ruthenium emission via the vessel vent exhaust system. Also, both the North and South sample galleries at Redox are known to have released several thousand radio-

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active particles per 1000 cubic meters of exhaust air during the months of February, March and April, 1952. Improvements in operating techniques reduced this problem somewhat in succeeding months, though complete cessation of particle emission from this area was dependent on installation of filters in the exhaust system.

Several glass wool particle frames (a sheet of glass wool suspended horizontally above ground on a frame) were positioned both inside and outside the Redox exclusion area during May, 1952. Routine surveys indicated a much reduced but continued emission or movement of radioactive particles until June 24, 1952, at which time a quantity of large flaky radioactive particles were found in and near the Redox Area. (Considered to be the fourth ruthenium emission incident and documented as Class I #225, HW-27431). The particles were observed to be 1/64 to 1/32 inches thick and up to several inches in diameter. Analysis revealed the activity to be primarily ruthenium, though the carrier crystal was predominately ammonium nitrate.⁽¹⁾ The stack monitor had not indicated any recent large emission of ruthenium, but it was possible that the monitor was not in operation at the time of the emission.⁽²⁾

The large flaky radioactive particles found near the eastern edge of the Redox exclusion area on June 24, 1952, rapidly disappeared and were not visibly present the next day, though spots of activity were still detectable. Since the flaky particles were quite fragile and also quite quite hygroscopic, they were probably broken up quickly by surface winds or dissolved in ground moisture. Following this emission incident, several short water flushes were periodically given to the main stack in an attempt to dissolve the adhering ammonium nitrate crystals. However, on the average, little activity or ammonium nitrate was picked up in the wash water, and the effectiveness of the operation was questionable. It is now believed that, since the air flow in the stack could not be completely shut off during these tests, a large portion of the water was blown back up the stack, reducing the efficiency of the cleaning operation. Some contamination (ruthenium) was picked up by the water; however, on two occasions considerable ground contamination, apparently from contaminated wash water blown out the stack, was observed primarily in the immediate vicinity of the base of the stack. On one of these occasions, numerous visible bubble-like masses were observed floating to the ground. Immediate attempts to pick up these "particles" were unsuccessful. The resultant activity levels of some of the surfaces on which these "particles" dropped and disappeared ranged from 1000 c/m to 50,000 c/m at one inch. Analysis of smears from typical locations revealed greater than 90% of the activity to be due to ruthenium with less than 1% due to I¹³¹. A positive ammonia test was also observed.

Routine surveys of ground surfaces and the use of glass wool frames positioned above ground around the Redox stack were continued during the following months and appeared to indicate the continued deposition of new particles. No large emission was again indicated until September, 1952, when approximately a 30-fold increase in the number of particles per unit area was observed on the glass wool control frames positioned around the stack and within the Redox exclusion area. This may be considered the fifth particle emission incident. Again the stack monitor did not indicate any abnormally large emission of ruthenium. Though on three occasions, September 9-10, 15-16, and 22-23, it did indicate the release of approximately one half a curie of ruthenium. This was above

- (1) A discussion of the formation of these crystals is presented in Section II of this report.
- (2) The stack air monitor was first installed in early June, 1952.

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the average for the month which was less than 0.1 curies per day.

The next major deposition of particles was observed by routine surveys performed in the Redox area on August 14, 1953. (This may be considered as the sixth incident and was documented as Radiation Incident, Class I #299, HW-29230.) Large fragments or chunks of radioactive material were observed on the ground surrounding and extending generally in a southeasterly direction from the stack. Laboratory analyses indicated that the bulk of the inert material was primarily ammonium nitrate and that the radioactive component was essentially all ruthenium. Some of the fragments were observed to be several inches in width and length and up to 1/2 to 3/4 of an inch thick. A maximum dose rate of 15 rads/hr at surface including 300 mr/hr at two inches, uncorrected for source size, was observed on one fragment. Some of them were observed to be concave-convex in shape as if they may have been formed on a circular base such as the inside of a pipe or the stack liner. The routine weekly survey of control areas around the stack performed on August 7, 1953, revealed only the usual number of new, comparatively small sized particles. Hence, the large fragments were released between August 7 and 14, 1953. Additional large particles were observed falling from the Redox stack effluent on August 18, 1953. The stack monitor did indicate an emission of approximately 2 curies of ruthenium per day between August 8-11 and about 3 curies on August 11-12, 1953. The stack monitor also revealed two large emissions in early September, 1953. Approximately 35 curies of ruthenium were emitted on September 5, and about 80 curies on September 6, 1953. This may be considered as the seventh ruthenium emission incident.

The eighth ruthenium-particle emission incident occurred initially on January 2, 1954, and again on January 5, 1954. (Documented as Radiation Incident Class I #333, HW-30764) Approximately 260 curies of ruthenium was estimated to have been released between January 2 and 3, 1954. An additional 70 curies was estimated to have been released on January 5, 1954. Both estimates are based on the stack monitoring effluent samples. Ground surveys performed between January 2 and 9, 1954, revealed extensive contamination (up to 7.5 rads/hr at surface) in the vicinity of Redox with considerable contamination being detectable over approximately half of the 200 West area. Most of the first emission was confined to the local area around Redox and a comparatively narrow fan-shaped area originating at Redox and extending roughly northeast towards the Wahluke slope. Failure of the H-5 caustic scrubber was believed the cause of the first of these two emissions, while stack flushing is credited with causing the second emission.

Though the following described Radiation Incident (Class I #335, HW-31344) is not directly concerned with the ruthenium-particle emission problem, it is believed relevant to any comprehensive review of the problem and incidents that are attendant to this subject. Following the second failure of the caustic scrubber (on January 2, 1954) and in an attempt to avoid future direct release of ruthenium in event of a 3rd failure of this system, it was decided to route the H-5 caustic scrubber off-gas line to the sand filter. An unsuccessful attempt to reroute this line was made by two employees on January 12, 1954. The work was being performed inside the Redox canyon crane cab and respiratory protection was prescribed and available and should have been worn for the entire operation. Nevertheless, respiratory protection was not worn for the entire period while the men were in the car and as a result some inhalation of contaminated air did occur with a subsequent nasal discharge from one employee showing 50,000 c/m or 15 mrad/hr at surface uncorrected for source size.

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Another radiation incident, Class II #69, HW-30783, which was related to the problem occurred during the period January 25, and February 3, 1954. Routine and follow up surveys revealed nine railroad employees to have personal clothing contamination during this period with one employee receiving a localized exposure in excess of permissible limits. Seven out of eight locomotives were found contaminated and a maximum reading of 100,000 c/m at one inch was observed. Also, the normally clean surfaces on seven cask cars were found highly contaminated with a maximum exposure rate reported on one coupling as 21 rads/hr at surface. The roadbed and railroad cuts within the 200 West areas were found to be quite generally contaminated, though not all the contamination can be attributed to Redox particles. Some of the activity is known to have been spread as a result of past burial operations, and also by spread of cask car contamination received during charging operations performed in the various facility railroad tunnels. The majority of the cases of clothing contamination were received as a result of poor radiation zone work practices and clothing removal techniques.

Widespread contamination of project vehicles became evident during February and March, 1954. Initial surveys made in March of nearly half of all the vehicles on the project revealed that approximately 20 percent of these were contaminated in excess of 100 c/m. The contamination was generally limited to tires, radiators and the under surfaces of the vehicles. Chemical analyses of some of the particles removed from automotive equipment found contaminated in March, 1954, indicated that vehicular contamination was not necessarily predominately ruthenium. A considerable percentage of rare earths was indicated by some analyses. For a more detailed report on vehicular contamination at HAPO, reference is made to the many and comprehensive reports on this subject issued by the Vehicle Emergency Study Group during March, April and May, 1954.

On April 23, 1954, a Minor Construction employee received a localized exposure in excess of permissible limits to a small skin area on his waist from contamination believed received as a result of work in a non-radiation zone area near Redox. The contaminating material in this case was not saved for analysis, but it probably was a ruthenium "particle", inasmuch as the general area in which he was working is known to have been subject to "showers" of particles from the nearby Redox stack.

On April 24, 1954, several hundred square feet of ground surface about a mile East and Southeast of Redox were surveyed and found contaminated. All spots checked had readings of a few hundred c/m and several spots found with a dose rate up to 750 mrad/hr at surface uncorrected for source size. The exact emission date for this material was not known. The area was known to have been comparatively free of contamination in September, 1953. Also, the contamination was not believed to have been associated with either the emission on January 2 or 5, 1954, as the contaminated areas resulting from those emissions were quite well defined and were located farther north.

The ninth emission of ruthenium-particles was detected in the 100-B area as a result of followup surveys after a pair of shoes were found contaminated on May 22, 1954. Particles with readings up to 80,000 c/m were found every ten feet or so around the 115-B building. Additional particles were found in the 100-B area and a maximum dose rate of 1.5 rads/hr at surface uncorrected for source size was observed. Analysis of the particles confirmed the activity to be primarily ruthenium and subsequent surveys revealed a well defined path of particles originating at Redox and extending northward over the 100 B area and on to the Wahluke slope.

On May 24, 1954, particulate ruthenium contamination was discovered in the major construction areas at 200 East. Surveys performed during the next few days revealed the contamination to be quite widely spread within the construction areas. During the early part of June, 1954, approximately 300 acres of ground area within the construction zone were surveyed and decontamination or removal of the more active particles was accomplished.

On June 7, 1954, an employee entered the Redox 291-S area without wearing the prescribed protective clothing. On his return from the job, he was found to have a spot of contamination on his right sock. Radioautograph revealed the contamination to be similar to a small particle and it is assumed that the activity was again principally ruthenium. The maximum corrected dose rate was calculated to be approximately 1.3 rads/hr at surface. In view of the short period of time that the employee was exposed to this contamination, no over-exposure was believed to have occurred.

On June 26, 1954, air, highly contaminated with ruthenium, was forced back from the Redox canyon into the operating and service side of the building. Approximately sixty employees were potentially exposed to this highly radioactive air. Positive nose smears were obtained from seven employees and initial bioassay results on two of these employees were quite positive. However, it is not believed at this time that the body deposition was in excess of permissible limits. This incident was investigated as Radiation Incident, Class I, #370, HW-32421.

On June 28, 1954, routine surveys of some of the control ground areas around Redox revealed a 10 fold increase in activity levels at some points over preceding surveys made during week ending June 25, 1954. A maximum dose rate of approximately 5 rads/hr was observed at some sites.

On June 20, 1954, some contamination was detected outside the perimeter barricade in the direction of Richland, but no contamination was detected in the city. Also, on June 29, 1954, highly contaminated air from the Redox canyon again reached the "clean" or service sides of the building. Personnel were again exposed to this activity without benefit of respiratory protection for varying periods. This incident was also investigated as a radiation incident.

II - Process Operations Associated with Ruthenium Particle Formation

A - H-5 Caustic Scrubber

Ruthenium is selectively removed in the H-4 "oxidation step" by air sparging the tankful of solution. The off-gases are directed to the H-5 caustic scrubber for removal of the ruthenium.

The H-5 scrubber assembly consists of a tank and a packed (Raschig rings) tower. The H-4 tank off-gases rise through the H-5 tower counter-current to a descending flow of caustic (15 to 25% solution of NaOH). The caustic liquor is recirculated from the tank below the tower. The system was designed on the basis that the ruthenium would be present as RuO_4 . In this state it can be readily absorbed in caustic. The exact mechanism by which this absorption takes place is not known for certain, though the ruthenium is probably reduced to the Ru (VI) valence which will form a soluble salt, probably $\text{Na}_2 \text{RuO}_4$. Unfortunately it is now known that at least part of the ruthenium coming to this scrubber has been previously reduced to the RuO_2 form which is not soluble in caustic. Ruthenium in this form

presumably passes directly through the scrubber and at least a portion of it then passes on through the glass wool filter which is in series with the scrubber. In the first ruthenium emission incident it is believed that recirculation of caustic did not occur due to solidification of the caustic liquor in the recirculation line.

Process changes have recently been made in this system and also the vessel vent system which should essentially prohibit further release of ruthenium to the stack. These changes include routing the H-5 off-gas through another caustic scrubber assembly (tank J-2, which is in the system but which is not yet charged with caustic), to the J-3 tank (an improved version of the old J-1 glass wool filter tank) and then to the sandfilter and the stack. The vessel vent system off-gas is now also routed through the sand filter.

B - Ammonium Nitrate Formation

The ammonium nitrate crystals are believed to have been formed in the main stack by the mixing and interaction of ammonia gas released during dissolution of the aluminum jackets and oxides of nitrogen released during the metal dissolution step. The crystals apparently built up on the stack liner and were then eventually coated with ruthenium released to the system. After a time the contaminated crystals would flake off and be carried up the stack to eventually settle out on the ground as radioactive particles. The two operations giving rise to the two gaseous effluents of concern were not carried on concurrently in the same cell but were carried on simultaneously in different cells. Process scheduling has been revised to insure that these two operations are not performed at the same time. This should aid in reducing the formation of the crystals of ammonium nitrate and thereby, in reducing the number of radioactive "particles" discharged from the stack. Some consideration is being given towards installing a water scrubber on each dissolver off-gas line to remove the ammonia and to prohibit formation of these carrier crystals. This would allow Operations more freedom in production scheduling than they now have under the present restrictions for dissolving vs. jacket removal operations.

III - Monitoring of Stack Effluents

There are two separate sampling systems currently in use to monitor the Redox stack effluents. Both systems have a common intake at the 50 foot level, and thus do not indicate the release of ruthenium particles that may be formed on the stack liner at heights above this level. This may account for the failure of both systems to indicate an emission when it is apparent by ground surveys that an emission has occurred.

One of the systems consists of a filter followed by a caustic scrubber in series through which the effluent gas flows at a rate of 1 to 2 cfm. The scrubber consists of a vessel in which a given amount of caustic solution is charged. The effluent gas is drawn (bubbled) through this system. The majority of the ruthenium activity and any particulate material will be retained on the filter while radiiodine will be found primarily in the caustic solution. A quantitative analysis for ruthenium is made on the filter.

The other sampling system, called the "CMS", is a constant monitoring system using a Victoreen Thyrode monitoring tube. This sytem does not have a filter

in it but does have a more efficient caustic scrubber assembly. The incoming effluent gas is made to rise counter-current to a descending flow of caustic through a packed tower. Fresh caustic is constantly supplied to the tower by a minipump. The caustic leaving the scrubber after being exposed to the effluent gas is passed through a steel cell which surrounds the gamma monitoring tube. Any gamma activity (ruthenium and iodine either absorbed or as particulate material) in the caustic solution is measured by the tube and recorded on a chart recorder. The caustic is collected in a container after passing the monitoring tube and is normally analyzed only for iodine. The system will pick up both ruthenium and iodine, but due to the non-uniformity of the caustic solution where particulate material is concerned and the low flow rate employed (~ 0.4 cfm), ruthenium is usually not determined by this system. The chart of the "CMS" system is connected to a range-changer which automatically changes the range of the chart as readings approach the upper limit of lower ranges. A duplicate recorder was installed in the 202-S building late in 1953 for use by operating personnel. (Note - this is the recorder referred to in Radiation Incident Class I, #333, HW-30764) This monitoring system has been in more or less continuous operation and has given good service during the past year and a half, though it was frequently inoperative during the first few months after initiation of the system in early June, 1952.

A recent (April, 1954) addition to the stack air sampling system is known as the Strip Air Sampler. The system consists essentially of a counter and chart recorder and a roll or strip of filter paper. A sample of the stack effluent is drawn through a small circular area on the filter paper. After a given period of time, the filter paper strip is automatically moved and the section of filter that was filtering the air is then automatically positioned under the counting tube. The length of sampling and counting time may be varied and a nearly-continuous record of the activity condition within the stack is readily available with a minimum lag time. The lag time is, of course, dependent on the length of sample period that is desired. The recorder is mounted in the Operational Dispatcher's office in the Redox process - 202-S Building, and the system in general has given very good service and has been helpful in correlating activity in the stack with process conditions. The filter collects ruthenium principally and, of course, any particulate matter. It probably gives an indication of some of the iodine activity present too, but the filter collection efficiency for this material is lower than for ruthenium. This system uses the same air intake as the other two systems.

IV - Composition and Structure of Particulate Contamination

The composition and structure of many of the particles recently observed in the 100-B and 200 Areas have been studied by the Biophysics Section. An excellent and detailed report of this study was made by F. E. Adley, J. M. Nielsen, and Z. E. Carey, in a letter to D. W. Pearce dated 6-15-54. According to this report, a total of approximately fifty particles were isolated and examined. Twelve particles from the 200 Areas and two from the 100-B area were analyzed for percent ruthenium. An average of $\sim 90\%$ ruthenium was observed on all particles. The activity ratio of $\text{Ru}^{103}/\text{Ru}^{106}$ ranged from 0.6 to 1.4, a value much lower than was generally observed in the past on the ruthenium air samples obtained in the Redox stack. However, the presence of ammonium nitrate in the contaminated material in addition to the high percentage of Ru tends to confirm the Redox stack as the probable source of the contamination.

One particle with an uncorrected surface dose rate of 1.2 rads/hr was found to have a total activity of 6.3 μ c and another particle with an uncorrected surface dose rate of 120 mrad/hr, a total activity of 0.49 μ c. There appeared to be no well defined relationship between particle size and observed dose rate. Particles of several thousand square microns were observed frequently, but little effort was made to separate the contaminating material from the inert material. The particles did show a tendency to fracture during the isolation procedure in the laboratory. There appeared to be a possibility that some of the larger particles may fracture or divide to smaller particles without attendant loss of active material. The particles were generally found to be rectangular in structure and opaque with frequent specks or flakes of color - black, yellow or reddish brown.

Several particles were forwarded to Biology for animal studies and several were retained by Methods for study of the solubility in solutions similar to those found in the G. I. tract. Additional studies are planned to confirm the relationship between dosage and activity.

Summary

At least nine specific incidents or periods involving significant ruthenium emission have occurred since startup of the Redox process. In addition, there are indications that ruthenium particles have been released almost continuously, to some extent, since startup.

It is believed that in all cases the ruthenium reached the stack effluent via either the H-5 tank (ruthenium caustic scrubber) off-gas line or the vessel vent off-gas line. Recent process changes to these systems have been effected and should prohibit further release of ruthenium to the stack effluent. Some of the ruthenium which was released prior to these changes may be still adsorbed on the stack liner or other piping surfaces and will, of course, contribute for a period to some further, though much reduced, radioactive particle emission.

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