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COBALT-60 IN GROUND WATER AND SEPARATIONS PLANT WASTE STREAMS

By: C. W. Thomas, D. L. Reid, H. A. Treibs
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RADIO-ANALYSIS LABORATORY UNIT
BIOPHYSICS SECTION
RADIOLOGICAL SCIENCES DEPARTMENT

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Co^{60} IN GROUND WATER AND SEPARATIONS WASTE STREAMS

Ground water samples are collected routinely by Earth Sciences or Regional Monitoring and radiochemically analyzed by the Radio-Analysis Laboratory for contaminating substances. Normally the samples are analyzed for the predominant radioactive isotopes shown by pre-cribbing analyses of the waste or for the isotopes critical with respect to M.P.C. even though the concentrations in the waste are relatively minor. In the past these have consisted of the following isotopes: Ru^{106}, Cs^{137}, Sr^{89} - Sr^{90}, U^{238} and Pu^{239} with the analytical frequency determined by the total activity level of the well water and the criticality of the isotope. Past history of ground water contamination has shown the radioactivity to be essentially all due to Ru^{106} - Rh^{106}.

Low level contamination of a strontium precipitate from the 241-BY-12 water sample collected late in February initiated a search for the offending material. This search was culminated with the identification of Co^{60} in the ground water underlying the T.B.P. scavenged waste disposal site, 241-BY.

SUMMARY

A few ground water samples previously analyzed for other radionuclides were analyzed for Co^{60} and showed concentrations ranging from 7.2×10^{-4} uc/ml in 241-BY-9 well water on 1-16-56 to 1.3×10^{-2} uc/ml in 241-BY-12 well water collected on 3-12-56. The ground water Co^{60} contamination exceeded the HAPO concentration limits by a factor of three hundred. The Co^{60} concentration in a well about 1000 feet from the cribbing site was 7×10^{-5} uc/ml.

It appears that the Co^{60} with the present T.B.P. scavenging procedure will possibly reduce the waste storage capacity of new cribs to three-fourths or one-half of the calculated volume.

The first cycle waste streams of the Redox and T.B.P. Plant, the feed solution to T.B.P., and pre- and post-nickel ferrocyanide scavenged T.B.P. wastes all contained Co^{60}. Cobalt-60 was not detectable in the second cycle T Plant waste or in the contaminated ground water underlying the second cycle cribbing site.

Cobalt-60 can be formed from one or more of the following reactions of copper, nickel and cobalt impurities in reactor materials: $Co^{59}(n,\gamma)\ Co^{60}$; $Ni^{60}(n,p)\ Co^{60}$; and $Cu^{63}(n,\alpha)\ Co^{60}$. The production of Co^{60} from minute quantities of one or more of the above impurities was shown by the analyses of the aluminum caps from a metal piece exposed to 650 M.W.D./T. The cobalt-60 activity density was approximately 6.4×10^{-3} uc/mg of aluminum. The cobalt-60 in first cycle separation waste streams could originate from impurities in both the irradiated aluminum can and uranium.

HISTORY

Two factors played on important part in the finding and identification of the cobalt-60. The more significant was a recent revision to the strontium procedure(1) to increase significantly the Ru^{106} decontamination factor which allowed detection of the contaminant in the strontium determination. The broader application and increased sensitivity of the gamma ray spectrometer made possible by a recently installed three-inch NaI(Tl) well crystal was a significant factor in the identification and expedition of the work.

Low energy beta particles from a strontium precipitate of a ground water sample from the 241-BY-12 well collected on 2-28-56 were investigated by an aluminum absorption study to determine the energy and to confirm the indication of Sr^{89-90}. These beta absorption curves showed that the energy was approximately 0.3 Mev, too low for either radioactive Sr or Rh^{106}, and indicated the presence of an isotope not previously detected in ground water samples. A larger volume aliquot

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was evaporated to dryness in the presence of perchloric acid to expel the high level Ru^{106} - Rh^{106} activity. The residue was dissolved in a small quantity of acid and scanned with the gamma ray spectrometer. Gamma energies of approximately 1.17 and 1.33 Mev and a small coincidence peak at approximately 2.5 Mev were found. The age of the material sent to the crib and the beta and gamma energies all indicated that Co^{60} was the unknown contaminant. Engineering and Manufacturing Laboratories were contacted relative to earlier work on the identification of isotopes present in waste streams and "Can" activation analyses. Their tests were not pointed toward the detection of Co^{60} and consequently, a review of these data did not indicate its presence. To further corroborate the findings a cobalt chemical separation procedure (see Analytical Methods) was developed. The procedure was formulated to quantitatively separate cobalt from any Fe^{59} that might be present since the beta and gamma energies are very similar to those of Co^{60} except for the gamma coincidence peak of 2.5 Mev. Beta and gamma energy studies and gamma-gamma coincidence counting of the cobalt precipitate confirmed the earlier measurements.

Two possibilities existed for the presence of Co^{60} in the ground water under the T.B.P. scavenged waste cribbing area. (1) An irradiated Co^{59} slug had inadvertently been dissolved with the uranium metal and had been sent to ground at some earlier date or (2) Co^{60} was being continuously produced in the reactors from impurities in the uranium, bonding material, or aluminum cans. A search was made for all the available samples of T.B.P. scavenged wastes previously sent to crib as well as samples of other plant waste streams that would provide data on the contemporary wastes to define the source of the cobalt-60. The procedures and methods used were varied to meet sample conditions and without concern for the radiochemical yield to expedite the analyses. From the data obtained and the

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procedure used, a fifty percent deviation in the assumed fifty percent radiochemical yield of these waste analyses appears reasonable.

ANALYTICAL METHODS

The analytical methods employed in determining the cobalt-60 concentrations in ground water, feed and waste streams from T.B.P., and first cycle waste from Redox varied due to the radioactive species present. In determining cobalt-60 ground water concentrations, it was necessary only to remove the large amounts of ruthenium-106 by perchloric acid distillation followed by a gamma scan.

The feed and waste streams from T.B.P. contained in addition to ruthenium large amounts of antimony-125, cesium-137, and the rare earths. The ruthenium was removed by distillation after which the addition of ammonium hydroxide complexed the cobalt and scavenged the rare earths by formation of an iron hydroxide precipitate. The insoluble antimony sulfide was removed by acidifying the supernate and adding hydrogen sulfide. Cobalt was isolated by a basic sulfide precipitation and any occluded cesium removed by a silicowolframic acid scavenge on a nitric acid solution of the cobalt sulfide.

The Redox first cycle waste contained in addition to the previously mentioned isotopes large amounts of zirconium-95 and niobium-95. The Zr and Nb was removed with successive acid iodate scavenges prior to the ruthenium distillation. Separation of the other isotopes was in the same manner as outlined above for T.B.P. waste solutions.

All activity measurements were obtained by transferring the cobalt fraction to a vial which was placed in a three-inch well NaI(Tl) crystal of a gamma spectrometer. No attempt was made to determine the radiochemical yield on the waste stream samples since only qualitative answers were necessary to determine the source of

the Co^{60}. However, from the relative data obtained (Table II), a deviation of fifty percent appears reasonable. The radiochemical yield for cobalt in ground water samples was assumed to be one-hundred percent since the method entailed only evaporation and distillation of ruthenium. The accuracy of this analysis is limited only by the accuracy of the gamma measurements.

RESULTS

At HAPO, the amount of radioactive material that can be cribbed to any one site is limited by the concentration of any critical nuclide in the ground water. A critical isotope may be defined as any radioactive isotope with a half-life greater than three years that exceeds one-tenth of the maximum permissible concentration (M.P.C.) in drinking water(2) for occupational exposure. The M.P.C. for Co^{60} in water is 4×10^{-4} uc/ml(3). The 241-BY-12 well water sampled on 2-28-56 exceeded the HAPO limit for Co^{60} in ground water (4×10^{-5} uc/ml) by a factor of approximately 100 and had further increased by a factor of three three weeks later.

The activity density of Co^{60} in ground water samples taken from wells adjacent to and downstream from the T.B.P. scavenged waste cribs (241-BY) is presented in Table I. Figure I, a map of the test well locations, indicates the area of water contaminated with cobalt-60 based on the samples analyzed to date. Contaminated equipment prevented sampling between 3-12-56 and 3-26-56. The samples collected prior to 2-28-56 were laboratory holdovers from previous analyses.

TABLE I

Co^{60} IN GROUND WATER UNDERLYING 241-BY CRIBS

241 Well No	Sampling Date	TB* Units of 10^{-4}	Co^{60} uc/ml	Ratio of TB/Co^{60}
BY- 9	1-16	1300	7.2	160
BY-11	2-20	430	2.4	160
	2-28	1500	7.4	200
BY-12	2-28	6100	38	160
	3- 5	7200	30	250
	3-12	8800	130	67
	3-28	10000	90	110
	4- 2	10000	76	130
DISTANT WELLS				
B-15**	3-12	150	1.9	79
B-16	3-12	32	0.7	45
B-17	3-12	45	0.8	55

*TB = Gross beta particle emitter concentrations

**Approximate ground distances from cribs: B-15 - 500', B-16 - 1000', and B-17 - 300'.

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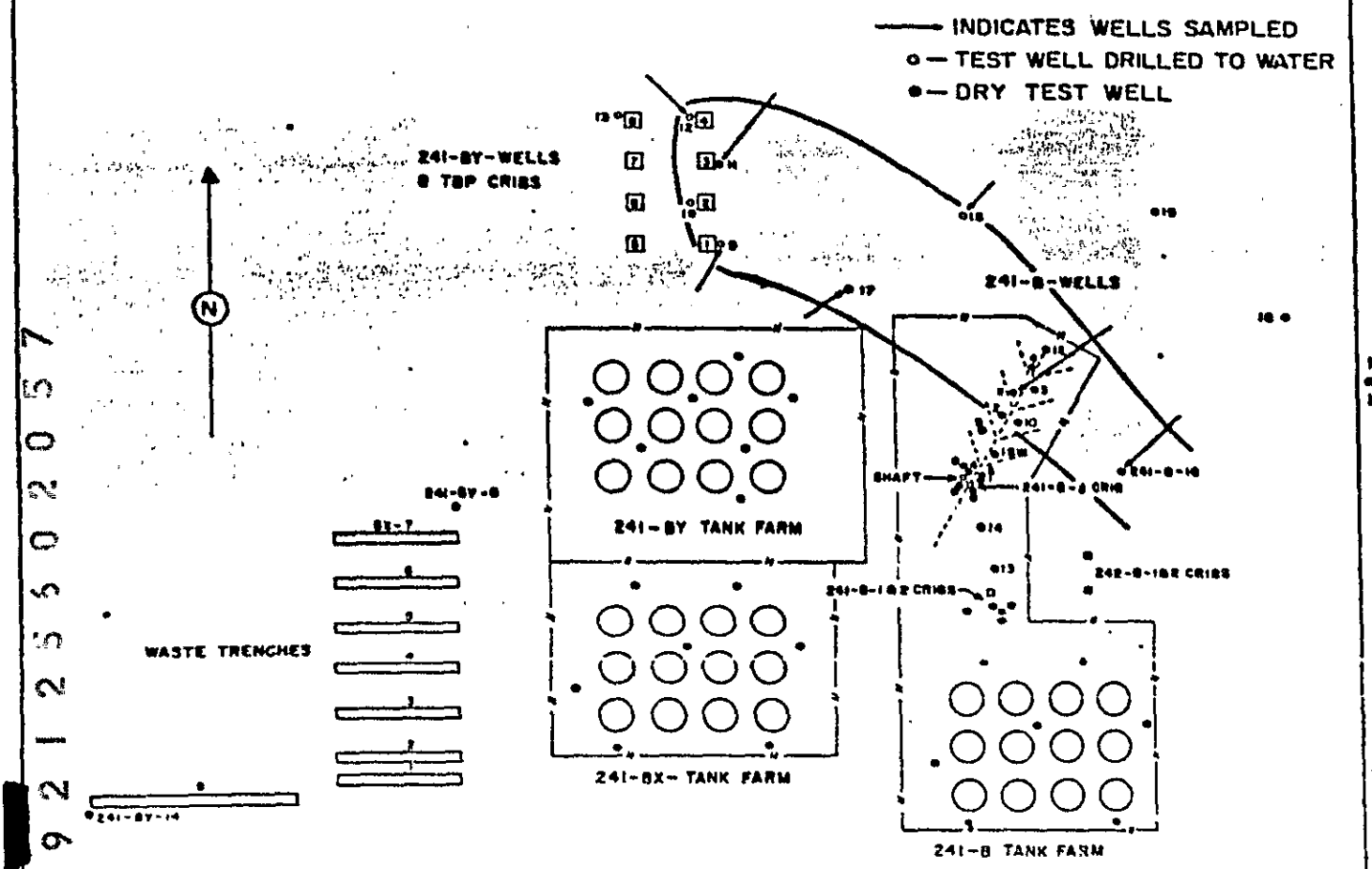
FIGURE — 1
TEST WELLS



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As shown by the data in Table II, all first cycle wastes analyzed contained Co^{60}. The T Plant second cycle stream, as predicted, did not contain a detectable quantity of cobalt-60. The presence of Co^{60} in both wastes approximately two years old and contemporary Redox waste confirms the assumption that Co^{60} is presently being and has continuously been produced in the reactor from impurities in the slug materials. The relatively small differences in the Co^{60} concentration in the various wastes could probably be accounted for by dilutions, yield deviations and small losses effected by the chemical treatment of the waste as indicated by the T.B.P. feed solution and wastes collected on 3-15-56 and 3-19-56 respectively, Table II.

An aluminum cap from a metal piece exposed to 650 M.W.D./T was obtained from Radiometallurgy and analyzed directly by gamma coincidence counting after removal of the occluded fission products and by gamma spectrometer scan of the chemically separated cobalt. The average activity density was 6.4×10^{-3} uc Co^{60}/mg aluminum or 780 uc/can assuming uniform distribution of Co^{60} throughout the aluminum. This would equal a Co^{60} concentration of 5.7×10^{-2} uc/ml in the Redox 1 AW waste assuming that all of the cobalt in the cans from a one ton charge reached this waste stream. This is not a logical assumption since cobalt precipitates as the hydroxide in the presence of strong alkalis and an appreciable portion of the sludge would probably be removed during the jetting of the coating waste. However, some fraction of the sludge produced during the chemical removal of the cans might remain in the vessel and be dissolved with the uranium. Thus, it appears that impurities in both the uranium and aluminum could be contributing to the total Co^{60}.

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TABLE

Co^{60} IN PLANT SEPARATIONS WASTE STREAMS

Solution	Date Sampled	Co^{60} uc/ml
First Cycle Redox Waste	8 - 8-55	7.6×10^{-2}
First Cycle T.B.P. Waste	5-11-53	5.0×10^{-2}
T.B.P. Feed	3-15-56	1.7×10^{-2}
First Cycle Redox Waste (acidic)	3-19-56	9.3×10^{-3}
First Cycle Redox Waste (scavenged)	3-19-56	5.2×10^{-3}
Tank 16-107-BY-Supernate	Cribbed 10-23-55	1.9×10^{-2}
Tank 12-110-BY-Supernate	Cribbed 12-12-55	1.4×10^{-2}
112T (2nd Cycle Waste, etc.)	2- 3-56	5×10^{-5}

DISCUSSION

Three possible modes of Co^{60} production from trace impurities in the uranium, aluminum can, or bonding material are $Co^{59}(n,\gamma)\ Co^{60}$, $Ni^{60}(n,p)\ Co^{60}$ or $Cu^{63}(n,\alpha)\ Co^{60}$. The most abundant reaction of these three in the reactor would be $Co^{59}(n,\gamma)\ Co^{60}$, but each reaction may contribute to the total Co^{60} produced. Values obtained from Metal Fabrication showed less than 2 ppm of Co^{59} in the uranium and less than 6 ppm in the aluminum can and bonding material. Nickel ranged between 50 and 100 ppm in the aluminum can and uranium. Calculations were made to determine the quantity of Co^{59} required to produce the Co^{60} concentration of 7.3×10^{-2} uc/ml in the first cycle Redox waste (Table II). Assuming an exposure of 200 M.W.D. per ton and 3436 liters of waste per ton of metal, only 0.12 ppm of Co^{59} in the uranium would be required to produce the quantity of Co^{60} in the Redox waste sampled in August of 1955. For 650 M.W.D/T, approximately 0.04 ppm would produce the same quantity of Co^{60}.

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Since the chemistry of cobalt and iron is very similar it would follow that Co like Fe should be strongly retained in the soil column unless in a complexed large molecule or un-ionized form. The chemicals for the formation of such a molecule are present in the T.B.P. waste scavenging process where a strongly complexed alkali double cyanide, or cobaltammine could be formed. Speculation as to the composition of the molecule is beyond the scope of this paper since there are many possibilities under the prevailing scavenging conditions and the physical and chemical properties of such compounds are most variable. A detailed chemical investigation would be required to determine the mechanism of formation, species and form of the compound.

Similar samples of the pre- and post-scavenged T.B.P. wastes were analyzed to evaluate the effect of scavenging upon the Co^{60} concentration. The results (Table II) indicate that a low decontamination factor of approximately two or less for Co^{60} is effected by the nickel ferrocyanide scavenging. This becomes insignificant since the variation in the Co^{60} concentration in the few scavenged wastes analyzed is greater than the indicated decontamination factor and would have relatively no affect upon the concentration in the ground water.

The 241-BY cribs were closed to waste disposal due to the Cs^{137} concentration in the ground water of 241-BY-11 well on January 9, 1956. The effect of an earlier discovery of Co^{60} on the closure date of the 241-BY cribs must be speculative until applicable experimental data can be obtained. However, from the data in Table I and a preliminary soil column test by Earth Sciences Unit[4] it appears that complexed Co^{60} approximates the soil percolation rate of Ru^{106}, the major radioactive component in the gross beta particle activity density (TB) of ground water. The average total β to Co^{60} activity ratio (TB/Co^{60}), Table I, was 150 to 1 for those wells in the immediate vicinity of the crib site. This ratio

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applied to previous TB values from 241-BY-11 well water indicated that the total volume of waste cribbed at the 241-BY site would have been reduced by approximately 2.3×10^6 gallons or from 8.5 to 6.2×10^6 gallons due to the Co^{60} concentration in the ground water.

From the results obtained on the more distant wells B-15, B-16, and B-17 (Table I) it appears that a lower TB/Co^{60} ratio prevailed at lower ground water TB concentrations prior to the major break-through of activity into the water table. For an average ratio of 50:1 the capacity of the 241-BY crib system would have been reduced to approximately 50 percent of the volume sent to crib.

CONCLUSIONS

The heretofore unknown presence of Co^{60} in the first-cycle separations waste and the subsequent formation of a complexed cobalt molecule or ion in the waste scavenging process resulted in ground water contamination in excess of the maximum permissible concentration[2,3].

It was indicated from the radioactive composition of the ground water and waste liquid and from preliminary soil column tests that the soil underlying the HAPO cribbing sites has little or no affinity for cobalt in the complexed state. This factor coupled with the present disposal limits for radioactive wastes[3] indicates a need for reducing the cobalt-60 concentration to prevent significant volume restrictions on cribbing sites.

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