Tritium and Nickel-63 at the Kansas City Plant

White Paper
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PURPOSE

Since writing the SEC-00210 Kansas City Plant (KCP) Petition Evaluation Report (ER), NIOSH has been made aware of KCP operations involving tritium and nickel-63. This white paper establishes exposure scenarios intended to bound worker dose resulting from use of these radionuclides.

At its June 10, 2014 meeting, the Work Group added Issues Matrix Item # 20 to ascertain the nature of tritium operations, potential worker exposures, and timeframes involved. As an action item from that meeting, NIOSH staff, members of the Board, ORAU Team staff, and SC&A staff visited KCP in October 2014 to review weekly activity reports and other documents.

As a result of the above visit and document reviews, it was discovered that radioactive Ni-63 had been used at KCP to electroplate Ni-63 sources for use within the tritium monitors manufactured at the facility. This Ni-63 electroplating operation was limited in scope and involved between four and eight workers (SRDB 138161, PDF pp. 7).

This white paper will address, in turn, bounding exposure scenarios for the following work involving tritium and Ni-63:

- Tritium: Using luminescent paint to fill engraved markings on the "HI-LO" switch plates
- Tritium: Manufacturing instrumentation for tritium analyses in air, urine, and water
- Nickel-63: Fabrication of a Ni-63 plated coupon for use as an internal calibration standard

TRITIUM: CONTAMINATION ON "HI-LO" SWITCH PLATES

NIOSH's first indication that tritium was being used, or was being considered for use at KCP, is a February 8, 1963 internal KCP memo from an industrial hygienist, [*redacted for privacy*] (SRDB 137154, PDF p. 16). This memo states that activated phosphor is associated with negligible radiation exposure. An unspecified Atomic Energy Commission (AEC) study on the topic was cited, but based on similar wording, the study was almost certainly the June 14, 1960 publication *USAEC Radiation Safety Evaluation of Tritium Activated Dials in Luminous Watches and Clocks* (SRDB 128438). This document was released just prior to the June 30, 1960 announcement "AEC to Permit Use of Tritium on Luminous Timepieces" which requested

comments on a general license for up to 25 mCi per device (SRDB 128438). Consistent with the AEC evaluation, the February 8, 1963 Industrial Hygiene memo said that no monitoring or protective clothing is required when working with this material, but that Industrial Hygiene should be notified in the event of breakage or destruction of the plastic matrix.

An April 16, 1964 interdepartmental KCP memo from [*redacted for privacy*] regarding tritiated phosphor is available (SRDB 137154, PDF p. 8). This memo discusses the need to expedite production of luminescent dials. The luminescent dial vendor, U.S. Radium, had a radioactive materials license condition that required a 7-day curing time prior to shipment. This curing-time requirement interfered with the production schedule that required 70 housings and 70 dials before the cure period would be completed. Each housing contained 10 µCi of tritium and each dial contained 25 µCi of tritium. The housings and dials were coated and shipped from U.S. Radium to Sargent and Greenlease Company in New York for assembly into a combination lock. Upon completion, this assembly was to be shipped to KCP.

A May 18, 1965 letter is available from U.S. Radium to [*redacted for privacy*] (with the Bendix Scintilla Division) regarding "tritium filled self-luminous plate" (SRDB 137154, PDF pp. 12-15). [Note: Bendix Corporation was the KCP site operator; Bendix Scintilla Division was located in New York.] This letter documents conversations establishing the KCP position that the luminous plates are unacceptable if contamination appears during their use. The letter documents wipe-test results, performed at U.S. Radium prior to shipment to KCP, on three batches (27 total luminous items) that showed increasing contamination over a one-week period. Each batch was wiped with one composite swipe on day zero, then again seven days later. Batch 1 increased from 0 to 1500 background-corrected counts per minute (cpm), which was equivalent to 0.0014 µCi. Batch 2 increased from 0 to 300 ccpm, which was equivalent to 0.0003 µCi. Batch 3 increased from 400 to 3500 ccpm, which was equivalent to 0.0032 µCi. U.S. Radium stated that these contamination levels were inconsequential, and that it was not possible to predict future performance without more testing.

On May 26, 1965, [*redacted for privacy*] wrote a letter to [*redacted for privacy*] of KCP (SRDB 137154, PDF p. 11) documenting discussions that had occurred during the prior week. The letter offered three options concerning the switch plate: (1) delete the requirement for the plate; (2) specify plates with improvements; or (3) remove the radioactivity.

A May 27, 1965 KCP interdepartmental memo regarding the "MC1831 Cable assembly (Hi-LO plates, tritiated phosphor)" documented a plan to develop a means to cover the plates via epoxy

or polyurethane at Bendix Scintilla Division as a way to contain loose contamination (SRDB 137154, PDF pp. 7). The plan called for a site visit to U.S. Radium after the coating method was developed so that the coating could be applied by the vendor.

A May 28, 1965 internal KCP memo is available from [*redacted for privacy*] to [*redacted for privacy*] regarding "tritium filled self-luminous switch plate for assembly CF-1831" (SRDB 137154, PDF p. 10). The Bendix Scintilla Division was due to ship the next lot of assemblies in early June; however, the contamination level exceeded the vendor's license limit. The memo also notes that KCP was faced with handling problems. Advice was requested by June 1, 1965.

A July 1, 1965 internal KCP memo is available from [*redacted for privacy*] to [*redacted for privacy*] regarding "Hi-Lo Switch Plates" used in the MC 1931 cable assembly (SRDB 137154, PDF p. 9). The memo states that tritiated phosphor filled the engraved letters so they could be read in the dark, and that the phosphor was a tritiated organic compound mixed with zinc sulfide and adhesive. It also states that the plates are covered with a protective coating. The radiation hazard was discussed and the memo pointed out that tritium contamination exposure involves a weak beta emission and no external dose. The activity of each plate was 40 mCi, which created no significant health problem handling the plates. The memo also notes that plates were marked with radiation labels to provide for better controls. The memo stated that the vendor, U.S. Radium, was placing a double coating of protective material on the plates.

NIOSH reviewed a patent filed by U.S. Radium on December 5, 1962 for their invention of the tritiated phosphor used on KCP's Hi-Lo Switch Plates (SRDB 141145). This patent was reviewed to understand the nature of the phosphor, its characteristics, and designed uses. The patent indicated that the phosphor was contained in a "Tung oil" matrix, which provided information that any personnel exposures would have been from organically-bound tritium (OBT) in the mixture rather than tritiated water (HTO) or tritium gas.

A report dated November 19, 1965 provides detailed removable-tritium-contamination results from swipe tests on Hi-Lo switch plates, made both after receipt and prior to use at KCP (SRDB 137063). A PAC-3A internal gas proportional counter was used to count the swipes. Each tested plate was swiped on the front with one swipe and on the back with another swipe. It was noted that the design specification for removable tritium on the switch plates was 10,000 dpm. Three hundred thirty Hi-Lo switch plates were received in four batches, and 55 of those were tested for contamination. Of the 55 tested, 13 (24%) exceeded 10,000 dpm. The highest observed contamination level was 35,395 dpm. The report concluded that the measured

contamination levels presented no significant radiation exposure while handling the plates. Table 1 summarizes the results. No additional information is available on whether or not additional switch plates received at KCP were routinely swipe-tested.

Table 1: Tritium Swipe Results from Luminescent Hi-Low Switch Plates								
Set No.	Receipt Date	Number Received	No. of Plates Tested Front and Back	Mean (dpm)	Standard Deviation (dpm)	Min (dpm)	Max (dpm)	Std Dev Mean
Set 1	10/21/1965	153	25	4796	6815	0	35395	142%
Set 2	11/12/1965	67	15	7044	5184	1810	24341	74%
Set 3	10/18/1965	4	4	2073	1148	0	3988	55%
Set 4	08/09/1965	106	11	7099	6380	1369	27142	90%
Summary	N/A	330	55	5672	6179	0	35395	109%

In a March 2, 1966 memo to [*redacted for privacy*], Sandia Livermore [*redacted for privacy*] documented a February 10, 1966 site trip to the U.S. Radium Corporation in Bloomsburg, Pennsylvania (SRDB 128439, PDF pp. 4-9). Also attending the site visit were [*redacted for privacy*] from KCP and U.S. Radium. The memo discusses the tritium contamination experience at U.S. Radium and the applicable AEC contamination limits (see Table 2). Allowable tritium contamination levels at the U.S. Radium facility in the areas where tritium was processed were 200 cpm on a 100-cm^2 swipe. The memo also discusses methods of counting and difficulties in obtaining reproducible swipe results. The consensus was that in the future, all contamination surveys would be counted using the liquid scintillation counter method. A summary of tritium removed in submersion water tests was reported. Acceptance sampling and vendor test certification requirements were defined. The acceptance test for contamination was to be done by the vendor between 5 and 7 weeks after the final protective coating was applied to the plate.

The trip report documents that the Bendix Scintilla contract with U.S. Radium would be terminated and that KCP would initiate a purchase contract with U.S. Radium to obtain the remaining plates originally ordered by Bendix Scintilla. A recap of the Bendix Scintilla procurement showed that:

- 181 units had already been shipped to Bendix Scintilla;
- 125 units were ready for shipment, pending leak test;
- 90 units were ready except for final coating;

- 42 units were ready for tritium application; and
- 62 units were in progress, having only been machined and engraved.

A May 27, 1966 internal KCP memo from [*redacted for privacy*] to [*redacted for privacy*] regarding "Inspection of Hi-Lo Switch Plates in Department 212" found that handling the switch plates should present no health hazard and that no special protective measures were indicated. The requirement was to contact Health and Safety in the event that phosphor paint was removed by accidental chipping or during any intended testing methods. Otherwise, hand-washing was the only routine required action (SRDB 128439, PDF p. 2). On the same date, [redacted for privacy] wrote a six-point set of health and safety requirements for "Handing Tritium Luminous Compound 115 GT" (SRDB 128439). The requirements included performing powder-mixing under a fume hood, properly labeling containers, covering work surfaces, requiring paper shop coats and rubber gloves, smoking restrictions, eating and drinking rules, hand-washing requirements, and instructions to bag waste and contact Health and Safety for disposal.

Shipping documents show that on June 26, 1967, KCP shipped 30 Hi-Lo plates to Seneca Army Depot (SRDB 137154).

An October 14, 1968 letter is available from [*redacted for privacy*] (KCP H&S [*redacted for privacy*]) to [*redacted for privacy*], Bendix Corporation, South Montrose, Pennsylvania) (SRDB 128438). This letter explains the regulatory analysis and framework associated with general and specific licensing of luminescent dials containing tritium. The referenced documents were included as attachments. These documents included Military Specification MIL-T-46343 (tritium solid form), 10 CFR 20, *Standards for Protection against Radiation*, 10 CFR 30, *Rules of General Applicability to Licensing of Byproduct Material*, and other tritium applicable notices. The radiological requirements in these documents applied to all organizations in the supply and user chain for possession, handling, or using these tritiated products.

Supervisor [*redacted for privacy*] stated, "We have handled these materials at the Kansas City Division and the following basic requirements were established…." Work rules describing "Preparation of Tritiated Phosphor" and "Handling of dials subsequent to painting…" were included. These appear to be similar to the work rules established by U.S. Radium (SRDB 128438). However, the first item under the KCP rules for preparation of tritiated phosphor is "Tritiated phosphor and adhesive binder were mixed in an exhausted hood to control airborne and surface contamination."

Three methods were used at U.S. Radium to determine the tritium contamination on the switches after the curing of the final cover coating.

1. A smear survey that involved removing any contamination from the part with filter paper and counting it on an internal proportional counter.

2. A water survey in which the part to be tested was immersed in 100 ml of distilled water for 24 hours at ambient temperature and pressure. Afterwards, a measured sample of the water was evaporated and counted with an internal proportional counter.

3. The same water-immersion method listed above except that the immersion water was counted in a liquid scintillation counter.

These methods were patterned after methods described in 10 CFR 32.101 (in place during that era and later).

The final criteria established for tritium contamination determination was: "Each plate of the sample size shall be immersed in 100 ml of distilled water for 24 hours at ambient temperature and pressure. The activity of tritium in the water shall be measured by a liquid scintillation detector that has been calibrated for tritium efficiency with a National Bureau of Standards tritium standard. The maximum allowable activity of tritium in the water shall be less than 5.5E8 dpm" (SRDB 128439, PDF p. 9).

Table 2 shows data reviewed by Lovell during his visit to U.S. Radium (SRDB 128439, PDF p. 5) and provides a comparison of the some of the standards of the day to the agreed-upon contamination criteria.

Table 2: Allowable Tritium Limits Established by the Military and AEC			
Source	**Description of Item and Quantity of H3**	**Allowable H3 Loss in 100 ml of Water**	**Allowable H3 Removable by 100 cm^2 Smear**
10 CFR 32.40	Auto Locks: 15 mCi	3.2E7	2.2E3 dpm
10 CFR 32.14	Watch Dials: 25 mCi	2.8E9	Not required
10 CFR 32.101	Aircraft Exit Signs: 4 mCi	8.8E9	2.2E3 dpm
Mil. Spec.	Luminous Signs	1.1E5	1.1E5 dpm

A November 6, 1968 memo is available from J[*redacted for privacy*] to Lt. Col. Edwin Engram (U.S. Army Seneca Army Depot) regarding Hi-Lo switch plates. The memo replies to a question regarding the required marking based on activity. The memo states that each plate contains approximately 40 mCi of tritiated phosphor mixed with adhesive binder for attachment to the aluminum. It states that markings and controls are appropriate considering the low hazard level of tritium. The memo also notes that, during fabrication, the plate is over-coated with clear plastic resin and cured. The luminosity design criteria is also reported (SRDB 137154).

TRITIUM: EXPOSURE BOUNDING SCENARIO FROM "HI-LO" SWITCH PLATES

This section describes a bounding scenario for exposure to tritium associated with radio-luminescent "Hi-Low" switch plates. Based on the period during which it is known that the switch plates were used, NIOSH assumes that tritium exposure occurred continuously between 1963 and 1968. It is also known that KCP had a formal method for controlling employee access to work areas via security guards, medical screenings, and qualifications.

In this bounding exposure scenario, only those workers who received, inspected, installed, tested, and packaged the switch plates may have been exposed to the tritium incorporated in the zinc sulfide scintillator. The chemical form of the tritium as it was incorporated into the phosphor was an organic compound known as Tung Oil, also known as China Wood Oil (used as a finish in woodworking). NIOSH reviewed a Sigma-Aldrich safety data sheet (SDS) that states that Tung Oil is an ester of eleostearic acid and other fatty acids (SRDB 140801). It is a waxy solid with a near-zero vapor pressure at room temperature, making inhalation unlikely. The SDS gives no precautions and instructs the user to wash it off with soap and water if it gets on the skin. In addition, NIOSH is aware that Eucerin pH5 hand cream contains stearic acid as a thickening agent. Since the tritium was also in a stearic acid similar to those used in common hand creams, with properties that would cause it to coagulate/thicken and dry on the skin, this provides a plausible skin-contact mechanism for transfers of OBT through workers' skin.

In consideration of these physical characteristics and KCP's operations, the most probable exposure pathway would have been through skin absorption. However, there would have been a slow and incomplete translocation of surface contamination across the skin membrane. In lieu of calculating the absorbed quantity, NIOSH will employ a claimant-favorable strategy and assume a bounding, instantaneous, and 100% activity transport across skin.

A February 1966 trip report recapping the order status from the prior year, states that 500 units were ordered and 181 were shipped prior to the report date. It is also known from swipe test records that 330 switch plates or components were received in four batches in 1965. This suggests that two different orders for switch plates were made in 1965. NIOSH can use this information on items received to estimate the daily chronic exposure that would have occurred.

Data collected in 1965 from 110 swipes used to assess the contamination level on 330 switch plates were fitted to a lognormal distribution. The data were found to have a geometric mean of 4,246 dpm/100 cm^2 and a geometric standard deviation of 2.32. The upper 95th percentile value of this distribution is 16,900 dpm/100 cm^2. NIOSH assumes this value for the contamination level in the bounding exposure scenario.

NIOSH has not found documentation on the size of the Hi-Lo switches other than their thickness of 3/16 of an inch. It is assumed they are approximately the size of a plate covering a light switch or standard wall outlet, two-sided (front and back), and nominally 100 cm^2 on each side for a total of 200 cm^2. NIOSH considers this a reasonable assumption based on the documentation that each plate was soaked in 100 ml of distilled water for the 24-hour leak test determinations. A plates of this size would have been covered and soaked in this volume of water. Thus, each switch plate would have had 33,800 dpm distributed over the entire surface.

NIOSH assumes that each switch plate was handled enough for all of the surface contamination to be transferred to the worker's skin where it was completely absorbed. Procurement records indicate that at least 500 of the plates were ordered by KCP; therefore, the handling could have been several per day over the intermittent tritium monitor manufacturing periods. Based on these procurement records, NIOSH will assume that a worker handled three switch plates each day. This means that the bounding intake rate of organically bound tritium through skin absorption would be 101,400 dpm (1690 Bq). This bounding intake rate would have been chronic through the year, for the period 1963 through 1968. Using the OBT ICRP 68 dose conversion factor of 4.19E-9 rem/Bq, the worker dose would be 7.08E-6 rem/day or 1.77E-3 rem/year (250 workdays).

TRITIUM: MANUFACTURING TRITIUM MONITORS

There is evidence that tritium-in-air instruments and tritium-in-urine monitors designed by Sandia were manufactured by Bendix at KCP over an extended period. This manufacturing involved use of tritiated water as a calibration standard. Radioactive Ni-63 was plated on a component of one of the tritium-in-air instrument models; exposure to Ni-63 at KCP is discussed later in this report.

Manufacturing of the instruments began in 1959 (SRDB 137065). Four monitoring kits were produced in February 1960 (SRDB 137065). Manufacturing of the tritium monitoring equipment continued in campaigns through the 1970s. This manufacturing effort was not in response to tritium used programmatically at KCP; rather, the manufacturing was done under contract to Sandia. The instruments were used by military organizations and by the U.S. AEC during nuclear testing.

The identification of the instrument models changed with time. In 1964, the U.S. Navy had the Model T-289 tritium-in-air monitor permanently installed on surface ships and submarines. Model T-290 was a less-sensitive, battery-powered, portable tritium-in-air monitor that was also on each monitored ship. Both could be used with the tritium-in-urine bioassay instrument called the Model T-329 Urinalysis Test Kit. In 1964, procurement of the next generation of instruments was in progress (SRDB 137822). Two each of the Model T-289 and the Model T-329A were available for use during atmospheric nuclear testing in the Pacific theater during the Operation Dominic series conducted during1962 (SRDB 77532). By 1972, the Tritium in Air Monitor Bendix/Sandia Model T446 and the Tritium Urinalysis Monitor Bendix/Sandia Model T449 were available, as documented in *Instrumentation for Environmental Monitoring*, published by Lawrence Berkeley Laboratory (SRDB 137183).

No evidence was found indicating that tritium gas or tritiated water vapor was used at KCP in direct association with the ion chamber production. Tritium-in-air monitors do not necessarily require tritium gas or water vapor to be available during the manufacturing process. These monitors are based on ion chamber technology. Ion chambers respond to any ions in the chamber, regardless of the source. They can be operationally challenged and functionally calibrated with minimal uncertainty using a standardized gamma radiation field. Typically, a cesium-137 source and a set of calibration jigs, used to reproducibly fix the source to detector distance, are used for this purpose. Therefore, the lack of documentation concerning tritiated gas and tritiated water vapor at KCP is not necessarily a data gap, but instead may reflect the fact that ion chambers were simply fabricated but not tested or calibrated at KCP, which is also

suggested in a March 27, 1965 memo (SRDB 137065). Sandia, known to have had extensive tritium-handling capabilities at their Livermore site, could have tested and calibrated the ion chambers with gamma rays and with high concentrations of tritium as part of a procurement acceptance test (SRDB 137065).

The tritium urinalysis instrument was not actually a radiation detector. It was a purpose-designed reaction system to disassociate hydrogen from water and inject that hydrogen into an ion-chamber air monitor where the tritium concentration could be accurately measured. This instrument reacted calcium metal with 7 ml of water or urine to produce hydrogen. If tritium were present in the water, it would also be proportionally-present in the evolved hydrogen. Due to uncertainties about the chemical reaction efficiency, the tritium bioassay instrument required tritiated water for testing and calibration. Consequently, KCP procured standardized tritiated water from Sandia. Initially, in 1959, the bottles were received and inspected without opening, then stored under ventilation until they were installed in instrument kits (SRDB 137065). This seems to have been thoroughly planned to the point of instructing Sandia to place a note on the exterior of the tritium package saying "Not to be Opened – Contact Health, Safety and Fire Departments." A hand-written note indicates that 14 bottles were received. An operational procedure for the Model T-329 requires that suitable standard solutions ranging from 5 to 250 µCi/l be prepared. The unit was reported to have a precision of ± 5% over the range of one to 150 µCi/l (SRDB 137065).

By 1964, the procurement practice had changed and the standard 250 µCi/l tritiated water solution was procured in gallon containers from Sandia and repackaged into smaller 400 ml bottles for inclusion in the monitoring kits (SRDB 137860). Eight gallons of tritiated water were purchased in August 1964 and seven gallons were purchased in November 1964. Nice and Weinstein (SRDB 137822) mentioned that standard tritium water was included in the Model 329 for calibration purposes and that the maximum permissible body-burden for tritium was 60 µCi per liter.

The market for the Model 329 and Model 449 tritium urinalysis instruments presumably ended by early 1970s when liquid scintillation counters became widely available. Direct counting of tritium in urine by liquid scintillation methods eliminated the need for the relatively complex equipment and reactive metal reagent, and so the method naturally fell out of favor.

TRITIUM: EXPOSURE BOUNDING SCENARIO FOR MONITOR WORK

This section describes a bounding scenario for exposure to the tritiated standard solution while handling and using the solution to test and calibrate the Model T-329 Urinalysis Test Kit and the Tritium Urinalysis Monitor Bendix/Sandia Model T449.

Initially, in 1959, small-sized bottles of standard solution (400 ml of 250 µCi/l) were purchased from Sandia and stored under ventilation until they were used or packaged for shipment with a completed urinalysis kit. Although it is unknown when the procurement policy changed, it is known that by 1964 the standardized tritiated water was purchased in one-gallon units and repackaged at KCP into 400 ml bottles. In 1964, there are records of two shipments of 8 gallons of standardized tritiated water for a total of 16 gallons (60,600 ml). A 400 ml bottle of the calibration standard solution was shipped with each urinalysis kit. Decanting the gallon-sized units into 400 ml bottles would result in nominally 150 bottles of standard solution. Based on this, it is reasonable to assume that approximately 150 decanting operations occurred in 1964. To ensure claimant favorability, it is assumed that some part of the decanting operation occurred in KCP's chemistry lab every workday (250 days per year) beginning in 1959 and ending in 1975.

Based on the care that went into the procurement process and cautionary notes about handling that were included in the purchase order, it is assumed that the chemistry technicians that handled the standardized tritiated water would have been careful with it due to its value and hazardous nature. It is known that the unopened bottles procured in 1959 were stored under ventilation when not in use; therefore, it is reasonable to assume that any process associated with standard tritiated water, including decanting from one bottle to another, would have taken place under a ventilated enclosure such as a fume hood.

Although decanting could have occurred on a single day soon after each shipment was received, it is possible that smaller bottles were filled in separate operations. The process of receiving and transfer tritiated water from Sandia in gallon bottles and transferring some of the liquid to smaller volumes (i.e., 400 ml and ~2.5 ml vials), could have provided reasonable opportunity for losses through splashes or spills that went unreported. It is plausible that these small splashes/spills occurred during the liquid-transfer processes that were used in the preparation of the final standard's volumetric configuration.

For this bounding scenario, it is assumed that the total volume of a 400 ml bottle of tritiated water was spilled over the course of a year and was absorbed by a worker. This is a claimant-

favorable assumption since NIOSH has not located Unusual Occurrence Reports (UORs) that describe incidents or spills that occurred during the tritiated water decanting transfers to other containers. It is also assumed that none of the water evaporated, which would have removed the tritiated water vapor from the room/hood through the ventilation systems. This assumption allows the entire spilled volume (i.e. 400 ml volume of 250 µCi/l tritiated water) to be absorbed through the skin of the worker. The activity in the 400 ml of standardized tritiated water is 100 µCi. A fully-efficient wipe test of the spill areas would yield a total removable contamination level rate of 2.22E+08 dpm. In this bounding scenario, this tritium contamination is completely transferred to the skin of the hand of the chemistry technician during the year. Thus, in this bounding scenario, the chemistry technician's skin is contaminated with 2.22E+08 dpm (3.7E+06 Bq) of tritiated water on an annual basis. This activity would be completely absorbed as tritiated water through the skin and into the blood stream. Using the tritiated-water ICRP 68 dose conversion factor of 1.8E-9 rem/Bq, the worker dose would be 6.66 mrem/year.

NICKEL-63: FABRICATION OF NI-63 CALIBRATION STANDARDS

There is evidence that KCP/Bendix used Ni-63 over an extended period of time in the manufacturing of tritium-in-air and urine monitoring instruments designed by Sandia National Laboratories. This manufacturing involved plating Ni-63 on a small aluminum metal coupon for use as an internal calibration standard.

Exposure to Ni-63 occurred during small-scale chemical-plating operations. Radioactive Ni-63 was included in the nickel-plating solution. A one-square-inch (SRDB 138164, PDF p. 8) Ni-63-plated area was incorporated into the precipitator plate (SRDB 138157, PDF p. 3) of the Tritium in Air Monitor, Bendix/Sandia Model T446 (SRDB 138159, PFD p. 2).

The nickel-plating solution was modified by adding the radionuclide Ni-63, as a liquid, from the standards prepared from the purchased Ni-63 dissolved in hydrochloric acid. Ni-63 is a low-energy beta-emitter with average beta energy of 17.4 keV, maximum beta energy of 66.9 keV (Figure 6) and half-life of 100.1 years. It emits no X-rays, gamma rays, or alpha particles. For comparison, the beta emission from tritium has an average energy of 5.7 keV and maximum energy of 18.6 keV. Based on waste records, the total activity of each one-square-inch nickel-plated spot was nominally 0.5 µCi (SRDB 138164, PDF p. 4). The plating process resulted in the plated portion of the precipitator plate to emit detectable amounts of beta radiation. Because of its low-energy beta emission, the Ni-63 plate can be used as a

self-contained calibration source in the Model T446 to simulate the beta radiation associated with tritium decay (SRDB 137183, PDF p. 2).

On at least four different dates, KCP engineering staff procured Ni-63 in 1 molar hydrochloric acid solution from ORNL. Three of the four orders referred to ORNL "Product 47," which has a nominal Ni-63 activity of 198 mCi/ml (SRDB 138157, PDF p. 3; 138151). Product 47 was reported to have two radioactive contaminants in trace concentrations: (1) "Silver (Au) 110" [sic], which most likely means silver-110, at a concentration of 0.03 mCi/ml [0.015% of the Ni-63 concentration]; and (2) an unspecified isotope of scandium in a concentration of 0.04 mCi/ml [equivalent to approximately 0.02% of the Ni-63 concentration]. The four documented purchase orders were (SRDB 138151, PDF pp. 2-6):

- 20 mCi at a concentration of 50 mCi/ml on April 25, 1967, referencing ORNL Product 47
- 120 mCi on June 20, 1967, ORNL Product 47
- 120 mCi on March 21, 1969, ORNL Product 47
- 1000 mCi on September 21, 1970

Each order placed with ORNL included instructions that ORNL mark the exterior package. A typical set of instructions is found on the April 25, 1967 order: "Do not open in receiving – radioactive material – notify health and safety, ext. 2638 for internal routing of material."

The Ni-63 plating operation occurred in the small volume-plating bath of the Finishes Development Facility. Floor plans and facility location maps are available (SRDB 138155, PDF pp. 3). A plan for upgrading the Finishes Development Facility was presented to KCAO-AEC on December 18, 1969 (SRDB 138155, PDF p. 2). The justification for the plan described safety issues that prompted KCAO-AEC to direct that the plating shop be immediately shut down. By December 23, 1969, corrections had been made and the Supervisor, Health and Safety, recommended that the facility could be restarted (SRDB 138155, PDF p. 5). On November 25, 1970, a project directive modification request for the Finishes Development Facility was submitted to AEC-KCAO (SRDB 138161, PDF p. 3). This document described the existing facility and the safety issues that were to be addressed by the capital improvement. It also stated that four chemical engineers, chemists, and engineering technologists worked in the facility full-time and another four personnel worked part-time. The time-frame of projects done in the facility ranged from a few days to a few years.

An August 31, 1970 memorandum documented the safety controls associated with Ni-63 plating operations (SRDB 138154, PDF p. 2). These were essentially no different from normal operational controls except for waste disposal and labeling requirements. The following is an edited summary of these controls:

- The solution will have to be stored in proper containers and identified
- Eventually, the solution will have to be disposed of in a method prescribed for radioactive wastes
- There is no danger for an operator using the small volume plating bath beyond the normal precautions that apply to handling and using acid solutions
- No special handling is required for rinse waters
- No special handling of parts except to identify radioactive parts in packaging

A September 29, 1970 memorandum more thoroughly documented the radiological safety controls associated with Ni-63 plating operations (SRDB 138163, PDF p. 2). The following is an edited summary of these controls:

- Workers will be given an orientation by Health and Safety prior to handling the material
- Workers will wear protective equipment including eye protection, gloves, and apron
- Workers will not eat, drink, or smoke while working with the material and will wash their hands at appropriate times
- The stock and plating solution will be identified and labeled with radioactive warning tape;
- Spills will be cleaned up immediately and Health and Safety will be notified to provide monitoring

Radioactive waste disposal records dated May and June 1984 show that at least five, and perhaps up to nine, Ni-63 panels with one-square-inch radioactive areas were disposed (SRDB 138164, PDF p. 8).

In summary, the records shows that both management and Health and Safety staff took careful interest in the procurement and use of the Ni-63 material during plating operations. Ni-63 was handled in liquid form until it was essentially immobilized in the form of durable metallic nickel plating. The radiological hazard was evaluated as operations progressed and was judged negligible, similar to the non-radiological hazards of metal plating. Other than waste management, spill response, and material labeling, no special controls or personnel dosimetry were required.

NICKEL-63: BOUNDING EXPOSURE SCENARIO FOR NI-63 ELECTROPLATING

The plating operations were all wet processes and offered minimal opportunity for exposure. The stock solution and the plating solution containing Ni-63 were considered chemical irritants because they were hydrochloric acid solutions. As with any plating-shop, adequate room exhaust ventilation can be assumed. The intake potential of the stock solutions of Ni-63 purchased from ORNL was minimal since they were delivered to KCP as liquids, most likely in sealed glass ampoules. The intake potential from the plating solutions was also minimal due to routine controls established for the plating shop.

Although there is no direct evidence or descriptions of the plating system used at KCP, the size of the coupons plated (1 in^2) is an indication of the size of the plating system required.

A plating technique for Ni-63 on small copper coupons, nominally one-square-inch, was reported by ORNL in 1989 (SRDB 128975, PDF p. 8). The ORNL plating cell system drawings are in Figures 1 and 2 (SRDB 128975, PDF pp. 10, 18). Assuming the width of the copper coupon shown in Figure 2 is one inch, the illustration can be scaled and the volume of the plating bath estimated to be one cubic inch, or 16 ml. This report documents how small bubbles, nominally 1 mm in diameter, were used to induce turbulence into the bath and achieve mixing. NIOSH finds this to be a plausible mechanism for creating and maximizing airborne radioactive material concentration in the air surrounding the plating bath.

The bounding dose scenario applied in this white paper is the calculation method shown below, derived from an U.S. Environmental Protection Agency (EPA) publication that estimates the solute emissions from aeration and electrical energy used in electroplating tanks or cells (http://www.epa.gov/ttnchie1/ap42/ch12/final/c12s20.pdf). Equation (1) in the EPA model can be used to predict uncontrolled emissions (EF_m) of nickel from electroplating tanks in units of grains/dscf (grains per dry standard cubic foot). Equation (4) uses the amount of air that was used to induce turbulence in the ORNL plating cell. It is estimated that 600 one-millimeter diameter bubbles per minute for 60 minutes created a volume of 38 milliliters of air through the plating solution during plating. It is important to note the instruction at the bottom of Equation (4) indicating that the E_2 emissions are calculated in per volume units of aeration air. The emissions from the NIOSH calculation are therefore normalized to the volume (38 ml) of aeration air through the ORNL plating cells shown in Figures 1 and 2.
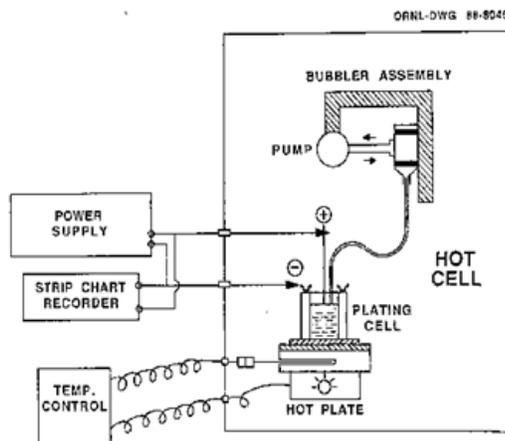
Figure 1: ORNL Plating System

Note that the operation occurred in a hot cell, probably due to the airborne activity release during the process.
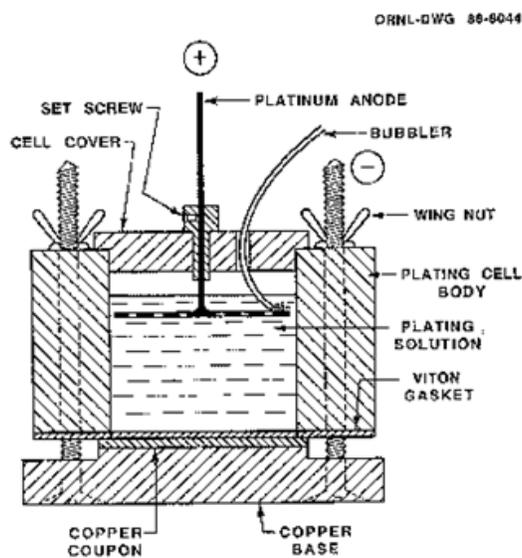

Figure 2: Detailed Drawing of ORNL Plating Cell

Assuming the copper coupon is one inch wide, NIOSH estimates the volume of the plating solution as 16 ml.

Equation (4) from the EPA equations (see Figure 3) was evaluated using an Excel spreadsheet with the following specific parameters and other general conversions factors:

Calculation of the constant "a" in Equation (4) below:

- Constant = 0.072
- R_b (in) = 0.02
- Sigma (lb-ft) = 4.96E-03
- a = 5.81E-03

Other constants used in calculations:

- ICRP breathing rate (m^3/hr) =1.2
- Volume of air breathed in one hour (ml) =1.20E+06
- Ni-63 DAC (μC_i/ml) = 1.0E-06
- Duration of one plating operation (hr) = 1
- Number of plating operations in one year = 100
- Volume of air aerated through the plating solution during one hour of plating (ml) =38

Calculation of E_2 in Equation (4):

- Constant = 1.9
- Calculation of coefficient in front of large square brackets = 4.71E-01
- E_2 (grains/ft^3) = 3.61E-02
- E_2 (mg/m^3) = 8.38E+01

E_2 normalized to the volume of air aerated through the plating solution during one hour of operation (mg/m^3) = 1.12E-01

Calculation of activity in normalized E_2:

- Specific activity of Ni-63 (mCi/mg) = 5.67E+01
- Activity of 1.12E-01 mg/m^3 of Ni-63 into 75 m^3 of room air (μC_i/ml) = 8.49E-11
- Room air concentration in DAC = 8.49E-5
- Activity breathed during one plating operation (μC_i) = 1.02E-04
- Activity breathed after 100 platings per year as an annual intake (μC_i) = 1.02E-02
- Annual intake rate (DAC-hr) = 8.49E-3

Emissions from plating operations other than chromium electroplating can be estimated using emission factors and operating parameters for chromium electroplating. Equation (1) below provides an estimate of uncontrolled emissions from non-chromium plating tanks from energy used to perform plating.

$$EFm = 3.3 \times 10^{-7} \times (EEm/em) \times Cm \times Dm \qquad \text{Equation (1)}$$

Where:

- EFm = Emission factor for metal "m" in grains/dscf
- EEm = Electrochemical equivalent for metal "m", A-hr/mil-ft2 = 19.2
- em = Cathode efficiency for metal "m", percent = 50%
- Cm = Bath concentration for metal "m", oz/gal = 2.34E-01
- Dm = Current density for metal "m", A/ft^2 = 2.55.

The above inputs lead to the following result:

$$EFm = 7.56E\text{-}06 \text{ grains/dscf}$$

The air concentrations produced by the two process methods and models can now be compared:

- EFm = 7.56E-06 grains/dscf $\equiv$ 7.56E-06 grains/ft^3 [emission value from electrical energy input using Equation (1)]

- E_2 = 3.61E-02 grains/ft^3 [emission value from air sparging/bubbling [using Equation (4)]

These air concentrations show that the E_2 concentration is approximately 5000 times larger than the EFm concentration. This means that the E_2 method air concentration would produce 5000 times the exposure to workers than the other model. It would be more claimant-favorable to use the higher air concentration to calculate worker exposures. Although the E_2 value is several thousand times larger than the annual exposure (2.83E-02 DAC-hr/yr), the dose consequences of this air concentration are very small. Thus, the Ni-63 plating process employed at KCP represented a very insignificant source of exposure to workers.

Equations 1 and 2 estimate emissions from the formation of gas as a result of the electrical energy applied to the plating tank; the equations do not account for additional emissions that result from air sparging or mechanical agitation of the tank solution. To estimate uncontrolled emissions due to air sparging, the following equation should be used:

$$E_1 = 100 \, k_1 R_b^2 \left[\frac{(1 - 2a + 9a^2)^{0.5} + (a - 1)}{(1 + 3a) - (1 - 2a + 9a^2)^{0.5}} \right]^{0.5} \tag{3}$$

$$a = \frac{6.45 \, R_b^2}{k_2}, \quad k_1 = \frac{56.7 \, \sigma}{c_s^2}, \quad k_2 = \frac{1.79 \times 10^5 \, \sigma}{(\rho_1 - \rho_g) \, g}$$

where:

E_1 = emission factor, grains/bubble;
R_b = average bubble radius, in.;
σ = surface tension of bath, pounds force per foot (lb_f/ft);
c_s = speed of sound, ft/sec;
ρ_1 = density of liquid, lb/ft^3;
ρ_g = density of gas (air), lb/ft^3; and
g = acceleration due to gravity, ft/sec^2.

Substituting typical values for constants c_s (1,140 ft/sec), g (32.2 ft/sec^2), and assuming values for ρ_1 of 62.4 lb/ft^3 and for ρ_g of 0.0763 lb/ft^3, Equation 3 can be reduced to the following equation:

$$E_2 = \frac{1.9 \, \sigma}{R_b} \left[\frac{(1 - 2a + 9a^2)^{0.5} + (a - 1)}{(1 + 3a) - (1 - 2a + 9a^2)^{0.5}} \right]^{0.5} \tag{4}$$

where:

$$a = \frac{0.072 \, R_b^2}{\sigma}$$

E_2 = emission factor in grains/ft^3 of aeration air; and
the other variables are as defined previously.

Figure 3: Calculation of the Emission Factor from Air Sparging/Bubbling

Ni-63 Internal Dose Bounding Scenario

The bounding dose to workers involves the potential inhalation of Ni-63 from a micro-aerosol that can be created in the laboratory room from aeration of the plating solution. It is assumed that the plating shop where the work occurred operated without ventilation. This assumption is very favorable to the claimant.

It is assumed that the plating bath was stirred using a bubbler, as shown in Figure 2. Bursting hemispherical bubbles at the surface of the plating solution provide the mechanism for the generation of aerosolized droplets of Ni-63, as illustrated in Figures 4 and 5.

Picture adapted from Sergio Blanco http://pixelado08.deviantart.com/art/water-bubble-drop-183430991

Figure 4: Photo of Bubble Bursting from Water Surface and Ejecting Droplets from the Surface
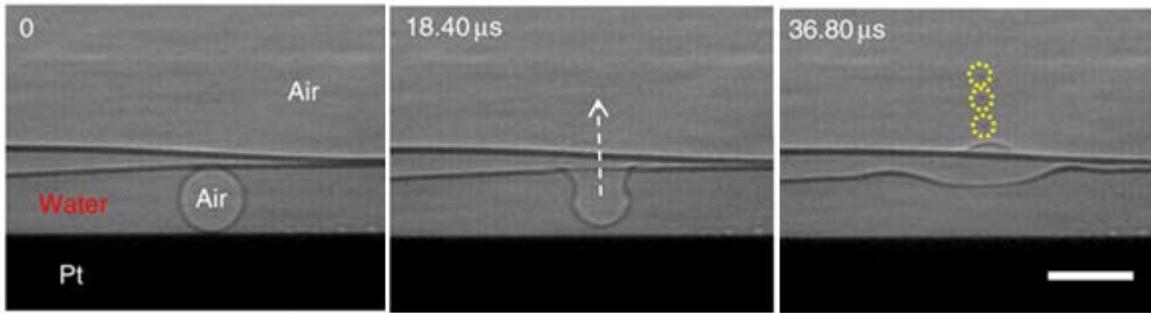
Photos from Nature Communications 2, Article number 367 doi:10.1038/ncomms 1369,
http://www.nature.com/ncomms/journal/v2/n6/fig_tab/ncomms1369_F2.html

Figure 5: Photographic Sequence Showing Small Bubble Formation and Droplet Ejection

For a bounding scenario, it is assumed that the radioactivity is uniformly mixed into the air of a 5 m x 5 m room with a 3 m ceiling height (75 m^3 volume) that is occupied by the worker who is breathing at the standard ICRP 66 occupational breathing rate of 1.2 m^3/hour. To be claimant-favorable, it is assumed that neither local exhaust ventilation nor room exhaust ventilation reduces the air concentration.

When 6.37E-03 µCi of Ni-63 is diluted into this air volume, the airborne activity concentration is 8.49E-11 µCi/ml. The Derived Air Concentration (DAC) for Ni-63 is 1.0E-6 µCi/ml. The air concentration predicted during a plating operation is 8.49E-5 times the Ni-63 DAC.

During the 60-minute plating operation, it is estimated that the worker will inhale 1.02E-01 nCi, which is equivalent to 3.8 Bq. Assuming this operation occurred 100 times each year, the annual intake rate would be 377 Bq. This is equivalent to an annual exposure of 8.49E-3 DAC-hr, and a dose of 2.1E-2 mrem/year.

Ni-63 External Dose Bounding Scenario

Figure 6 is derived from data in Radiological Toolbox. The average beta energy is 17.4 keV and the maximum beta energy is 66.9 keV. The half-life of Ni-63 is 100.1 years.
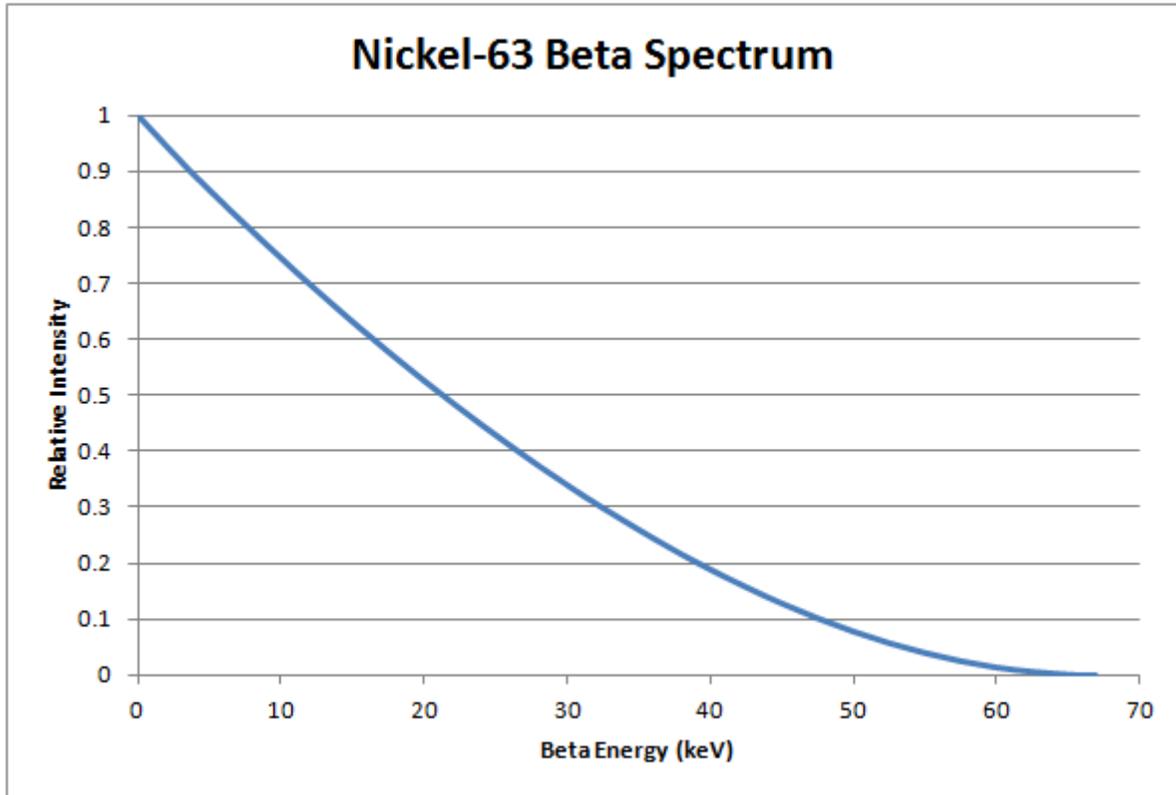

Figure 6: Ni-63 Exposure Rate vs Beta Energy

The Katz-Penfold equation predicts the range of an electron in units of g/cm^2. For electron energy below 0.1 MeV, Equation 5 applies. (http://holbert.faculty.asu.edu/eee460/IonizationRange.pdf)

$$R_{max} = 0.412 * E_{\beta}^{1.265-0.0954*\ln(E_{\beta})}$$

Equation (5)

Using this equation and the maximum beta energy emitted by Ni-63 (0.0669 MeV) gives a range of 0.0067 g/cm^2. This value can be divided by the ICRP soft tissue density of 1.060 g/cm^3 to calculate that the range of the maximum energy beta in soft tissue is 63 µm. Since the maximum energy beta cannot reach to depth of 70 µm, where skin dose is calculated, no external dose from a Ni-63 source can occur.

TRITIUM AND NICKEL-63 BOUNDING CONCLUSIONS

KCP SEC Issue #20 reflects the Working Group's desire to better understand tritium operations and worker exposures. This paper provides details to respond to Issue #20 and provides additional details to address associated Ni-63 operations.

- Tritium Bounding Scenario for HI-LO Switch Plate Handling: A worker's skin is contaminated with 1690 Bq of organically bound tritium (OBT) each workday. This bounding intake rate would have been chronic through the year (250 workdays). Using the OBT ICRP 68 dose conversion factor of 4.19E-9 rem/Bq, the worker's dose would be 1.77 mrem/year.

- Tritium Bounding Scenario for Tritium Monitor Manufacturing: The chemistry technician's skin is contaminated with 3.7E+06 Bq of tritiated water on an annual basis. This activity would be completely absorbed as tritiated water through the skin and into the blood stream. Using the tritiated-water ICRP 68 dose conversion factor of 1.8E-9 rem/Bq, the technician's dose would be 6.66 mrem/year.

- Nickel-63 Bounding Scenario: The annual intake rates to workers assigned to plating shop operations were 377 Bq, which amounts to a dose of 2.1E-2 mrem/year. The external exposure associated with any operation involving Ni-63 is zero because the range of emitted radiation is less than the depth of sensitive tissues in skin.

Considering the information regarding KCP operations documented here, the contamination conditions, and the potential for exposures discovered thus far, it is concluded that exposures to workers from tritium and Ni-63 can be bounded.

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