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A STUDY OF CERTAIN PROPERTIES OF
RUTHENIUM COMPOUNDS FOUND IN
THE REDOX PROCESS

By
W. E. Gill
D. E. Wisehart

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Hanford Atomic Products Operation
Richland, Washington

UNITED STATES ATOMIC ENERGY COMMISSION
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A STUDY OF CERTAIN PROPERTIES OF RUTHENIUM COMPOUNDS
FOUND IN THE REDOX PROCESS

During the current study by the Industrial Hygiene Unit of the penetration by ruthenium compounds of certain respirator filters and canisters used at the 202-S facility, some information was obtained which may be useful to others at HAP0.

In order to study the character of ruthenium compounds involved in the problem, laboratory study of non-radioactive ruthenium and field study of accessible parts of the process were made.

A 500 ml round-bottomed boiling flask was set up as an RuO_4 generator to simulate oxidation. Ball and socket connections were used so that U tubes, scrubbers, and other units could be readily placed in the sampling train. Commercial ruthenium chloride that had been fumed with H_2SO_4 and diluted, was

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used as a source of ruthenium. Potassium periodate was used as the oxidizing agent. The RuO_4 was removed from the flask by drawing an air stream through the generator solution in a manner similar to sparging in the process.

As will be shown in detail in a final extensive report, from 40% to 99% of the gaseous RuO_4 passed through the various paper filter media tested. The use of activated charcoal and silica gel as adsorbing agents for gaseous RuO_4 was also investigated. Using the characteristic orange color produced qualitatively by RuO_4 in NaOH solution as the indicator of penetration, 200 mg of RuO_4 was collected on one gram of charcoal before it was sufficiently saturated to show penetration into the NaOH solution. However, within a few minutes the charcoal exploded with a flash of flame. For this reason, silica gel was tried. It was observed that at 25°C, the RuO_4 caused an immediate blackening of the silica gel at the upstream surface, and that this blackening progressed through the bed of silica gel as long as the passage of RuO_4 continued. It seems probable that the black deposit was RuO_2 , resulting from the rapid decomposition of RuO_4 as it was adsorbed on the silica gel.

It is likely that the RuO_4 adsorbed on the activated charcoal also decomposed to RuO_2 and oxygen in the same manner as that observed on the silica gel. The explosion could well have been due to the secondary reaction of the oxygen with charcoal resulting in spontaneous combustion.

It was further observed that the black deposit on the silica gel was readily removed by leaching with hot HCl. One gram of the blackened silica gel was boiled for twenty minutes with six successive 25 ml portions of concentrated HCl. This treatment removed all evidence of the black deposit on the silica gel, and the ruthenium was recovered in the leach solution.

Gaseous RuO_4 was passed through a 5 foot coil of 10 mm glass tubing for 30 minutes at 95°C. No evidence of decomposition of RuO_4 to form black RuO_2

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particles was observed.

Silica gel was also used as a collecting agent for radioactive material in the ruthenium off-gas sample line. During the oxidation step at 202-S on May 28 between 1:32 and 1:47 P.M. an aerosol sample was collected below the J1 filter by means of a silica gel tube backed up by a sodium hydroxide scrubber. The silica gel tube contained 1.7 microcuries of ruthenium (measured as total beta) and 6.3×10^{-4} microcuries was found in the backup scrubber. For this single trial the silica gel tube had an efficiency of 99.96%.

Possibly silica gel could be used effectively in respiratory equipment to filter out both gaseous RuO_4 and the microscopic particles of ruthenium compounds that characterize the aerosol in the ruthenium off-gas line.

It is suggested that silica gel might be used to advantage in the process for the recovery of the radioactive gaseous ruthenium tetroxide. Periodic leaching of the silica bed would dissolve the radioactive ruthenium and it could then be disposed of in the waste liquor.

The only readily accessible material from the ruthenium oxidation at the 202-S facility was in the ruthenium off-gas line. In order to study actual samples of ruthenium aerosols from the process, samples were collected below the J1 filter in the off-gas line.

Samples were collected by means of cascade impactors, and with a sampling train consisting of parallel filter holders backed up on one side by a silica gel tube followed by a sodium hydroxide scrubber, and on the other by a sodium hydroxide scrubber alone. Individual flow meters were placed in each parallel line, and the plant vacuum line was used.

Because of the sub-microscopic character of the ruthenium particles, electron micrographs were deemed necessary for adequate study. Representative electron photomicrographs are shown on pages 5 and 6.

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The particles shown in Figure 1 were prepared in the laboratory from non-radioactive ruthenium, and vary in size from less than 0.5 micron down to 0.01 micron. A deposit of film that is probably composed of discrete particles below the limit of resolution of the electron microscope is also shown. A few aggregates and chains are larger. An interesting ring pattern is shown which indicates that much of the particulate matter may have been deposited as part of a microscopic droplet. Photomicrographs taken with the light microscope before the droplets were dry show a size and shape similar to the ring pattern of the electron photomicrographs.

Particles collected in the process off-gas line showed marked similarity to those produced in the laboratory. In Figure 2 are particles collected on the fourth stage of the cascade impactor from the ruthenium off-gas line at the 202-S Building. The material collected on this stage comprised 99.4% of all radioactive material collected in the sample. Most of the particles were spheroids from 0.3 to 0.4 microns in diameter. Some chains and aggregates of these particles are shown which are from 3 to 5 microns in length. Some smaller particles less than 0.1 micron are also present. Most of the particles shown here appear to have been deposited within microscopic droplets similar to those shown in Figure 1. In Figure 3 the particles have been shadowed to show their spheroid character, and the characteristic droplet pattern is obvious. Figure 4 shows a single drop pattern with particles and a dark deposit of film in the center. This was collected on stage 3 of the cascade impactor at the 202-S Building.

The material shown in Figure 5 was collected by passing the air stream from the ruthenium off-gas line over the electron microscope screens placed in the filter sampling unit. A few 0.3 μ spheroids are shown, with a large number of particles less than 0.01 micron in diameter.

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ELECTRON PHOTOMICROGRAPHS

FIGURE 1

Particulate matter resulting from the passage of gaseous non-radioactive RuO_4 through a laboratory NaOH scrubber and subsequently collected in an electrostatic precipitator. 6000X

FIGURE 2

Particulate material collected on the 4th stage of a cascade impactor downstream from the J1 filter in the ruthenium off-gas line. 6000X

FIGURE 3

An electron photomicrograph which has been shadowed to show the spheroid character of some of the particles. This material is part of the same sample shown in Figure 2. 6500X

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ELECTRON PHOTOMICROGRAPHS

1 μ

FIGURE 4

This material was collected on the 3rd stage of a cascade impactor and is part of the same sample shown in Figure 2. 6000X

1 μ

FIGURE 5

Particulate material collected in sampling head upstream from a AAA glass fiber sampling filter during air sampling in the ruthenium off-gas line downstream from the J1 filter. 6000X

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It seems to be characteristic that gaseous RuO_4 passing through a sodium hydroxide scrubber produces submicron droplets and particles. Also, that a deposit of material so small that it appears as a film even in an electron photomicrograph is associated with the deposition of these materials on the surface of sampling devices. While the droplets either contain or produce many particles that are below the electron microscope limit of resolution in size, more than 99% of all the radioactive material in the ruthenium off-gas line below the J1 filter collected in the sample shown here was on the fourth stage of the cascade impactor. It has been shown* that approximately 95% of the droplets of unit density, collected on the fourth stage of a similar cascade impactor, were in the 0.7 to 2.0 micron range.

It is also notable that AAA glass fiber sampling filters removed more than 99% of the material at this point in the off-gas line.

CONCLUSION

Silica gel had an efficiency on the order of 99.9+% for the collection of both gaseous RuO_4 and droplets and particles from the ruthenium off-gas line below the J1 filter.

A silica gel bed is suggested for consideration as a collecting agent for gaseous RuO_4 in the process.

The material passing through the off-gas line below the J1 filter was composed of particles and droplets which were filtered out with AAA glass fiber filters. The droplets either contained or produced ruthenium particles ranging in size down below the limit of resolution of the electron microscope (0.01 micron).

* Instruction Sheet No. 3018/RD, Casella and Company Ltd., London.

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A temperature of 90-95°C did not in itself cause decomposition of RuO_4 when it was distilled from an aqueous solution through a clean all-glass unit.

W. E. Gill

W. E. Gill
Industrial Hygiene

D. E. Wischart

D. E. Wischart
Industrial Hygiene

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