

DECONTAMINATION STUDIES OF SIMULATED  
PWR PRIMARY COOLANT SYSTEM COMPONENTS

by  
Ernesto David Cabello

S.B. Nuclear Engineering, Massachusetts Institute of Technology

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Signature of Author \_\_\_\_\_  
Department of Nuclear Engineering  
May 11, 1990

Certified by \_\_\_\_\_  
Michael J. Driscoll Thesis Advisor  
Professor Emeritus, Nuclear Engineering

Certified by \_\_\_\_\_  
Otto K. Harling Thesis Advisor  
Professor, Nuclear Engineering

Certified by \_\_\_\_\_  
Dr. Gordon Kohse Thesis Advisor  
Research Scientist, MIT NRL

Accepted by \_\_\_\_\_  
Allan F. Henry  
Chairman, Department Committee on Graduate Students

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# DECONTAMINATION STUDIES OF SIMULATED PWR PRIMARY COOLANT SYSTEM COMPONENTS

by

Ernesto D. Cabello

Submitted to the Department of Nuclear Engineering on the 11<sup>th</sup> of May 1990, in partial fulfillment of the requirements for the Degree of Master of Science in Nuclear Engineering

## **ABSTRACT**

An in-pile loop has been constructed at MIT for PWR coolant chemistry studies (PCCL). As a result of this work an inventory of simulated components (Inconel steam generator tubes, Zircaloy fuel surfaces, stainless steel plena) with radionuclide deposits laid down under carefully controlled chemistries, pH in particular, have been generated. The purpose of the present work was to develop decontamination techniques for chemical and radiochemical analysis of the surface oxide deposits, and to advance the state of the art in PWR decontamination methods.

A variety of decontamination and de-scaling tests were performed on more than 120 Inconel samples and 32 highly-activated Zircaloy samples. The PWR Oxidative Decontamination (POD) chemical process has been qualified for use on PCCL samples, and appropriate electropolishing and ultrasonic decontamination procedures have been established for the tubing sample geometry used. In the de-scaling of the Zircaloy tubing section using aqua regia, bulk metal dissolution occurred, which made radionuclide assay difficult, and chemical separation of zirconium necessary. A separation method for zirconium removal from solutions containing transition metal ions was qualified. Corrections for bulk metal dissolution of both Inconel and Zircaloy were developed.

The optimized ultrasonic de-scaling method for the Inconel was shown to virtually totally de-scale all samples except those created under low pH conditions ( $\text{pH}_{300^\circ\text{C}} = 6.5$ ). Aqua regia de-scaling of Zircaloy gave decontamination factors of 100, and the chemical separation method using sodium arsenate precipitation was successful: Zr-95 content was decreased by a factor of ~200, while over 90% of Fe, Ni, Co remained in solution.

Electrolytic separation of zirconium from transition metal was unsuccessfully attempted, as were bench test simulations of the effect of boric acid and hydrogen peroxide additions during plant cooldown.

Thesis Supervisor: Dr. Otto K. Harling  
Title: Professor of Nuclear Engineering

Thesis Supervisor: Dr. Michael J. Driscoll  
Title: Professor Emeritus of Nuclear Engineering

Thesis Supervisor: Dr. Gordon Kohse  
Title: Research Scientist

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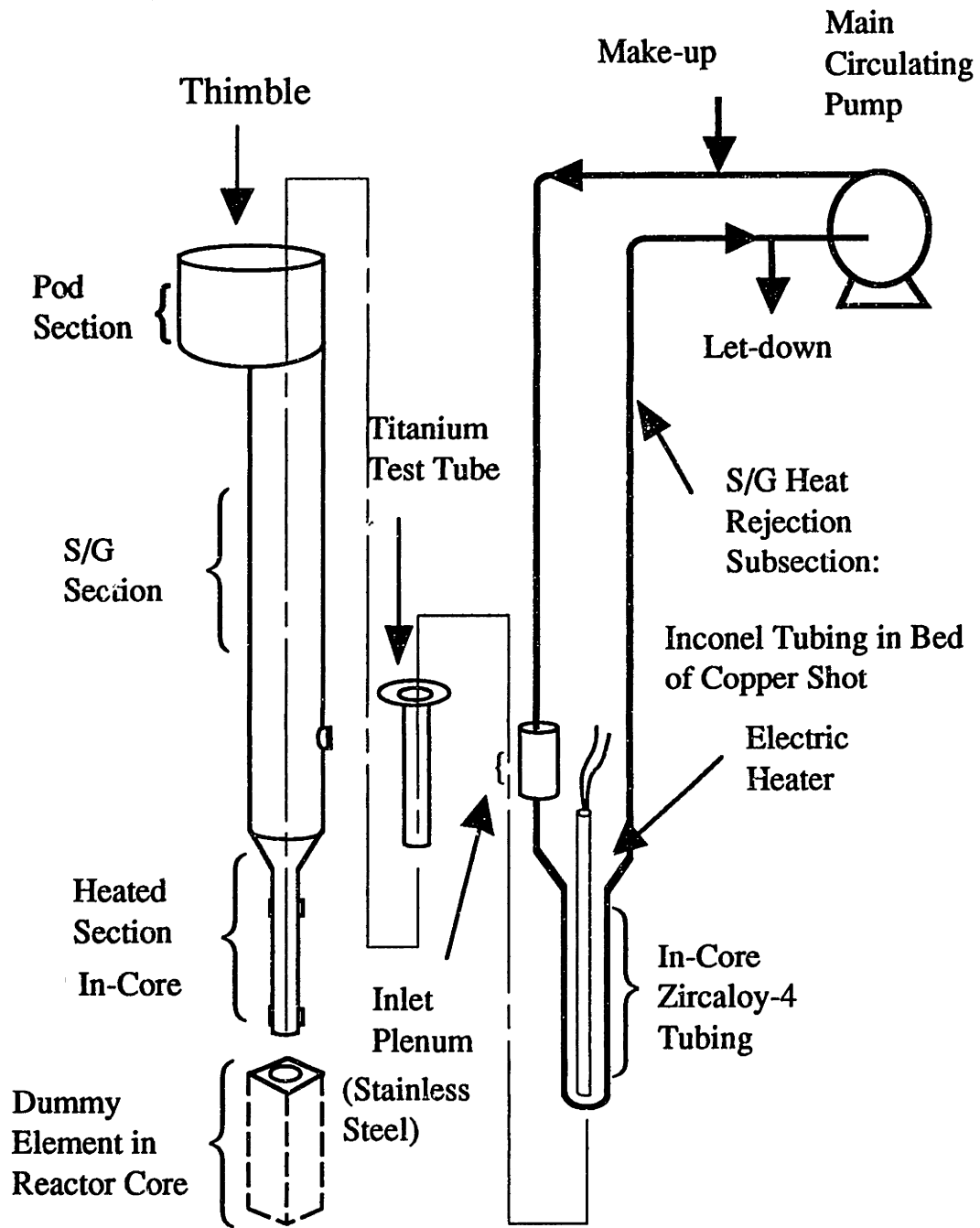
## 1. INTRODUCTION

### 1.1 Foreword

The primary long-term source of radiation fields in LWR nuclear power plants is cobalt-60. Cobalt-58 can also be a significant source, especially early in life, i.e. during the first few years in early plant designs, and may even dominate in new plants where extensive cobalt replacement has been achieved. Fission products from failed fuel contribute only rarely to radiation field buildup. Cobalt-60 is formed as a result of slow neutron absorption by cobalt-59, which is the only cobalt isotope present in naturally occurring cobalt. Cobalt-58 is formed from fast neutron bombardment of nickel-58, which is the isotope present as 68% of naturally occurring nickel by an (n,p) reaction, (threshold 1 MeV). Nickel is a primary alloying constituent in most reactor coolant primary pressure boundary materials, whereas cobalt is found as an impurity in these materials, present at about a few tenths of a percent by weight. However, cobalt is the major constituent in hardfacing materials, such as the Stellites, used in valve seats, pump journals, and other components that require outstanding wear resistance. A review of the chemistry of corrosion product transport in water reactor coolant circuits has been presented in reference [L-1], and here only a summary of the key processes will be outlined.

An in-pile loop facility to simulate PWR primary coolant system behavior has been constructed at the MIT Nuclear Reactor Laboratory (Figure 1.1 taken from Fig. 2.1 in reference [S-1]) under

Electric Power Research Institute (EPRI) and Empire State Electric Energy Research Corporation (ESEERCO) sponsorship. The purpose of research using the loop, now completing its first campaign and beginning the second, has as its initial objective the optimization of coordinated  $\text{LiOH}/\text{H}_3\text{BO}_3$  pH control to minimize radionuclide deposition on plant surfaces. As a result of this work an inventory of simulated components (Inconel steam generator tubes, Zircaloy fuel surfaces, stainless steel plena) with radionuclide deposits laid down under carefully controlled and prototypic chemistries are being generated. One principal objective of the EPRI/ESEERCO project is to analyze these components for their radionuclide inventories, which is also a principal goal of this thesis. Also, segments of these loop components are made available for complementary research including post shutdown decontamination experiments, which constitutes the second major focus of the present work: a task undertaken under MIT Electric Utility Program sponsorship.



\* To hold molten lead bath which thermally couples heater and Zircaloy tubing

Figure 1.1 Diagram of Major PCCL Components

As noted above, there are two primary objectives of the current research, the first is to determine and qualify a method of decontamination for the MIT PWR coolant chemistry loop (PCCL) project [S-1] to obtain deposition data on activated portions of the loop. The in core Zircaloy section of the loop, the stainless steel plenum, and portions of the lower Inconel steam generator tubing are activated by the ambient neutron flux in the MITR core tank, and direct measurements of the deposition on the tubes are not easily obtained due to the induced bulk activity. The second objective is to evaluate potential alternative procedures for component decontamination. Numerous recipes and procedures exist in the literature which exhibit a wide range of decontamination factors. Comparative evaluations are often difficult because of the differences in the manner of application and the lack of a complete pedigree for the specimens.

## 1.2 Background

After the irradiation period the MIT loops are disassembled and unactivated regions (out-of-flux parts) are then directly measured for crud deposition using a high purity Ge gamma detection system [S-2]. However, there are segments of the loops in which bulk metal is activated and where the degree of activation is not quantified. The problem then of measuring the crud activity by subtracting out the contribution due to bulk metal activation. One might at first assume that direct measurement on Zircaloy tubing segments would not be a problem, since activation of cobalt and

nickel would be minimal compared to that of the corrosion products, but this is not the case for reasons that will be discussed in subsequent sections. In the lower zone of the Inconel (SG) section, where there is considerable chromium, nickel, and some cobalt impurity there is a significant contribution of bulk metal activation which effectively prohibits direct measurements. Here, the only way to properly measure the crud activity (or radionuclide composition) without having the activated bulk metal skew the results is to chemically or mechanically decontaminate the pipe surfaces and then measure the specific activity of the removed corrosion products. Two new problems arise in this approach. First, there is the problem of finding a suitable decontamination procedure that will effectively remove all of the crud from the surface of interest while minimizing the amount of base metal removed. Secondly, one must devise a method of subtracting the contribution due to dissolved base metal in the solution after decontaminating the test piece.

As mentioned earlier, the primary long-term source of radiation fields in nuclear power plants is cobalt-60, with cobalt-58 also being a significant contributor to radiation exposure for workers in PWR plants. Radiation fields on primary system surfaces outside the reactor shield are responsible for most of the radiation exposure of nuclear plant maintenance personnel. Removal of the radioactive corrosion products that cause these fields is one of the most effective ways of controlling radiation doses, and chemical decontamination is the most widely applied means of doing so. This technology has be-



come widely used for BWR recirculation system piping repair and PWR steam generator maintenance.

The primary goal of decontamination procedures is to remove radioisotopes, produced from corrosion products, from pipe surfaces and other components in order to reduce the radiation fields in areas of the plant where maintenance, inspection, and repair tasks have to be performed. Non-chemical techniques are used mainly on specific components or easy to reach components but are not viable options for full system decontaminations or steam generator piping decontaminations. Therefore, at present only chemical decontamination can be used in full system or part system pipe decontamination. There are two major concerns that must be addressed before attempting any sort of full system, or even part system, decontaminations in plants. The first concern is to use a chemical agent which will minimize the amount of corrosion to the existing system. The second concern is to be sure that this solution will lend itself to inexpensive waste disposal. There is a fine line to be drawn in selection of such a chemical agent. The basic idea is to use the weakest dilute chemical agent that will provide an adequate decontamination factor (DF). The DF is defined as the ratio of radiation field before the decontamination to the field after decontamination.

Developments in this technology over recent years have been directed primarily at the use of dilute chemicals, with the goal of increasing decontamination effectiveness. Several dilute chemical systems, providing good decontamination factors, are now available.

It is quite likely that most future decontamination at operating power plants will use dilute chemical processes.

Much of the work described in this thesis is intended to develop methods for quantitative measurement of deposited activities in the presence of activities generated by in-situ activation of the base metal. The measurements are generally performed at the conclusion of PCCL runs and degradation of the structural properties of the materials is therefore unimportant. In contrast, most decontamination procedures developed by the nuclear industry must be proven to be benign with respect to degradation of material performance and, with the exception of the specialized case of crud/oxide sampling, are not concerned with activated substrates. The discussion in sections 2.4 to 2.8 is largely concerned with issues arising from the special nature of PCCL decontamination, which is intended to generate activity deposition data.

The de-scaling process of interest is for three sections of the MIT PCCL; the bottom (activated) section of the Inconel, the stainless steel plenum, both of which are activated due to leakage of neutrons from the core of the MITR-II reactor, and the Zircaloy section, of which 70% is directly in core.

### 1.3 Organization of Present Work

This report is divided into five chapters. The present (first) chapter presents the introduction to the subsequent work.

Chapter 2 discusses the general considerations related to the experiments conducted as part of the present work and provides the basic background underlying the current work on methods for decontamination and deposition determination. The subsections of this chapter review the characteristics of radioactive corrosion films, decontamination solutions and processes, and base metal composition studies, including assay by neutron activation analysis, and base metal dissolution corrections. Electropolishing as a decontamination method is discussed, as is chemical separation of zirconium from the transition metals of interest. The chapter concludes with an introduction to considerations involving post-shutdown peroxide/boric acid addition.

Chapter 3 describes the procedures used in the current work. The experimental facilities used for decontamination are described. Test tube pre-screening procedures, which give a potential indication of crud removal effectiveness, are described, as is a crud "toughness" comparison based on Inconel tube chemical decontaminations. The Zircaloy tube decontamination procedures are described, as are the zirconium separation procedures which accompany the Zircaloy tube decontaminations. The electropolishing decontamination procedures used for crud deposition descaling are discussed in this chapter. The chapter concludes with the description of the test matrix carried out for the post-shutdown pre-screening experiments involving boric acid addition and peroxide injection.

Chapter 4 describes the results for all the component decontaminations methods conducted, including a qualitative analysis of the findings as they relate to the MIT PCCL and to decontamination studies in general.

Chapter 5 provides a summary of the present work, and conclusions which follow from it. Some recommendations for future work are also presented in this chapter.

## 2. GENERAL CONSIDERATIONS

### 2.1 Introduction

This chapter provides the basic background underlying the current work on decontamination and deposition determination methods. Theoretical considerations directly related to the experiments conducted for the present work are discussed.

Before one can consider developing a decontamination method for corrosion product films, one must first consider the origin of the radioactive films in question and the method of their production. In this chapter, a description of radioactive corrosion films is presented as an overview. Section 2.2 in this chapter addresses this issue by discussing typical chemical compositions of PWR crud films. Section 2.3 of the chapter gives an empirical description of how chemical solvents react with corrosion films and which types of chemical steps are believed to be necessary.

Another issue that is of importance in characterizing crud layers and decontamination methods is that of base metal impurities. Base metal composition, including impurities, and the elemental solubilities are important in determining corrosion film composition. Knowing the extent to which impurities are present is therefore important in determining what contribution their activation makes to crud and base metal activities. Sections 2.4 and 2.5 address these issues, especially as they pertain to MIT PCCL materials.

Electropolishing is a technique whereby metals are electrolytically etched under conditions which produce smooth surfaces. The technique has been shown to reduce subsequent corrosion and/or activity deposition in some cases. Electrolytic etching can also be used to decontaminate small system components. There are several methods in the literature which will be investigated for comparison using MIT PCCL specimens. This technique is described in section 2.6.

As described in section 1.2, the primary focus of this work is to obtain PCCL deposition data, including the in-core Zircaloy section. The decontamination of Zircaloy will include base metal removal which results in high zirconium radionuclide activity in the subsequent decontamination solution. Section 2.7 gives a description of zirconium separation by precipitation methods, which are of interest for the present work because of the necessity to reduce zirconium activity in the Zircaloy segment decontamination solutions.

The evaluation of decontamination methods becomes complicated when one decontaminates regions which are activated due to exposure to neutron flux. Most decontamination methods can not perfectly discriminate corrosion film from base metal, and therefore some base metal material is also removed. This base metal activity appears in the subsequent decontamination solution, and skews the results by making it difficult to distinguish between removed crud and neutron activated base metal dissolution. Section 2.8 describes

possible corrections for this effect. In this section, the impurity levels determined from section 2.5 are used in the corrections.

Finally, section 2.9 gives an overview of post shutdown decontamination considerations. Conventional wisdom as well as new theories are discussed here.

## 2.2 Radioactive Corrosion Films

Radioactive films in PWR plants are considerably more difficult to dissolve than those in BWR plants. In both cases spinel structures composed of chrome-iron-nickel oxides are predominant, but between the plant types there exists a significant difference in the chromium content. PWR primary circuit chemistry is reducing, as a result of the presence of dissolved hydrogen concentrations which are high enough to consume radiolytically generated oxygen. Steam generator corrosion films are primarily iron-nickel chromites with up to 30% chromium. PWR fuel crud is mainly nickel ferrite. BWR chemistry, however, is oxidizing, and films are spinel structures with much less chromium, since the oxidizing coolant conditions cause it to be present as soluble chromate.

The higher chromium content of PWR oxides makes these films more intractable to the dilute organic acid mixtures used in most decontamination processes [L-2]. It is necessary to modify processes which are effective in BWRs for PWR use by adding an oxidizing pretreatment that dissolves the chromium predominant in the corrosion

film. This makes the remaining material, which includes most of the radioactivity, more readily soluble in dilute acid. The chromium content in BWRs is variable, and it has proved necessary on a few occasions to use a chromium removal step along the lines noted above for PWR applications. These oxidizing processes need to be evaluated carefully, as their application has been shown to require as much attention as the subsequent decontamination step.

It is important to note that the recent trend of hydrogen addition to BWR plants, to suppress stress corrosion cracking, means that a more reducing environment is created, which will tend to make BWR corrosion film layers more like those in PWRs, and thus make them equally difficult to remove. Thus one can anticipate convergence of decontamination techniques toward methods more like those currently applied in PWRs: the focus of the present work.

Crud compositions and amounts have been determined for a typical Westinghouse PWR after 1 cycle; Table 2.1 summarizes such data (from [B-10]). Comparable values are to be expected for the MIT PCCL; measurements of activity and crud composition will be made for various sections of the PCCL. Crud build-up in core for the subject PCCL segments is expected to be about  $1 \text{ mg/dm}^2$ , again based upon [L-1] interpolated values for build-up after 30 days.



**Table 2.1      Crud Composition and Weight for a Typical Westinghouse PWR (1 cycle)**

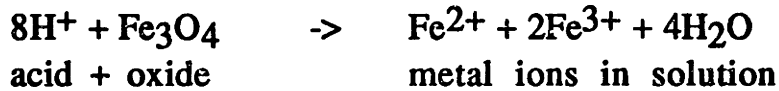
	Composition (%)				Weight (Fe + Ni + Cr)
	Fe	Ni	Cr	Co	
Fuel Crud	68	29	3	0.17	Core Total = 12 kg (20 mg/dm <sup>2</sup> )
Circulating Metals in Coolant	76	19	6	0.2	Conc. = 26 ppb
Make-up Water	86	10	3		Conc. = 100 ppb
Inconel 600					Areal weight = 6.3 (mg/dm <sup>2</sup> )
Base Metal	8	73	19	0.05	
Fixed oxide	27	30	43		
Loose oxide	39	40	21		
Total oxide	27	33	39	0.61	
304 S.S.					Areal weight = 88 (mg/dm <sup>2</sup> )
Base metal	71	10	19	0.07	
Fixed oxide	41	21	38	0.62	
Loose oxide	55	34	11	0.22	
Total oxide	47	23	30	0.54	

Note: 1 dm<sup>2</sup> = 100 cm<sup>2</sup>, the SS values are the average of 4 samples, the Inconel values averaged over 14 samples, and all core values are averaged over 9 different plants and for 11 different cores after 1 cycle [B-10].

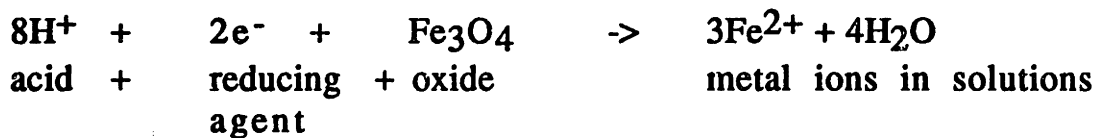
### **2.3 Decontamination Solutions and Processes**

Two types of dilute decontamination systems are common today. One type consists of organic acids (such as the citric acid used in

the Citrox process) and chelating agents (such as EDTA) which are mildly reducing in nature. The reagents dissolve oxides by simple acidic dissolution [A-1], e.g.



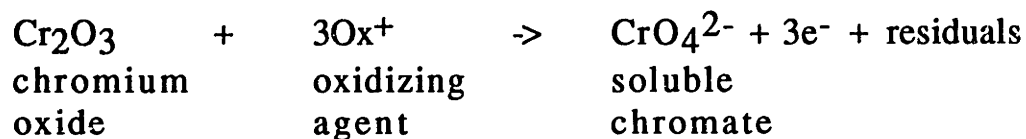
and reductive dissolution [A-1]:



In order to reduce and/or prevent redeposition of the metal ions, a chelating agent (for example, EDTA) is used to increase the solubility of the metal ions in solution by forming a chelating complex. A corrosion inhibitor may be necessary for some applications, depending on the materials in the system, the process temperature, its duration, and reagent strength.

The second category of decontamination reagents is based on low oxidation state metal ions (LOMI), which are more strongly reducing and do not require a corrosion inhibitor. The most widely used LOMI reagent is vanadous picolinate/formate in which vanadous ions ( $\text{V}^{2+}$ ) reduce the oxidation state of the iron in the oxide, enabling it to be rapidly dissolved in picolinic acid, which is also a mild complexing agent. A drawback of the LOMI process is the necessity of anaerobic administration. This can be very difficult to control for component decontamination.

As mentioned above, both types of processes may require an oxidizing pre-treatment for use in PWRs. Potassium permanganate is often used for this purpose, dissolving chromium oxides by oxidizing them to soluble chromate [A-1], e.g.



Potassium permanganate is administered in acidic treatments as NP (nitric acid permanganate) or in alkaline treatments as AP (alkaline permanganate). The form used depends on the materials involved [W-1] and some experiments show that perhaps both should be used [W-1], and [P-1].

The chemical reagents can be added in the solid form (such as Can-Decon) or in solution as liquids (e.g. LOMI). Depending on the type of circuit to be decontaminated, feed and bleed methods or fill and drain methods may be used. In most cases, the radioactive waste is removed on ion-exchange resins. A review of decontamination waste management issues is given in reference [S-3], which describes regulatory requirements and waste processing.

## 2.4 NAA Studies

A neutron activation analysis study of all MIT PCCL materials was performed to determine base metal constituents and to characterize the amount of impurities present. This characterization is nec-

essary to determine possible crud contribution origins and contribution ratios from various sections.

For the MIT Reactor (MITR-II) the fluxes of both thermal and fast neutrons, and neutron cross-sections for each activation reaction of interest in the present work were obtained from measurements made for this reactor in reference [B-9]. Table 2.2 below summarizes these values.

Table 2.2 Average Neutron Fluxes and Cross Sections in MITR-II

Reaction	Core Average Neutron Flux (n/cm <sup>2</sup> sec)	Cross Section (energy spectrum averaged)
Co <sup>59</sup> (n,γ)Co <sup>60</sup>	$\bar{\phi}_{2200} = 2.6 \times 10^{13}$	$\bar{\sigma}_{2200} = 37 \text{ b}$
Ni <sup>58</sup> (n,p)Co <sup>58</sup>	$\bar{\phi}_{E>1 \text{ MeV}} = 5.0 \times 10^{13}$	$\bar{\sigma}_{E>1 \text{ MeV}} = 100 \text{ mb}$
Fe <sup>54</sup> (n,p)Mn <sup>54</sup>	$\bar{\phi}_{E>1.5 \text{ MeV}} = 2.5 \times 10^{13}$	$\bar{\sigma}_{E>1.5 \text{ MeV}} = 134 \text{ mb}$
Fe <sup>58</sup> (n,γ)Fe <sup>59</sup>	$\bar{\phi}_{2200} = 2.6 \times 10^{13}$	$\bar{\sigma}_{2200} = 1.1 \text{ b}$

Cobalt impurity in the Zircaloy is of particular importance. Cobalt 60 is the primary crud activity in mature PWRs and the existence of significant elemental cobalt in the Zircaloy could become a problem due to its high rate of activation (as opposed to cobalt in the coolant which does not have constant flux exposure). This cobalt, which will also exist in the zirconium oxide (ZrO<sub>2</sub>) layer, may participate in corrosion product transport and deposit on ex-core surfaces.

Since the impurities found in various materials are not necessarily uniform throughout the metal, several neutron activation analysis studies were performed on the metals of interest. The results are shown in table 2.3 for the first two sample sets taken.

Table 2.3 Neutron Activation Analysis of PCCL materials

Element	Inconel 600			316 S.S.			Zircaloy 4		
	1989	1988	spec.	1989	1988	spec.	1989	1988	spec.
chromium (%)	12.5	14.1	15.5	12.8	6.4	17	0.09	0.06	0.1
iron (%)	6.3	7.5	8	51	47.9	68	0.3	0.49	0.22
nickel (%)	81.2	78.4	76	-	-	12	-	0.01	<.007
cobalt (ppm)	369	234	-	742	524	-	3.7	4.6	<20
antimony (ppm)	6	-	-	14	10.8	-	8.3	3.3	-
tungsten (ppm)	23	-	-	352	-	-	8	-	-

The PCCL materials shown above were analyzed twice for comparison using two separate batches, one in 1988, and one in 1989. The specification column gives ASTM specifications for the composition.

As shown in Table 2.3, the specification for cobalt content in Zircaloy 4 is given as "less than 20 ppm". If the cobalt concentration in Zircaloy is 10 ppm, for example, there can be a very significant

cobalt contribution from the base metal to the crud (see section 2.5). The initial measurements of cobalt content in the MIT PCCL Zircaloy were relatively high at 3 or 4 ppm as noted in Table 2.3. Hence, additional Zircaloy NAA studies were made to more thoroughly characterize cobalt content.

The expanded NAA study was conducted on Zircaloy samples from the MIT loop tubing and from other Zircaloy sources to see how MIT PCCL Zircaloy compares with standard fuel vendor Zircaloy. Table 2.4 displays the results.

The results clearly show that all samples have a cobalt content on the order of 1 ppm. At this level, Co-60 produced in Zircaloy should not be a problem in either the MIT loops or in full-scale PWRs. The only point worthy of note is that the above values represent bulk metal data; hence surface contamination is not necessarily ruled out.

It is important to point out that Vendor 1, sample c is intentionally suppose to be a low impurity Zircaloy alloy and therefore it is anomolous compared to other Zircaloy except for cobalt content.

Table 2.4 Zircaloy Neutron Activation Analysis

	Sc (ppm)	Cr (ppm)	Fe (ppm)	Co (ppm)	Sb (ppm)	Ni (ppm)	Eu (ppm)	Hf (ppm)	Ta (ppm)
<b>Vendor 1</b>									
Sample a		1010	1915	1.1	2.7			48	
Sample b		1070	2290	1.1	1.1		0.06	45	0.79
Sample c		75	1070	1.0	12.6			70	5.1
Sample d	0.006	1030	1950	1.6	8.9			41	0.31
<b>Vendor 2</b>									
Sample a		1070	2290	0.48	2.1		0.076	40	0.70
Sample b		1045	2180	0.55	2.2			43	0.59
Sample c		1105	2145	0.79	1.4			45	
Sample d		930	1840	0.68	2.1		0.14	43	
Sample e		965	1940	1.1	1.7			43	
<b>Vendor 3</b>									
Sample 1		1110	2230	0.58	1.8			40	0.90
Sample 2		1130	2340	0.9	<1.0			44	0.56
<b>MIT CCL</b>									
ZIR2		984	1450	0.5				48	
ZIR4 #1		1029	2180	0.72				52	
ZIR4 #2		1060	2070	0.67	2.1	<25		54	
ZIR4 #3		1070	2080	0.68	2.2	<25		54	

## 2.5 Impurity Cobalt in Zircaloy

As stated before (section 2.4), the ASTM specification for cobalt content in Zircaloy for nuclear service is 20 ppm or less. Even at 10 ppm, impurity cobalt in Zircaloy fuel cladding can be shown to be a potentially significant source of coolant-born activity..

From reference [M-1], the amount of crud on the core of a representative PWR after one year is about 26 kg. Therefore, the amount of cobalt in the crud in core is about 20 g based on a 0.17% cobalt content in core crud (from table 2.1). Also from [M-1], the core surface area is  $6.1 \times 10^5 \text{ dm}^2 = 6.1 \times 10^7 \text{ cm}^2$ . From [G-1] the loss of Zircaloy metal is about 0.64 times the measured oxide thickness. Since typical oxide thickness (after one cycle) is about 20 microns, the Zircaloy metal equivalence is about 13 microns which, over the total core area, gives 512 kg of Zircaloy oxidized (see Appendix A). For Zircaloy containing 10 ppm of cobalt, the oxide layer would contain 5 g of cobalt, which is approximately 25% of the cobalt in the crud, as cited in [M-1]. Exchange of transition metals between the zirconium oxide and the deposited crud and coolant is expected to be significant. In addition, cobalt in the Zircaloy will have a longer effective in-core residence time than that in transported crud. If one considers the limiting case of rapid homogenization of all primary side crud, then on average a given Co-59 atom will only spend about 1/5 of its time in the core(see Appendix A). This would make 10 ppm cobalt impurity in Zircaloy approximately as important a contributor to transported cobalt-60 as sources in the remainder of the primary circuit.



Since the results for cobalt content in the Zircaloy (section 2.4, table 2.4) show less than 1 ppm for the MIT samples, which is consistent with the samples from industry, cobalt impurity is not deemed to be a problem, as less than 5% of the total cobalt in crud can be attributed to cobalt in the Zircaloy using the above estimate. It is still important, however, to reiterate that a large potential cobalt source in PWR plants could be attributed to the Zircaloy if Zircaloy with close to current specification levels of cobalt were to be used.

## 2.6 **Electropolishing**

Electropolishing is an electrochemical process which is used to produce smooth polished surfaces on metal or alloys. It is the opposite of electroplating, which adds a metal layer as a coating to the surface of interest. Electropolishing removes metal from the surface of interest in order to smooth it out.

The object of interest is generally immersed in an electrolyte and the object serves as the anode in an electrolytic cell. The cathode, which is typically copper or stainless steel is also immersed in the electrolyte a short distance from the object of interest. Figure 2.1 shows a schematic of a typical electropolishing system taken from reference [G-2].

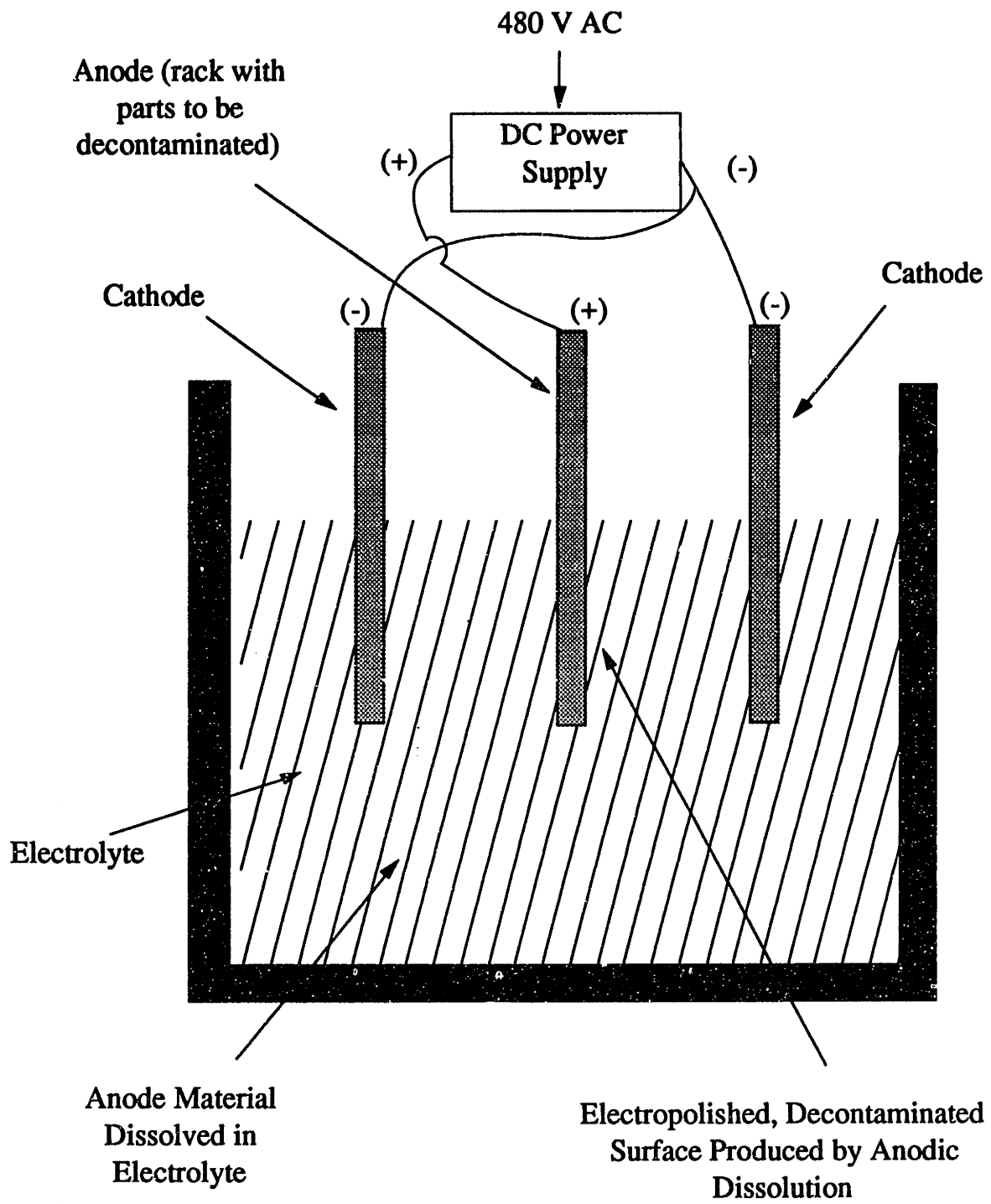


Figure 2.1 Electrochemical Decontamination System

When a voltage is applied to the system, the passage of electric current results in the anodic dissolution of the surface material, and a progressive smoothing occurs under proper conditions. Surface radioactive contamination is removed and released into the electrolyte by this surface dissolution process. Proper control of the polishing parameters produces a uniform surface with no pitting or preferential attack of grain boundaries [G-2]. The material removed in the electropolishing process resides in the electrolyte as metal ions or as a metal phosphate precipitate when using phosphoric acid as the electrolyte, or as a sludge precipitate if sodium sulfate ( $\text{NaSO}_4$ ) is the electrolyte used.

Phosphoric acid is commonly used as an electrolyte for electrochemical decontamination. Important characteristics of phosphoric acid include: stability, safety, and applicability to a number of alloy systems [G-2]. Phosphoric acid also minimizes recontamination from the electrolyte.

Corrosion by the phosphoric acid of the object being electrochemically decontaminated is a concern, with an incomplete answer to date; "Although there is no direct evidence to indicate that electrochemical decontamination with phosphoric acid will cause any adverse effects on stainless steel or carbon steels, it should be recognized that no comprehensive, rigorous study or investigation of this interaction has been made." [G-2].

A critical factor when decontaminating a component of intricate shape is the position of the cathode. Depending on the component, a

number of anode connections should be considered to provide the necessary current distribution characteristics [R-1]. If the cathode(s) are not properly positioned or shaped and if optimum current distribution characteristics are not achieved, an unsuccessful decontamination will result [R-1].

Typical operating conditions for phosphoric acid electropolishing [R-1] are:

Operating temperature of electrolyte: 104° - 176°F

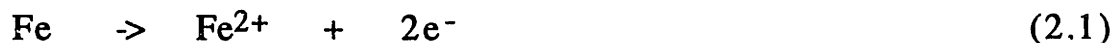
Phosphoric acid (s.g. 1.70) concentration: 40 - 85% by weight

Electrode Potentials: 8 - 12V(DC)

Current Density: 50 - 250 amp/ft<sup>2</sup>

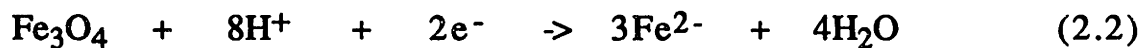
When sodium sulfate (FW 142.04) is used as the electrolyte, typical operating conditions are the same as above with the exception of solution strength, which is given in [G-2] as 200 g/l.

There are three types of processes involved in electropolishing regardless of the of choice electrolyte; anodic electrolysis, cathodic electrolysis, and alternation of the two. In the conventional type of electrolytic decontamination, anodic electrolysis, the surface metal is dissolved and the removed material is proportional to the electrolysis time:



The surface oxidation film cannot be electrochemically dissolved [I-1]. Therefore the removal rate of the metal is reduced because of the restricted diffusion of the electrolyte through the film.

The surface oxidation film is reduced in cathodic electrolysis and the material removal is proportional to the electrolysis time:

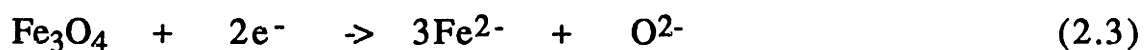


This is an advantageous method because there is no metal dissolution and the contaminated oxide film is removed. The removal rate is extremely slow and application times of up to 10 hours [I-1] are reported.

Alternating electrolysis consists of both anodic and cathodic electrolysis. There is a postulated three step sequence involved in alternating electrolysis [I-1]:

1. the change to an amorphous structure for the oxidation film by cathodic electrolysis.
2. the dissolution of iron or  $\text{Fe}^{2+}$  from the amorphous structure
3. the ionic reaction in the electrolyte.

The (cathodic) reduction process removes oxygen anions from the oxidation film, and ferric ion ( $\text{Fe}^{3+}$ ) is simultaneously reduced to ferrous ion ( $\text{Fe}^{2+}$ ) or iron (Fe):





As a result,  $\text{Fe}_3\text{O}_4$  of a spinel-type structure is reformed into an amorphous structure containing FeO and iron, and the concentrations of  $\text{O}^{2-}$  and  $\text{Fe}^{3+}$  in the oxidation film decrease, while  $\text{Fe}^{2+}$  and iron increase. With the subsequent (anodic) oxidation process,  $\text{Fe}^{2+}$  and iron are dissolved from the reformed oxidate film.  $\text{O}^{2-}$  and  $\text{Fe}^{2+}$ , which are dissolved from the oxidate film form  $\text{H}_2\text{O}$  and  $\text{Fe}(\text{OH})_2$  by reaction with  $\text{H}^+$  and  $\text{OH}^-$ , respectively [I-1].

## 2.7 Zirconium Separation

As mentioned earlier, the Zircaloy sections of the MIT PCCL are highly neutron activated due to in-core exposure. Interference of this in-situ activation with deposited activity measurements is of concern for several PCCL regions. The zirconium activity in solutions resulting from activated Zircaloy decontamination is large compared to crud activities, and creates difficulties in the crud radionuclide assay by gamma spectroscopy. A method of zirconium removal from the decontamination solution is therefore necessary for measurement of radionuclides in the crud layer.

Techniques to separate zirconium from cobalt, iron, and other transition metals are described in the literature, [M-2], and are described as easy to employ with reliable results.

Precipitation is the oldest method of chemical separation. Precipitation conditions can often be chosen so that a considerable amount of the major constituent of a chosen solution can be precipitated with minimal, if any, coprecipitation of the trace constituents to be determined [M-2]. Thus, the trace elements of interest will remain in solution while the 'contaminant' is almost completely precipitated. Precipitation techniques for removing zirconium from cobalt, iron, manganese, and chromium (crud constituents of interest) or vice versa are of particular interest in the present work. Chemical precipitation methods exist for the elements of interest [M-2], which usually involve the addition of a selective complexing agent to prevent precipitation of the elements of interest.

Electroplating may also be used for removal of components from a solution. By the use of electrochemical stripping analysis, traces of the species to be determined or separated are concentrated electrolytically from the solution onto the measuring electrode, then the concentrated traces are stripped back into the solution by the reverse electrolytic process, which is monitored by any suitable electrochemical technique [M-2].

## 2.8 Correction to Activities For Wall Dissolution

It is clear that no matter what type of method is used to decontaminate a material, if a large decontamination factor is desired, there will most surely be some base metal dissolution and removal by the decontamination method used. This is a concern for the pre-

sent work because it is desirable to determine deposition data for the entire MIT PCCL, including regions which are neutron activated. In order to obtain deposition data from the neutron activated regions, the entire crud layer must be removed by some decontamination method, with minimal base metal removal. This is necessary because direct measurements of these regions are not possible due to the large interference by the neutron activated base metal activity.

Assuming that some base metal removal will occur during a decontamination process, there is a way to subtract out this base metal activity contribution based on the differences in concentrations of the corrosion products in the base metal and the crud layer.

One method of correction for the activities from wall dissolution is that of using the ratio differences of two isotopes of interest in the base metal and in the crud layer. If two isotopes have significant differences in their ratio in the base metal compared to that in the crud, their ratio can be used as a tracer for base metal dissolution. Their initial ratio in the decontamination solution should be close to their crud ratio, and as base metal is dissolved, their ratio should start to change towards that of their base metal ratio. The decontamination process can be stopped at that point and the solution can be corrected for the base metal dissolution using the ratio differences of the two isotopes of interest. Below is a derivation for this method using, as an example, Cobalt-58 and Iron-59 as the isotopes of interest and Co-58 as the isotope to be determined.



## Calculated Correction to Cobalt 58 for Wall Dissolution

Let

$A^{59}$  = Measured Fe-59 activity in solution

$A^{58}$  = Measured Co-58 activity in solution

$$A^{59} = A_c^{59} + A_w^{59} \quad A^{58} = A_c^{58} + A_w^{58} \quad (2.5)$$

where:  $A_c$  = activity from crud

$A_w$  = activity from wall

$$R = \frac{A^{58}}{A^{59}} = \frac{A_c^{58} + A_w^{58}}{A_c^{59} + A_w^{59}} = \frac{A_c^{58} + A_w^{58}}{\frac{A_c^{58}}{\alpha} + \frac{A_w^{58}}{\gamma}} = \frac{A^{58}}{\frac{A_c^{58}}{\alpha} + \frac{A_w^{58}}{\gamma}} \quad (2.6)$$

where:

$$\gamma = \frac{A_w^{58}}{A_w^{59}} \quad \text{and} \quad \alpha = \frac{A_c^{58}}{A_c^{59}} \quad (2.7)$$

$$A_c^{58} = A^{58} - A_w^{58} = A^{58} \left[ 1 - \frac{A_w^{58}}{A^{58}} \right] \quad (2.8)$$

so that

$$R = \frac{\alpha A^{58}}{A_c^{58} + \left(\frac{\alpha}{\gamma}\right) A_w^{58}} = \frac{\alpha A^{58}}{A^{58} - A_w^{58} + \left(\frac{\alpha}{\gamma}\right) A_w^{58}} \quad (2.9)$$

$$R = \frac{\alpha}{1 + \left(\frac{\alpha - 1}{\gamma}\right) \frac{A_w^{58}}{A^{58}}} \quad (2.10)$$

$$\frac{A_w^{58}}{A^{59}} = \frac{\left[\frac{\alpha - 1}{R}\right]}{\left[\frac{\alpha - 1}{\gamma}\right]} \quad (2.11)$$

$$A_c^{58} = A^{58} \left[ 1 - \frac{\left(\frac{\alpha - 1}{R}\right)}{\left(\frac{\alpha - 1}{\gamma}\right)} \right] = A^{58} \left[ \frac{\frac{\alpha - \frac{\alpha}{R}}{\gamma}}{\frac{\alpha - 1}{\gamma}} \right] \quad (2.12)$$

Thus,

$$A_c^{58} = A^{58} \left[ \frac{1 - \frac{\gamma}{R}}{1 - \frac{\gamma}{\alpha}} \right] \quad (2.13)$$

Therefore, if for example  $R = 2$  (the observed ratio in the decontamination solution),  $\gamma = 1/8$  (ratio of Co-58 to Fe-59 in the base metal), and  $\alpha = 8$  (ratio of Co-58 to Fe-59 in the crud),  $A_c^{58} = 0.95A^{58}$  which is only a small correction. This crud correction formula can be applied to any element provided its ratio to another element is known in both the crud and the base metal. All one need do is sub-

stitute the appropriate isotopes of interest for the Co-58 and Fe-59 in the above formula.

Both Fe-59 and Mn-54 come from iron activation. Hence the Co-58/Mn-54 ratio can be used in place of and as a check on the Co-58/Fe-59 ratio correction factor for Zircaloy wall effects. The PACTOLE [B-6] code predicts a Fe-59/Mn-54 ratio equal to 2.35 in the Zircaloy base metal compared to 2.29 in the crud. This clearly shows that a 1:1 substitution is acceptable. In some respects Mn-54 can be considered a better correction because it too is a fast neutron reaction, and hence local spectral effects need not be a concern.

An error calculation is necessary for base metal removal with crud. The determination of how much base metal dissolution is significant is a straight-forward calculation involving the ratio of the crud to base metal weight per unit area times the ratio of the activity of the base metal to that of the crud.

Let

R = the measured ratio of tubing activity to crud activity of any particular element per unit length of tubing.

M = mass per unit length of tubing (for PCCL Zircaloy tubing  $M \approx 1$  g/cm)

S = surface area per unit length of tubing (for PCCL Zircaloy tubing  $S \approx 2$  cm<sup>2</sup>/cm)

M/S = mass per unit area (PCCL Zircaloy tubing  $M/S \approx 0.5$  g/cm<sup>2</sup>)

$m$  = mass per unit area of crud (30 day build up  $\approx 1 \text{ mg/dm}^2 = 10^{-5} \text{ g/cm}^2$  in core [L-1])

Therefore, the tube wall mass per unit area is 50000 times the crud mass per unit area. The ratio of the tube specific activity ( $A_t$ ) to crud activity ( $A_c$ ) is:

$$\frac{A_t}{A_c} = \frac{SmR}{M} = (2 \times 10^{-5})R \quad (2.10)$$

This means that if equal masses of crud and base metal are removed, then it would take a ratio,  $R$ , of 20000 to increase the activity of interest in the decontamination solution by 10%. Or, if the crud itself is deposited at the beginning of the run, it will only get 10% of its activity from in-situ activation (provided that  $R = 20000$ ). Either situation would be acceptable.  $R$  is measured by first determining the activity per  $\text{cm}^2$  of the activated Inconel piece and then dividing it by the activity per  $\text{cm}^2$  measured for the Inconel section in the unactivated region. This can be used as a cross check with the electropolishing correction described below.

### 2.8.1 Correction for Electropolishing

The use of electropolishing for Inconel and Stainless Steel as a method for de-scaling will inevitably remove base metal in the process. It is however possible to estimate the amount of subsequent

base metal removal due to electropolishing. This amount can be calculated using Faraday's law.

Faraday's law says that 96500 coulombs will electrolyze 1 formula weight of metal. Therefore 96500 amp seconds are needed for 1 gram mole per valence electron. Since transition metals are di-valent, then assuming an average transition metal molar weight of 58 grams, 96500 amp sec (= 1608 amp minutes) will remove 29 grams, for a removal rate of 18 mg/amp minute.

A 10 minute test was performed for verification under the following conditions:

3 cm Inconel tube with no oxide layer, having a weight of 4.1582 g, measured using a Metler analytical balance.

Electropolished for 10 minutes at 0.7 amps at 70°C using 70% by volume phosphoric acid.

The calculated weight loss is  $(18 \text{ mg/amp min})(10 \text{ min})(0.7 \text{ amps}) = 126 \text{ mg}$ . The measured weight using a Metler analytical balance after the electropolishing was 4.0370 g, a difference of 121 mg, about 3%: in good agreement with the theoretically calculated value. Therefore, Faraday's law will be used for correction of base metal activities when electropolishing is used as a method of decontamination. Note, however, that this should be an upper limit, since a specimen coated with an oxide film will probably not exhibit 100% effective base metal removal. It is also important to note that in practice, the correction is only on the order of 10% of the total re-

moved oxide activity and small correction errors are therefore deemed unimportant.

### 2.8.2 Correction for Zircaloy De-scaling

For the case of activated Zircaloy decontamination a correction can be made for base metal contribution to measured activities based on the activity of Zr-95 measured in the decontamination solution, the flux in the reactor, and the transition metal impurity levels in the Zircaloy. The NAA studies (section 2.4) of Zircaloy composition provide impurity levels that are accurate to within 20%. The flux has been measured experimentally in the past [B-9], and is currently being measured and calculated using a flux wire and the Zircaloy itself [M-3]. Using activation rates from reference [B-9] and assuming that transition metal activities in the decontamination solution are proportional to those in the base metal, corrections were calculated on a base of  $10\mu\text{Ci}$  of Zr-95 activity. This data is summarized in Table 2.5 and was used to adjust the data for in-core activities as reported in Chapter 4.

Table 2.5 PCCL Relative Elemental Activation in Zircaloy

Element	Activation	Reaction	Conc.	relative activities
Zr-95	0.01 Ci/g	$Zr^{94}(n,\gamma)Zr^{95}$	100%	10 $\mu$ Ci
Fe-59	0.0066 Ci/g	$Fe^{58}(n,\gamma)Fe^{59}$	2000 ppm	13 nCi
Mn-54	0.0029 Ci/g	$Fe^{54}(n,p)Mn^{54}$	2000 ppm	5.8 nCi
Co-58	0.286 Ci/g	$Ni^{58}(n,p)Co^{58}$	25 ppm	7.2 nCi
Co-60	2.02 Ci/g	$Co^{59}(n,\gamma)Co^{60}$	0.7 ppm	1.4 nCi
Cr-51	1.87 Ci/g	$Cr^{50}(n,\gamma)Cr^{51}$	1000 ppm	1900 nCi

Note: 10  $\mu$ Ci Zr-95 corresponds to 0.001 g Zr

## 2.9 Post Shutdown Peroxide/Boric Acid Additions

One of the major objectives of the overall decontamination effort associated with the present work is the evaluation of the decontamination/recontamination consequences of chemistry changes (such as H<sub>2</sub>O<sub>2</sub> addition) during plant cooldown evolutions.

The recent water chemistry conference at Bournemouth [B-2] has documented considerable information relevant to the subject of addition of H<sub>2</sub>O<sub>2</sub> during cooldown. This new input provides valuable information when considering potential studies.

**Several variables are considered important:**

**temperature**

**concentration of boric acid/lithium hydroxide (hence pH)**

**concentration of dissolved hydrogen**

**presence of dissolved air (hence O<sub>2</sub>)**

**H<sub>2</sub>O<sub>2</sub> addition**

The large increase in transition metal ion solubility as the temperature decreases explains the obvious importance of the first variable, temperature. This solubility can vary by as much as a factor of one thousand between hot and cold. This effect is seldom allowed to occur in isolation: boric acid is added to provide additional reactivity hold-down; the coolant make-up needed to compensate for the hot-to-cold change in water density may be aerated; and some utilities add hydrogen peroxide as a further means to alter the redox potential.

References [B-3] and [B-4] discuss in some detail the strong solubilizing effect of heavy boration in the startup/shutdown regime, especially in the low-temperature (50-100°C) phase. There is evidence that the borate ion has an effect even if the pH is kept constant (e.g. by LiOH addition). UK investigators [B-3] in fact recommend pre-operational boric acid treatment to reduce transportable cobalt inventory. The spring 1990 campaign for the MIT PWR loop



runs includes plans to test for comparable boron effects during normal hot operations.

According to reference [B-2], aeration has an even more profound effect: coolant-borne activity increases by another order of magnitude over its already-enhanced level. The French find that the temperature at which this is done is crucial: if done at temperatures exceeding 50-90°C, there is an observed increase in activity deposition on ex-core surfaces. The French claim that their overall procedure does not reduce plant dose levels. Neither they, nor the Japanese add H<sub>2</sub>O<sub>2</sub> however.

The overall combined effect of residual H<sub>2</sub>, added O<sub>2</sub> and/or H<sub>2</sub>O<sub>2</sub> is a complex issue. It may well be that a single parameter (redox potential) can be used to measure the status of the coolant in this regard, but only Finnish researchers [B-5] appear to have made detailed measurements of this parameter during normal and shutdown operations.

## 2.10 Chapter Summary

This chapter has presented general background information concerning the decontamination and deposition determination methods used for the current work.

The chapter began by describing, in sections 2.2 and 2.3, some typical chemical compositions of PWR crud films and how some chemical agents react with these crud films. These first two sections

give a general chemical background to help explain how one addresses the chemical removal of radioactive corrosion films. PWR films are significantly more difficult to remove than BWR films due to the chromium content in the crud. Crud, being primarily  $\text{Fe}_3\text{O}_4$  (i.e.  $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ ) and or  $\text{NiO}\cdot\text{Fe}_2\text{O}_3$ , is thought to be removable with dilute chemical reagents, such as citric acid, after an oxidation step using potassium permanganate is used to oxidize the chromium to a soluble form, since some  $\text{Cr}_2\text{O}_3$  exists in the oxide layer as insoluble chromium.

The characterization of impurities in PCCL materials is stressed in chapter sections 2.4, and 2.5. Section 2.4 discusses the role of neutron activation analysis (NAA) in the determination of base metal impurities with particular attention to Zircaloy impurities. It is shown that the Zircaloy used at MIT has about 0.7 ppm cobalt, and other Zircaloy samples provided by industrial vendors also show approximately 1 ppm cobalt. Section 2.5 describes the significance of these impurities, placing particular importance on cobalt content in Zircaloy. As much as 25% of crud cobalt could be attributed to Zircaloy if levels are at half of the ASTM specification value of < 20 ppm.

Section 2.6 introduces the basic ideas behind electropolishing as a decontamination method as it pertains to the current work. Electrolytic descaling usually involves phosphoric acid or sodium sulfate as the electrolyte with current densities of about  $0.1 \text{ A/cm}^2$ .

Section 2.7 discusses zirconium separation from transition metals - a step needed to remove zirconium activity from Zircaloy test piece decontamination solutions. The separation techniques reviewed involve chemical precipitation in the presence of a complexing agent to prevent coprecipitation, and electrolytic stripping, which electroplates trace elements of interest out of the zirconium. Finally, section 2.9 introduces post shutdown activity transport considerations that are addressed in the present work. Issues of importance include peroxide addition during shutdown and boration of coolant during shutdown.

Section 2.8 discusses the correction needed to subtract the base metal activity contribution in chemical decontamination solutions. This result underlines the need to set much lower limits for cobalt in the specification for Zircaloy; the author suggests  $< 2$  ppm since it seems readily attainable based on table 2.5. A very small correction is found to be needed (errors on the order of 10%) if anticipated base metal dissolution occurs. The correction for electropolishing is also less than 10%.

### **3. OUTLINE OF EXPERIMENTAL WORK**

#### **3.1 Introduction**

In the following sections in this chapter, the experiments carried out for this thesis are described in detail. The procedures chosen are described along with the reasoning for the particular procedure adopted.

Section 3.2 begins the chapter by describing the laboratory facilities used for the decontamination experiments. Section 3.3 describes a crud "toughness" comparison which uses methods discussed in the chemical and mechanical decontamination procedure sections. The Inconel tube chemical decontamination trials are described in Section 3.4, including comparisons of chemical effectiveness.

Section 3.5 describes the Inconel tube de-scaling procedures used. Preliminary electropolishing procedures are described as are ultrasonic de-scaling for MIT PCCL deposition determination. The final procedures used for de-scaling are outlined.

Sections 3.6 and 3.7 describe the Zircaloy tube section deposition determination procedures. The chemical decontamination method used is described along with the decontamination solution evaluation in section 3.6, and the zirconium separation techniques used to improve gamma counting of the subsequent decontamination solutions are presented in section 3.7.

The chapter concludes with section 3.8, which describes procedures for pre-screening experiments associated with post shutdown

peroxide injection and high boric acid concentration effects on crud release during shutdown.

### **3.2 Experimental Facilities**

This section gives an overview description of the laboratory facilities used for the subject work. There are three facilities of particular importance: first, the gamma spectroscopy facility provides radionuclide counting capability, second, the analytical chemistry lab where solutions for decontamination, separation, and electrochemistry are prepared, and third, the reactor radiochemistry lab where highly radioactive samples are handled and processed.

#### **3.2.1 Gamma Spectroscopy Facility**

To determine the specific activity of decontamination solution samples, and S/G Inconel tubes, the data acquisition system assembled as shown in Fig. 3.1 (taken from [S-1]) for the post irradiation analysis of the MIT PCCL is used. The hardware for this system consists of a high purity Germanium (HpGe) detector, a Series 35 multi-channel analyzer (both from Canberra Industries), a stepping motor controller (MITAS), a stepping motor, an IBM-PC AT computer, and a printer (Epson EX-1000). The arrangement and integration of the components mentioned above is described in detail in reference [S-2]. The stepping motor and controller are used for scanning the full length of the MIT PCCL Inconel tubes, but this feature is not used for

the decontamination studies since the tube samples used are only 3 cm long. The software used is the Spectran-AT software package by Canberra Industries. Software integration is also described in detail in reference [S-2].

There are only two basic counting geometries of interest for the decontamination work. One applies to 110 ml samples in a 4 oz. (standard polypropylene) bottle, and the other to Inconel tubes. The 110 ml bottle geometry was chosen because that is the configuration already calibrated for the MIT PCCL daily water samples [S-1], and it is a convenient quantity. The Inconel tube geometry is a 2 cm collimated window geometry viewing a 5/16" OD, 0.025" wall, tube placed approximately 4.5 inches from the detector face. Most counts are for 2000 seconds, and pre-counted background is automatically subtracted for the appropriate geometry. When activity is low, longer counts are performed to obtain better counting statistics.

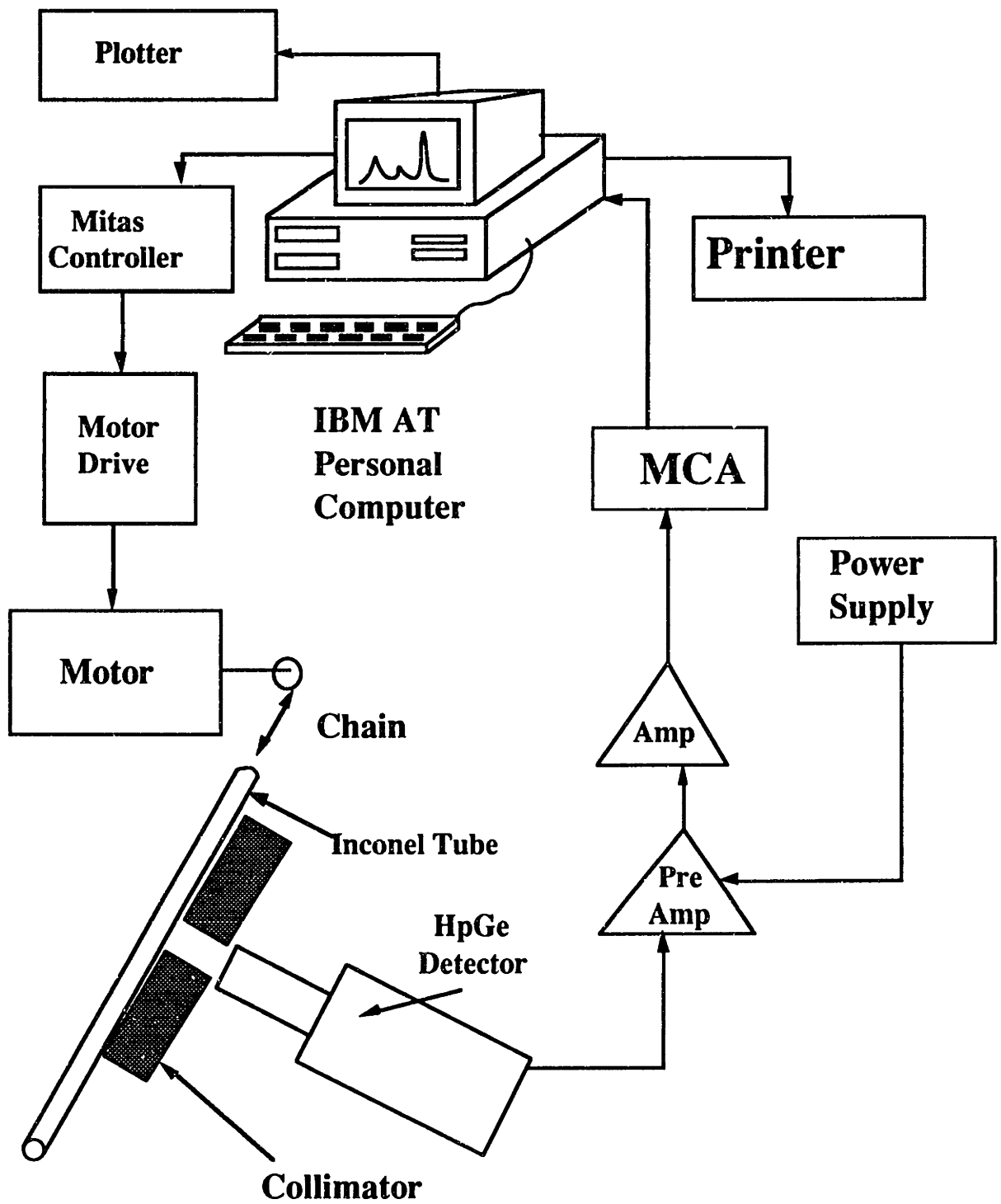


Figure 3.1 Post-Irradiation Data Acquisition System

### **3.2.2 Analytical Chemistry Lab**

The analytical chemistry lab (MIT room NW13-247) is where all chemical reagents and acids are kept. A fume hood is available for those procedures where it is required. All chemical solutions and acids are prepared in this laboratory. The room is also authorized for radioactive material use, and some low level radioactive experiments are conducted in this facility. The test tube pre-screening experiments (section 3.3), Inconel tube decontaminations (section 3.4), electropolishing experiments (section 3.7), and post shutdown experiments (section 3.8) were all performed in this facility. Any resulting radioactive waste was transferred to the reactor radiochemistry lab (section 3.2.3) for waste disposal.

### **3.2.3 Reactor Radiochemistry Lab**

All high level radiation decontamination experiments are conducted in the reactor radiochemistry lab, located within the reactor restricted gate area. This facility contains three chemistry hoods, a ventilated and shielded hot box with manipulators, and a shielded lead "coffin" for waste storage. All Zircaloy tube decontaminations are conducted here in the hot box and all separation experiments with Zircaloy tube decontamination solutions are also conducted in this facility. All decontamination solutions and tube specimens generated during the work are stored in the coffin until proper disposal occurs. Typical radiation levels for the waste range from less than 1 mR/hr to about 8 mR/hr on contact (gamma dose only, with a 110 ml



bottle) for the aqua regia Zircaloy decontamination solutions. The Inconel tube dose rates are about 4 mR/hr on contact. The 3 cm Zircaloy segments, from the in-pile part of the loop, measure approximately 1 R/hour at about 2 cm. All dose rates given are for about 1 month cooling after the 21 full power (4.5 MW) days irradiation of the loop.

### 3.3 Crud Toughness Comparison

One of the secondary purposes of the present work is to investigate the possibility of a difference in decontamination effectiveness as a function of the pH during crud formation. As a result of PCCL runs there exists an inventory of tubing pieces with crud layers created at  $\text{pH}_{300} = 6.5, 7.0$  and  $7.5$  (all at 800 ppm boron). It is entirely possible that crud produced and deposited at one pH may be more or less resistant to a particular decontamination procedure than crud created in a different pH environment.

A chemical method and a mechanical method of crud removal were used to compare Inconel (steam generator) pieces from the different pH runs. The chemical method used was the P.O.D. process, described in the following section. The "mechanical" method used was ultrasound.

### 3.4 Inconel Tube Chemical Decontamination

A quick comparison between established chemical decontamination methods is desired in order to compare the relative effectiveness of such processes when applied under the same conditions. Inconel SG tubes taken from MIT PCCL post mortem examinations were used for this procedure.

It is clear that the crud layers on these specimens are not of the same thickness as those typically obtained in full scale PWR plants after years of exposure, nevertheless they were created under similar coolant chemistry. Because the crud layers on the subject Inconel pieces are much thinner than in plants, the decontamination factors (DFs) achieved are expected to be much lower than those realized using actual PWR specimens.

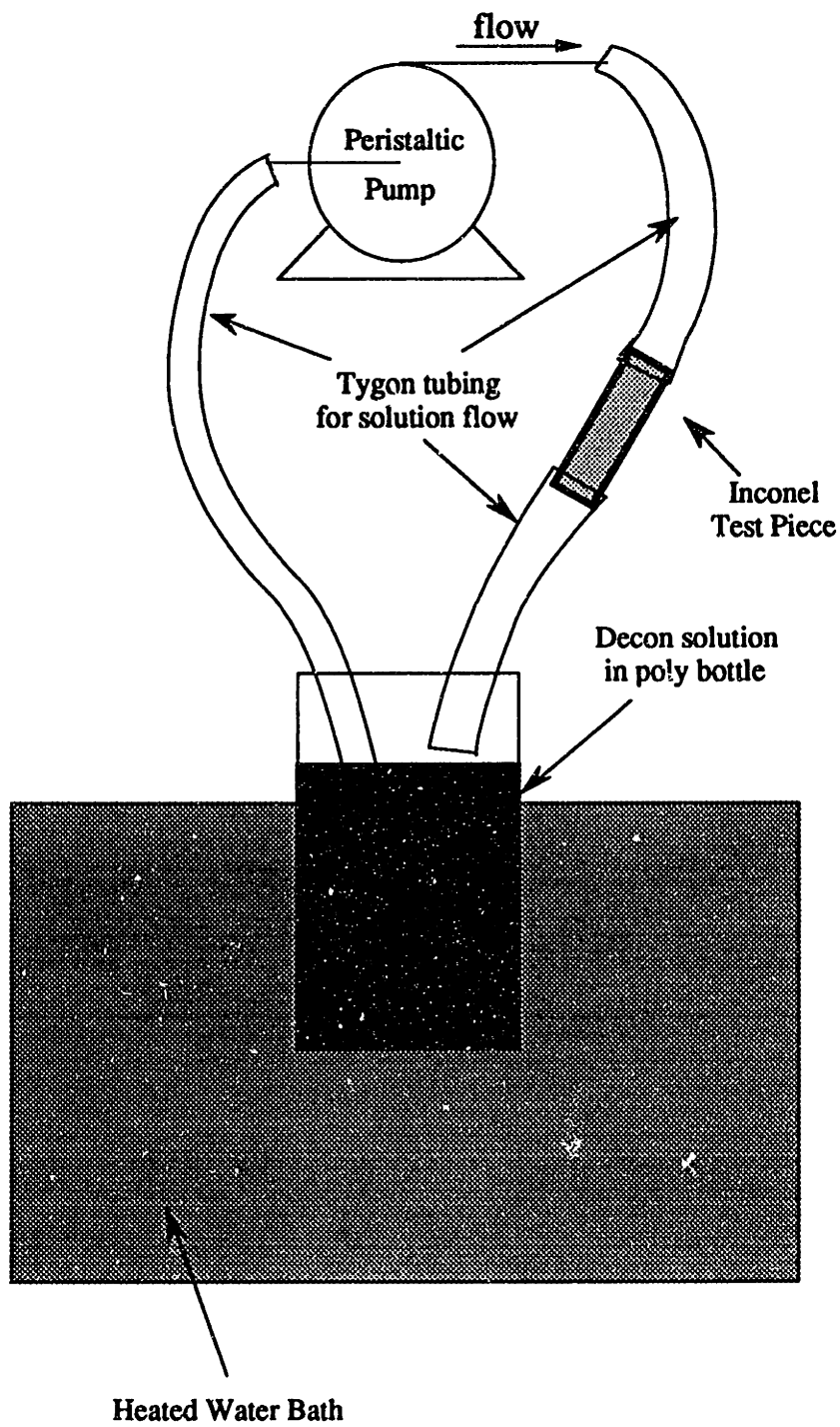
The first runs conducted involved soaking the test pieces in Citranox™, Citric acid, Citric acid + Oxalic acid + EDTA, H<sub>2</sub>O<sub>2</sub> + EDTA, and H<sub>2</sub>O<sub>2</sub> alone. The subject decontamination solution was placed into a standard 4 oz. polyethylene bottle. The bottle was placed into a heated water bath with an approximate temperature of 50°C. The Inconel specimens were counted at the gamma spectroscopy lab (section 3.2.1) and then placed into the bottles. The soaks were conducted for about 4 hours at temperature. The sample Inconel tubes were then recounted to determine DFs.

The next runs involved flowing acids through the test pieces using a tubing pump. For these runs, concentrated HNO<sub>3</sub>, HNO<sub>3</sub> followed by hydroxylamine, and aqua regia were tried. The strong

acids were chosen as an extreme to determine what sort of maximum chemical decon should be attainable. The acids are believed to give a maximum DF under given conditions since all commercial decontamination solutions are of dilute chemical form to preserve bulk metal integrity and acids are only used in decommissioning or de-scaling of samples. Inconel test pieces are counted before and after the decontamination procedure to determine DFs.

### Chemical Flow Through Tests

A peristaltic pump is used with tygon tubing as shown in figure 3.2. The sample bottle is filled with approximately 90 ml of the desired chemical agent and then placed in the heated water bath where it is heated to approximately 50°C. The tygon tubing is attached to the Inconel tube by sliding the ends of the tygon tubing over the ends of the Inconel tube. The pump is used to flow the chemical through the Inconel tube for the desired time.



**Figure 3.2 Inconel Tube Decontamination Setup**

The second generation trials of Inconel tube decontaminations involved the use of a modified POD (PWR Qxidative Decontamination) process, as used by reference [L-3] for their deposition studies. The process, as used in the present work, is as follows:

NP step: Soak tubes in 90°C NP solution for 5 hours.

NP: 1 ml/l nitric acid (s.g. 1.42),

2 g/l potassium permanganate (KMnO<sub>4</sub> FW 158.03)

Rinse: Thoroughly rinse tubes in wash solution

wash: 10 ml/l 35% H<sub>2</sub>O<sub>2</sub>, 6 ml/l nitric acid

Soak: Soak at 80°C for 30 minutes in acid solution

acid: 1.4 g/l oxalic acid (FW 126.07), 1.15 ml/l nitric acid

Citrox: Soak at 95°C for 2 hours in Citrox

Citrox: 0.45 g/l oxalic acid,

0.95 g/l citric acid (FW 210.14)

For the POD process assessment, three Inconel tubes were used. One piece was cut from each of the three different pH MIT PCCL runs. The activities per cm<sup>2</sup> of the tubes were determined by counting them in the counting facility (section 3.2.1). After the subsequent POD process, the tubes were recounted and decontamination factors determined. Also compared was DF as a function of the pH under

which the crud layer was created. The results are discussed in section 4.2.

A second test was performed to repeat the above experiment with a further modified POD process. Six tubes were cut for this run. Three were cut adjacent to the original three, all having different crud activities per  $\text{cm}^2$  of tube, and three purposely cut in a region where all three have approximately the same activity per unit area. The three pieces cut with the same inferred crud specific activity will provide the test for crud toughness (section 3.3) by comparing DFs on the three after decontamination. The three tubes having different crud activities per unit area, a repeat of the first trial, will provide an indication of decontamination factor difference between the use of both an AP and NP step or just the NP step alone.

The modification to the original POD process referred to above is the addition of an alkaline permanganate (AP) step to the process. The NP step is retained, but for a soak of only three hours following the AP step (also a three hour soak), rinsing in between with the wash solution. The new POD process is:

**AP: Soak in AP solution for 3 hours**

**1 g/l sodium hydroxide (NaOH FW 40.0)**

**1 g/l potassium permanganate (KMnO<sub>4</sub> FW 158.03)**

**rinse with wash solution (as before)**

**Acid soak (as before)**

**NP (as before but for only 3 hours)**

**rinse with wash solution (as before)**

**Citrox (as before)**

The motivation for the additional AP step comes from references [W-1], and [P-1] where it is stated that while an NP step is a superior step for stainless steel surfaces, and the AP step is superior for Inconel surfaces, the combination of the two yields better DFs than either applied separately under all tested conditions. The results of the second POD procedure are discussed in section 4.2.

Table 3.1 is a summary list of all the chemical decontamination methods tested on PCCL Inconel tube sections.

**Table 3.1 Chemical Decontaminations of Inconel Tubes**

Solutions tested on PCCL Inconel tubes
P.O.D. [L-3]
Modified P.O.D.
Citranox™
Citric acid
Citric acid + Oxalic acid + EDTA
H <sub>2</sub> O <sub>2</sub> + EDTA
H <sub>2</sub> O <sub>2</sub>
HNO <sub>3</sub> (20%)
HNO <sub>3</sub> followed by hydroxylamine
HNO <sub>3</sub> (40%)
aqua regia

### 3.5 Inconel De-scaling

In the following two subsections, the procedures for the two mechanical descaling methods are described. They are of interest because of the need to completely remove all the crud from the activated sections of the PCCL Inconel (steam generator section) and to characterize the crud layer specific areal (nCi/cm<sup>2</sup>) activity, while also avoiding base metal removal.



The two regions of interest for de-scaling have extrapolated lines drawn at positions 0-40 and 320-360 in Figure 3.3. These are the regions from which 4 samples were taken, at 10 cm intervals, to de-scale and therefore properly plot the complete graph. The following positions were taken from each of the four runs:

Table 3.2 Steam Generator De-scaling Positions

Inlet Position (cm)	Outlet Position (cm)
0-3	357-360
12-15	345-348
24-27	333-336
36-39	321-324

### Cobalt 58 Activity Profile

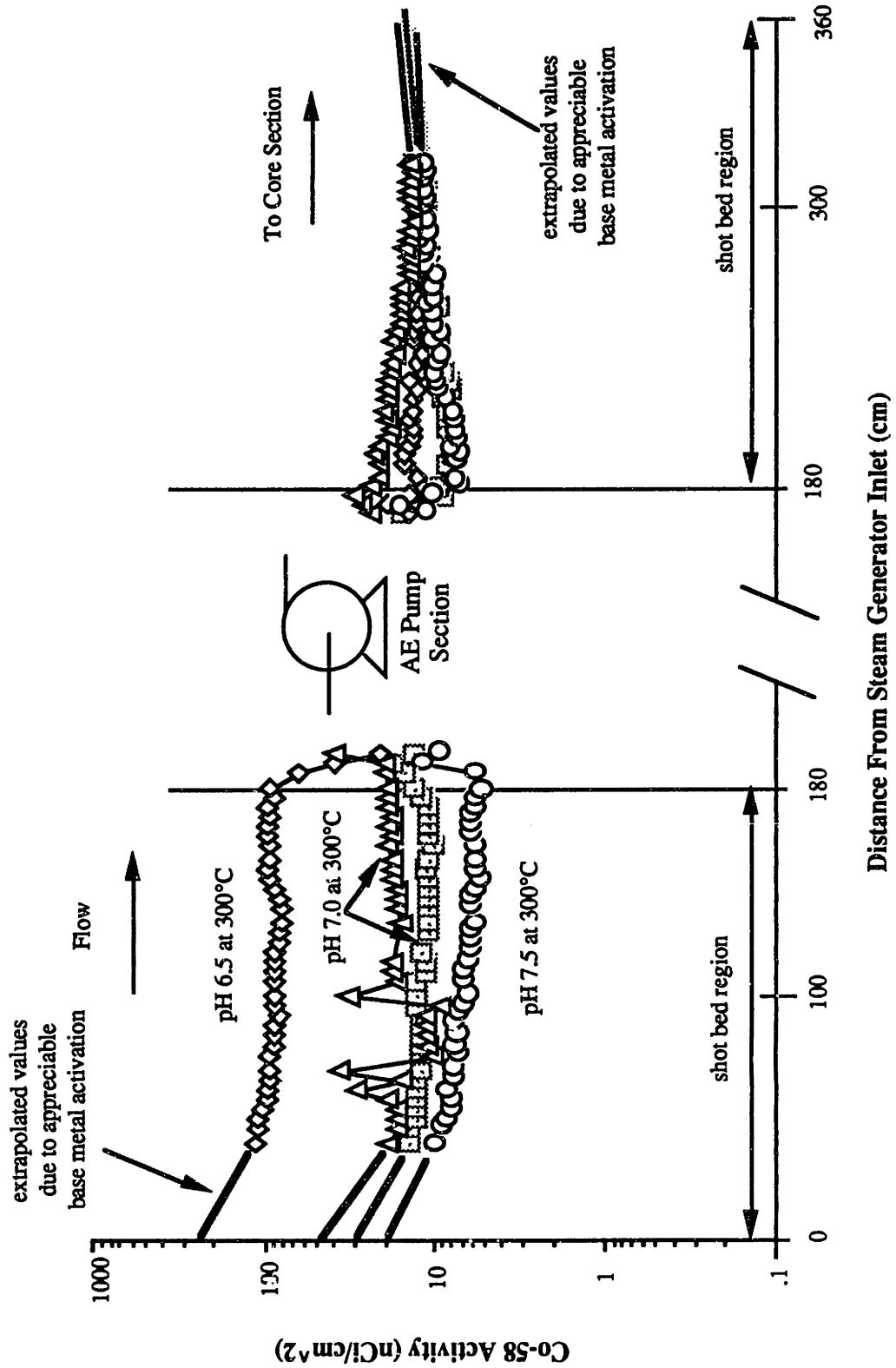


Figure 3.3 Inconel Cobalt 58 Linear Activity Distribution

### **3.5.1 Ultrasonic De-scaling**

Ultrasound is a very common method of component decontamination, but is not necessarily consistent in outcome. It is desirable to develop an effective ultrasonic de-scaling procedure which removes no significant base metal, since one cannot accurately characterize base metal removal using ultrasound, although corrections such as those discussed for chemical methods can be applied.

The ultrasound device employed in the present work is a Cole Palmer (model number 8560) unit which operates at 55 kHz. The sample piece is placed in a beaker filled with the desired enhancing fluid and the beaker in turn placed in the center of the ultrasound bath. The bath has a maximum temperature of 60°C when used in conjunction with the ultrasound.

After some preliminary tests where unactivated Inconel pieces were used to compare subsequent decontamination solutions with measured tube removal using the Inconel piece itself, a general procedure was adopted for all ultrasonically de-scaled activated Inconel samples:

#### **Ultrasonic Descaling of Activated Inconel Section**

Prepare 5% by volume HNO<sub>3</sub> by diluting with deionized water.

Heat up ultrasonic bath to 60°C along with beaker containing 70 ml of HNO<sub>3</sub> solution.

Place Inconel tube sample in beaker, inside ultrasonic bath and turn power on for 5 minutes rotating tube sample occasionally.

Visually inspect tube to be sure oxide is removed, otherwise place in solution and ultrasonically clean for another 2 minutes.

Dilute solution with 50% HNO<sub>3</sub> solution to 110 ml and evaluate for radionuclide content.

### 3.5.2 Electropolishing

There are several processes in the literature that show potential promise and merit investigation. There are three methods that will be investigated as potential activated Inconel de-scaling procedures, anodic electrodecontamination, alternating anodic/cathodic electropolishing with a basic electrolyte, and alternating anodic/cathodic electropolishing with electrolytes recommended by Mitsubishi.

Conventional electrodecontamination, as described in section 2.6 and in references [R-1] and [G-2], shows decontamination factors as high as 500. For conventional anodic electropolishing, a phosphoric acid (s.g. 1.70) electrolyte was used at a concentration of 70% by volume. The current density utilized was 100 A/ft<sup>2</sup> (0.1 A/cm<sup>2</sup>) with an application time of 2 minutes at 70°C.

The alternating cathodic/anodic step electropolishing technique is described in two references: [B-1] describes ELDECON, as presented

by the Swedish delegation from ABB Atom at the Fall 1989 Bournemouth Conference with claimed DFs of 1000, and [I-1], which gives a detailed procedure for the same process. The electrolyte used for this procedure was  $\text{Na}_2\text{SO}_4$  ( $1.7 \text{ mol/dm}^3$ ) with a current density of  $0.3 \text{ A/cm}^2$  at room temperature.

The final procedure investigated was that given by Mitsubishi as their electrodescaling procedure. It involves a 0.15 N sulfuric acid (s.g.1.84) electrolyte cathodic step followed by a 0.1 N nitric acid (s.g. 1.42) electrolyte anodic dissolution step. The current densities required are  $0.1 \text{ A/cm}^2$  and  $0.015 \text{ A/cm}^2$  respectively.

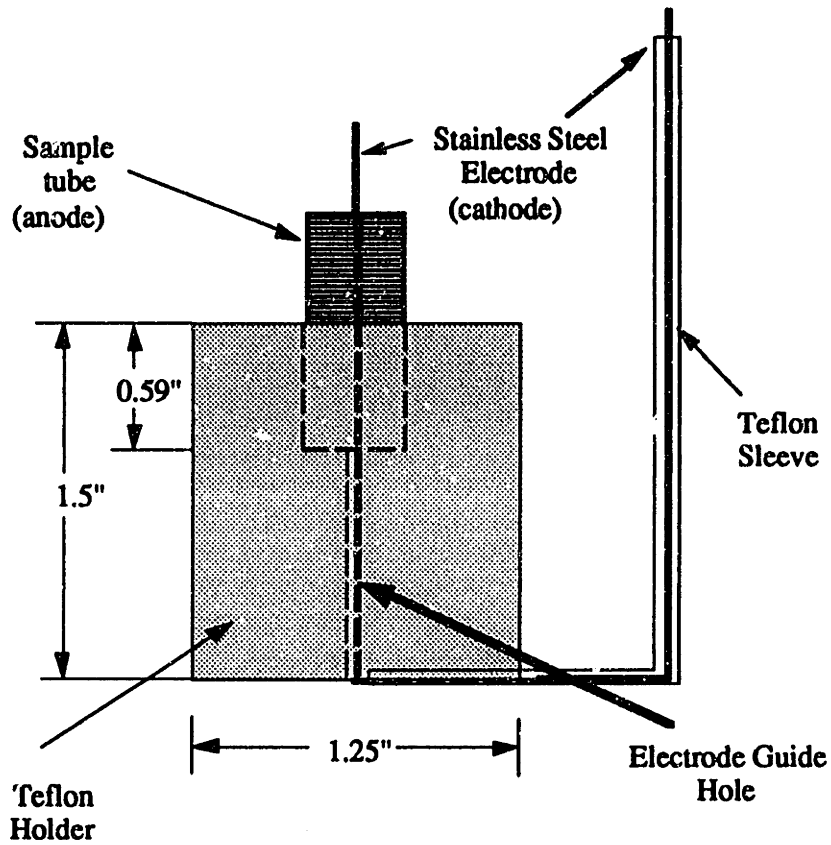
Based on the techniques recommended in the above mentioned literature, several experiments were performed to attempt qualification of the method for future testing.

A device was designed and constructed to hold the subject Inconel piece with a stainless steel cathode passing through the middle of a teflon holder. Figure 3.4 shows a schematic of the electropolishing tube/cathode holder.

A spring clip connects the positive lead from the power supply to the tube. The stainless steel shaft located on the tube holder is the negative connection, making it the cathode in the electrolytic cell. The cathode lead is shielded with teflon tubing outside the teflon tube holder, as shown in Fig. 3.4, to prevent unnecessary reaction with the anode clip. The tube to be decontaminated is placed in the holder and the holder is placed in a small beaker containing about 70 ml of the desired electrolyte. An ammeter and voltmeter are used to

characterize the operating conditions, along with a thermometer located inside the controlled temperature heated water bath. The entire electropolishing setup is shown in Figure 3.5.

Electropolishing, even though virtually always successful, is a method that will always cause some base metal removal. The base metal removal may be satisfactorily characterizable using Faraday's Law (see section 2.8.1), but it is desirable to use this method only as a last resort.



Cross sectional Views: Vertical (Above) and Horizontal (Below)

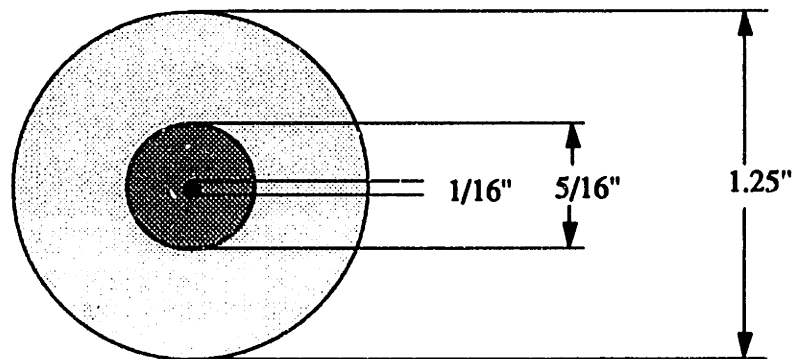


Figure 3.4 Electropolishing Tube Holder

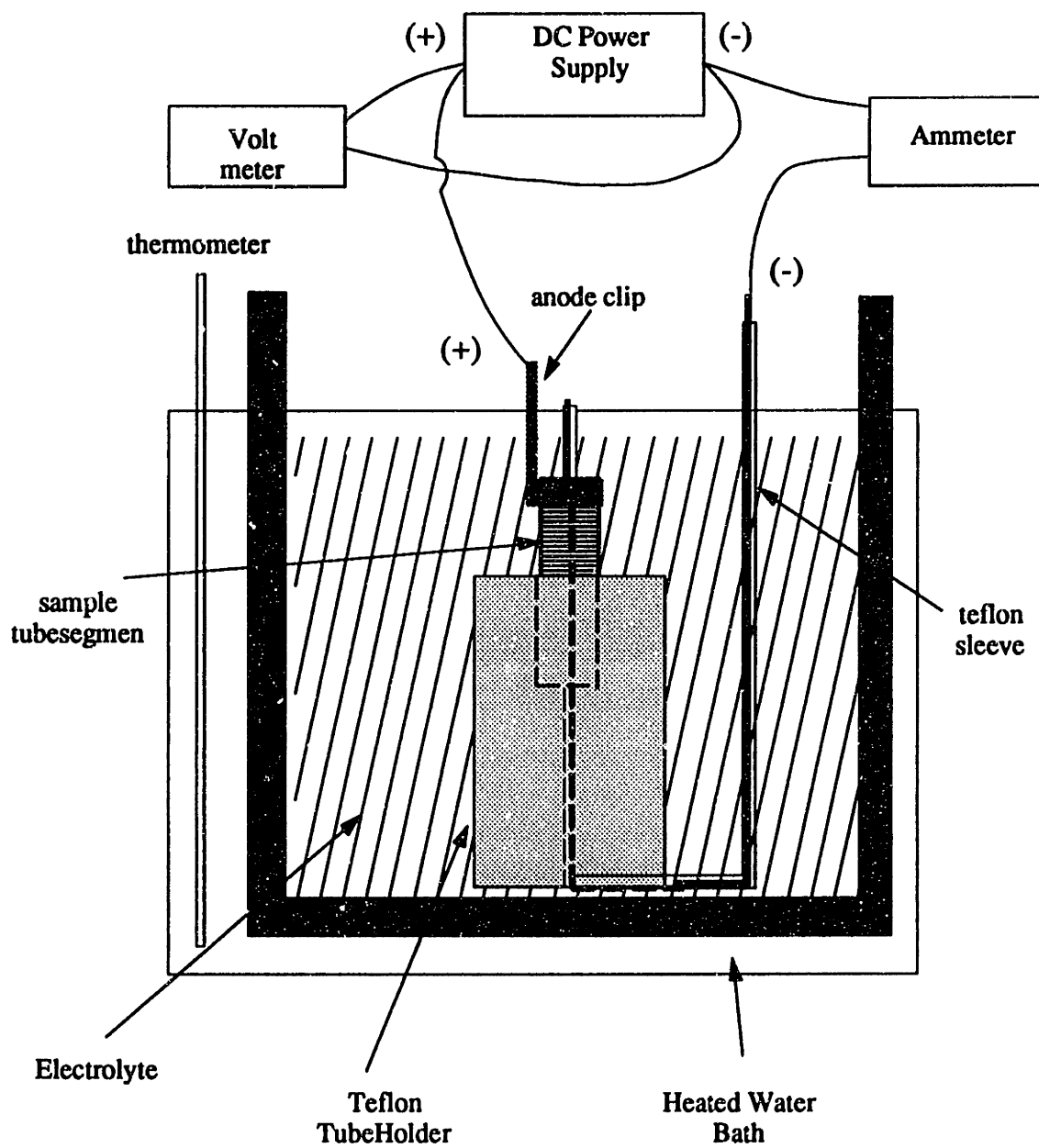


Figure 3.5 Electropolishing Setup



### 3.6 Zircaloy Tube Decontamination

The MIT PCCL in core section is constructed of 5/16" OD, 0.025" wall Zircaloy-4 tubing approximately six feet in length, bent into a U-tube configuration. After an in-pile run, the in-core section is typically cut into 27 segments of alternating 3 cm and 10 cm sections so that fourteen 3 cm segments and thirteen 10 cm segments result. Figure 3.6 shows the cutting diagram. Details of the remotely operated mechanical shear used for cutting the tube are discussed in reference [S-1]. The above mentioned 3 cm sections were subjected to decontamination procedures to obtain a deposition distribution map of the Zircaloy section.

The Zircaloy section is approximately 3 ft. in length with a bend of approximately 2 inch diameter at the bottom (see fig 3.6). The vertical length of the tube from the bottom of segments Z7, and Z8 to the bottom of the tube is approximately 2 inches. The MIT reactor core depth is about 24 inches. The distance from the bottom of segment Z7 to the top of segment Z3 is 21.65", so that the total Zircaloy length from the top of Z3 to the bottom of the Zircaloy section is approximately 23.65". It is therefore assumed that all segments from Z3 to Z12 are in core.

The pieces are labeled by position as shown in Figure 3.6, and by PCCL run as summarized in Table 3.3 for the 3 cm pieces of interest for the present work.

Table 3.3 Zircaloy Segment Nomenclature for 3 cm Sections

$pH_{300} = 6.5$	$pH_{300} = 7.0$	$pH_{300} = 7.0$	$pH_{300} = 7.5$
PL1-Z1	PR1-Z1	PR2-Z1	PH1-Z1
PL1-Z3	PR1-Z3	PR2-Z3	PH1-Z3
PL1-Z5	PR1-Z5	PR2-Z5	PH1-Z5
PL1-Z7	PR1-Z7	PR2-Z7	PH1-Z7
PL1-Z8	PR1-Z8	PR2-Z8	PH1-Z8
PL1-10	PR1-10	PR2-10	PH1-10
PL1-Z12	PR1-Z12	PR2-Z12	PH1-Z12
PL1-Z14	PR1-Z14	PR2-Z14	PH1-Z14

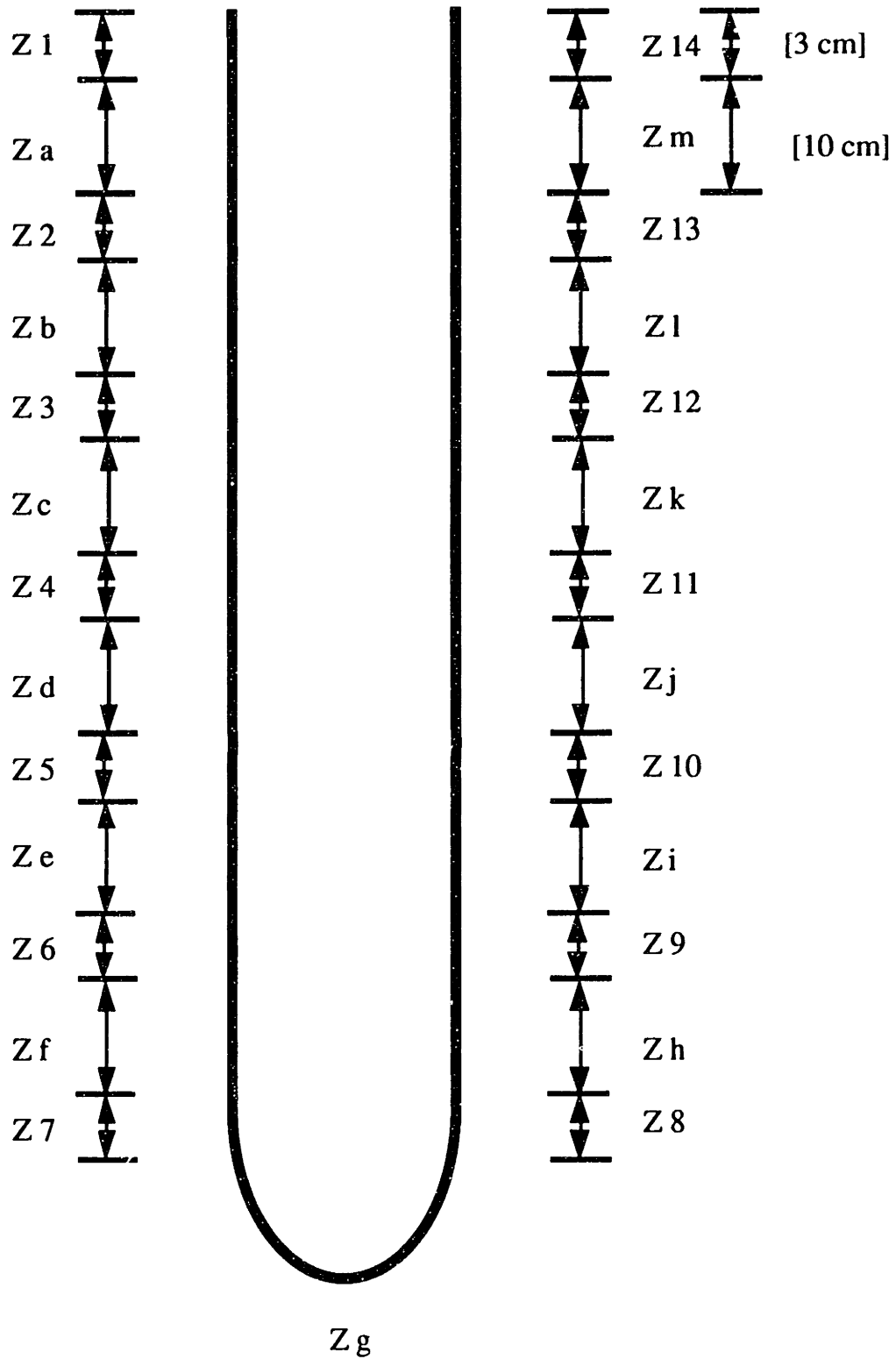


Figure 3.6 Schematic of Zircaloy Section Segmentation

De-scaling of the Zircaloy tubes presents a considerable challenge. Directly counting using the HpGe gamma detection system, discriminating against the high zirconium activity, is not feasible. It has been determined that even with the discriminator on the multi-channel analyzer set above the zirconium 95 gamma energy peaks (756.7 keV, and 724.2 keV), the amplifier (designed to handle about 20000 MeV/sec) of the MCA is overwhelmed by interactions such that the dead time, and background from pulse pileup/random summing is still so large that the (much lower in gross activity) cobalt 58 peak (810 keV) is undeterminable.

Another consideration is that there may be a considerable amount of base level nickel and even some cobalt impurities in the Zircaloy itself, which contribute to a problem in determining its contribution to the cobalt 58 and cobalt 60 signals emitted by the crud.

The method chosen for decontaminating the Zircaloy sections was the use of an aqua regia soak. Aqua regia is a very strong acid which proved to be effective in dissolving virtually all the crud and dissolving a minimal amount of base metal. Aqua regia is a mixture of 3 parts concentrated hydrochloric acid (s.g. ), 1 part concentrated nitric acid (s.g. ) and 2 parts water. After several qualification tests, a general procedure for Zircaloy section decontamination was developed:

### Zircaloy Section Aqua Regia Decontamination

The 3 cm pieces are prepared by first applying a piece of heat shrinkable tubing. The tubing is alpha FIT 750 adhesive wall polyolefin tubing. The inner coating of thermoplastic adhesive melts when tubing is shrunk and completely coats the object. Upon cooling, the material reverts to its solid state and forms a waterproof bond.

Approximately 70 ml of aqua regia (defined in section 3.4) is poured into a 4 oz. standard polyethylene sample bottle.

The sample tube is placed into the bottle for a 12 hour soak.

The tube is removed from the bottle using 12" forceps and placed into a plastic funnel back on the sample bottle.

The sample tube is thoroughly rinsed and then placed into the hot box (section 3.2.3) for storage.

The solution in the sample bottle is diluted to 110 ml from which 20 ml is taken and diluted for gamma spectroscopy (3.2.1) and another 20 ml is taken to be used for zirconium separation (section 3.7).

### 3.7 Techniques for Zirconium Separation

Two types of separation methods have been attempted, chemical and electrolytic. The chemical methods employed involve the precipitation of zirconium from the solution of interest leaving crud radionuclides in solution. The electrolytic technique, on the other

hand, plates the radionuclides of interest in preference to zirconium, leaving the zirconium in solution and the electrode with the radionuclides of interest.

### **3.7.1 Chemical Separation Methods**

Cobalt/zirconium separation has been attempted to establish the basis for future testing. Two different precipitation methods were evaluated: ammonium hydroxide in the presence of a cobalt carrier; and sodium arsenate.

All precipitation experiments were conducted in the reactor radiochemistry laboratory (section 3.2.3) in a chemical hood with ventilation.

A set of precipitation experiments to evaluate cobalt/zirconium separation was carried out to determine the extent of cobalt coprecipitation. It is known that in a zirconium solution containing cobalt, iron, etc, it is impossible to precipitate 100% of the zirconium, and to selectively precipitate only zirconium, with 100% of the other trace elements remaining in solution. Some of the elements of interest will coprecipitate along with the zirconium, and not all of the zirconium will precipitate out of solution.

#### **Precipitation for Ammonium Bifluoride Samples**

The following procedure was followed to give a cobalt coprecipitation factor and qualify a separation method for solutions of

partially or fully dissolved Zircaloy in ammonium bifluoride; the procedure follows suggestions from reference [M-2]:

A 1 cm piece of Zircaloy-4 tube, weight 0.99 grams, was cleaned in a 50% nitric acid ( $\text{HNO}_3$  s.g. 1.42)/deionized water solution.

The Zr-4 tube was then dissolved in about 80 ml of ammonium bifluoride ( $\text{NH}_4 \text{HF}_2$ , FW 57.03) solution (45 g/l).

2 grams of cobalt chloride ( $\text{CoCl}_2$ ) were added to the solution to provide additional cobalt in solution along with 1 ml of 26.3  $\mu\text{Ci}/\text{gram}$  (12/1/1979) Co-60 solution as a tracer.

The solution was diluted up to 110 ml, the pH checked, and the solution counted at the gamma counting facility (sec. 3.2.1) to get a baseline Co-60 concentration.

Progressive amounts of concentrated (56.6%) ammonium hydroxide ( $\text{NH}_3\text{OH}$ , s.g. 0.90) were added with periodic pH checks between additions. Five milliliter additions were first done until the pH approached the theoretical precipitation range ( $\text{pH} = 6.8$ ). One milliliter steps were then taken until the target pH of 6.8 was achieved.

The solution containing the precipitate was then filtered, and the filter rinsed thoroughly with deionized water before it was removed to be dried.

The solution was then counted and its Co-60 activity compared with the original count to determine cobalt retention effectiveness.

Results are discussed in section 4.6.1

From all of the precipitation trials attempted, a general procedure was adopted for all subsequent zirconium separations from aqua regia Zircaloy tube section decontaminations. The following procedure is extrapolated from reference [A-2] for zirconium separation from iron, nickel, and cobalt.

#### Zirconium Separation from Co, Fe, Cr and Mn in Aqua Regia:

##### **Solution preparation:**

A 1.5 M solution (50 grams/100 ml H<sub>2</sub>O) of sodium arsenate (FW 312.01) was prepared by mixing sodium arsenate in heated water.

A wash solution was prepared by diluting 1 ml of the sodium arsenate solution (above) to 100 ml using 2.4 N hydrochloric acid (HCL s.g. 1.19).

A 0.1 M zirconyl chloride (ZrOCl<sub>2</sub>·8H<sub>2</sub>O, FW 322.262) solution was prepared by mixing 3.22 grams of ZrOCl<sub>2</sub>·8H<sub>2</sub>O in 100 ml of deionized water at about 80°C.

Pipet 20 ml of the sample solution into a 50 ml centrifuge tube and another 20 ml into a 4 oz. bottle, dilute the bottle to 110 ml and count at the gamma counting facility to get baseline measurements.

Pipet 2 ml of the zirconium chloride solution into the centrifuge tube, add a small amount (about 200 mg) of cobalt chloride, and mix well.

Pipet 2 ml of the sodium arsenate solution into the centrifuge tube, mix by vortex agitation, and wait 30 minutes.



Put the centrifuge tube into the centrifuge and centrifuge at 3000 rpm for 15 minutes.

Decant the resulting solution through a standard 9 cm paper filter (Schleicher & Schuell Analytical Paper #595) into a 4 oz. poly bottle.

Add 5 ml of wash solution to the centrifuge tube containing the precipitate, mix by agitation, and centrifuge at 3000 rpm for 8 minutes. Pour off liquid into filter, adding to original filtered liquid.

Repeat above step twice so that a total of three washes are performed.

Dilute liquid in 4 oz. bottle up to 110 ml and count on gamma counting system to determine radionuclide concentration.

Compare post precipitation radionuclide concentrations with baseline measurement to obtain zirconium removal factor and transition metal retention factor.

It is important to mention that precipitation is desirable over counting by dilution because there are some elements of interest (Mn-54, and Co-58) which have gamma energy peaks close to the Zr-95 gamma energy peaks and are of much less specific activity in the solution.

### 3.7.2 Electrolytic Separation Methods

Electrolytic separation is a potentially good way of separating crud nuclides from zirconium [M-2]. Zirconium is very difficult to electroplate onto any surface under most conditions; transition metals such as nickel, cobalt, manganese, chromium, and iron are much easier to electroplate. The basic idea of the procedure is to attempt to plate the crud radionuclides onto an electrode out of the zirconium solution and then either count the resulting electrode, or remove the transition nuclides from the electrode into a clean electrolyte by reversing the process.

A stainless steel anode was used and the cathode used as the plating electrode was an 18 gauge copper wire 6 in. in length. Both electrodes were placed into a pre-counted decontamination solution containing both zirconium activity and transition metal activity.

Table 3.4 shows the electrolytic test matrix for the transition metal separation from the zirconium solution. All tests were performed at room temperature with a pre-counted solution.

**Table 3.4 Electrolytic Separation Test Matrix**

<b>Trial</b>	<b>Solution ID</b>	<b>Applied Voltage</b>	<b>Solution pH</b>	<b>Plating Time (minutes)</b>
1	PR1-Z3 #1	1.0	0	10
2	PR1-Z3 #1	1.0	0	20
3	PL1-Z8 #1	1.0	0	10
4	PL1-Z8 #1	1.0	0	20
5	PL1-Z8 #1	2.0	0	20
6	PL1-Z8 #1	2.0	14	20
7	PL1-Z8 #1	3.0	14	20
8	PL1-Z8 #2	14.0	3.5	20
9	PL1-Z8 #3	9.0	3.5	20

Note: Solution made basic (trials 6 and 7) by adding NaOH

### **3.8 Post Shutdown Peroxide/Boric Acid Additions**

The issues of interest are described in section 2.9; tests carried out involved variation of temperature and pH. A test matrix of runs using 3 cm sections of Inconel from the reference pH = 7.0<sub>300°C</sub> runs were subjected to various coolant conditions. Table 3.5 shows the test matrix.

**Table 3.5 Test Matrix For Boric Acid/Peroxide Additions**

Case	T°C	Boron (ppm)	Lithium (ppm)	pH <sub>(300°C)</sub>	Oxidant
1	90	800	1.84	7.0	aerated
2	90	2000	1.84	6.6	aerated
3	90	2000	5.15	7.0	aerated
4	90	2000	5.15	7.0	10 ppm H <sub>2</sub> O <sub>2</sub>
5-8	Repeat above at room temperature				

The above test matrix was carried out in containers open to the atmosphere. In the future, tests under anaerobic conditions are planned to better simulate the coolant environment during the initial steps of a reactor plant shutdown.

The 3 cm sections of Inconel tube from the reference pH PCCL runs were first counted for specific activity at the gamma spectroscopy facility (section 3.2.1) and then put into 4 oz. bottles containing about 50 ml of the desired coolant. The bottles requiring the 90°C condition were then placed in a heated water bath and kept at 90°C for eight hours of exposure. The other four bottles (room temperature) were just kept on a lab bench, uncovered. After the exposure time, the tubes were recounted and the radionuclide removal and DF were determined. The results are discussed in section 4.7.

Following this initial series of runs, the results (discussed in section 4.7) were reviewed to develop recommendations for future work.

### **3.9 Chapter Summary**

This chapter has surveyed potential approaches to component decontamination and focused on several which will be subjected to detailed evaluation. The procedures described adaptation of methods that are generally employed in larger scale applications than to present needs, with an overall emphasis on simplification.

The chapter describes the procedures used in the decontamination methods examined. Section 3.2 begins the chapter with a brief description of the specific facilities used for the decontamination experiments. The gamma spectroscopy facility, analytical chemistry lab, and the reactor radiochemistry lab are described as they pertain to the current work. Section 3.3 describes the planned procedures for a "crud toughness" comparison between three crud samples deposited at different coolant pH values. Section 3.4 describes the chemical trials attempted on Inconel test pieces, to provide a comparison of established methods under controlled conditions.

Section 3.5 gives the Inconel de-scaling procedures used for the MIT PCCL activated Inconel sections. A discussion of procedures for electropolishing using different electrolytes and different current

densities to evaluate its potential for further optimization is presented. An alternating electrolysis procedure suggested by Mitsubishi using nitric acid and sulfuric acid as the electrolytes is described, as are conventional electrochemical descaling using phosphoric acid or sodium sulfate as electrolytes.

Section 3.6 gives the procedure for decontaminating the Zircaloy section for deposition determination. Aqua regia is the solution of choice, as all crud is eventually dissolved. Section 3.7 follows with precipitation procedures for zirconium removal from the Zircaloy decontamination solution. This procedure proved to be necessary as some base metal dissolution occurs, and the resulting zirconium activity hinders transition metal radionuclide analysis.

Section 3.8 concludes the chapter by introducing screening tests to develop data relevant to work on the evaluation of post-shutdown peroxide and boric acid additions. High boron addition (2000 ppm) in the presence of hydrogen peroxide and in an aerated environment are investigated.

## **4. RESULTS AND DISCUSSION**

### **4.1 Introduction**

This chapter summarizes and evaluates all the data obtained during the subject work. Section 4.2 gives the results for the chemically decontaminated Inconel tubes. Each trial is described, focussing on deviations from the general procedure. All activity results presented in this thesis are corrected back to the end of irradiation.

Section 4.3 discusses the results obtained from the descaling experiments on contaminated Inconel tubes. Two different techniques were employed, ultrasonic descaling in the presence of nitric acid and electropolishing using phosphoric acid. All electropolishing results and ultrasonic de-scaling results are presented in this section.

Section 4.4 discusses the crud "toughness" comparison results obtained by application of the POD process and the ultrasonic process.

Sections 4.5 and 4.6 discuss the Zircaloy decontamination results. Section 4.5 gives the results for the aqua regia decontaminated samples, including dilute counting of the subsequent solutions. Section 4.6 describes the results obtained from the two methods used for zirconium/transition metal separation. Both chemical separation and electrolytic separation were attempted.

The chapter concludes with the results of the post shutdown peroxide/boric acid addition experiments, in section 4.7.

## 4.2 Inconel Tube Chemical Decontamination Results

Experiments were conducted under a variety of conditions to characterize candidate chemical decontamination methods. The PCCL tubing samples 3 cm long were measured before and after decontamination to determine decontamination factors.

The first set of Inconel chemical decontamination tests were done at a low temperatures (20-50°C), for 4 hours and were unsuccessful. Table 4.1 displays the results of the chemical decontamination soaks.

Table 4.1 Chemical Soak Results

Sample Tube	Chemical Reagent Soak	Co-58 Activity (nCi/cm <sup>2</sup> )		Tube DF
		before	after	
PR1 81-84	2 ml/l Citranox	13	9	1.4
PR1 93-96	Citric Acid	13	8	1.6
PR1 96-99	Citric +Oxalic Acid	12	6	1.7
PR1 109-112	Citric + Oxalic + EDTA	13	6	2.2
PR1 112-115	H <sub>2</sub> O <sub>2</sub>	12	9	1.3
PR1 115-118	H <sub>2</sub> O <sub>2</sub> + EDTA	12	8	1.5
PR1 118-121	Citric + H <sub>2</sub> O <sub>2</sub>	13	9	1.4
PR1 87-90	2 M Citric + EDTA	13	7	1.9

Citric and Oxalic acids prepared at 1 M concentration unless otherwise noted. EDTA prepared at 0.01 M, and peroxide prepared at 10% by volume.



The chemical soaks gave DFs of less than 2, with one exception at 2.2. These results are not comparable to results reported in the literature [W-1]. Either the PCCL crud is very resistant to chemical decontamination because it has a different structure or the conditions were not optimal.

The second series of tests involved flow-through experiments, using a peristaltic pump. Both unactivated Inconel samples, and specimens with some bulk metal activation were used for these tests. The 4 individual tubes used for the flow-through tests were as follows:

Piece #1 = Bulk-metal-activated Inconel piece 3 cm long from steam generator inlet at shot bed bottom (sample PR1 0-3).

Piece #2 = Unactivated Inconel piece 3 cm long from steam generator inlet in center of tube approximately 90 cm from shot bed bottom (sample PR1 90-93).

Piece #3 = Unactivated Inconel piece 3 cm long from steam generator inlet, approximately 84 cm from shot bed bottom (sample PR1 84-87).

Piece #4 = Bulk-metal-activated Inconel piece 3 cm long from steam generator inlet, 6 cm from shot bed bottom (sample PR1 6-9).

Table 4.2 below summarizes the conditions used for the 9 tests performed on the 4 Inconel specimens described above. It is impor-

tant to note that the following tests were done using strong acids since it was assumed that they would be most effective in crud removal, and base metal integrity is not important in this application.

Table 4.2 Flow-Through Inconel Tube Chemical Decontamination Results

Test #	Piece Id.	Solution Tested	Time (min)	Crud† nCi/cm <sup>2</sup>	Removal nCi/cm <sup>2</sup>
1	PR1 0-3	20% Nitric	30	12†	7
2	PR1 0-3	20% Nitric	60	12†	3*
3	PR1 90-93	20% Nitric	120	13	0.8
4	PR1 90-93	Hydrox.†	120	12	0.2*
5	PR1 84-87	Aqua regia	15	11.3	2
6	PR1 84-87	Aqua regia	30	9.5	9.5*
7	PR1 6-9	Aqua regia	20	12†	108
8	PR1 6-9	Aqua regia	15	12†	7.5*
9	PR1 0-3	Aqua regia	30	12†	126.5

† Total crud before decontamination, extrapolated values are given for activated sections.

\* This is additional removal and should be added to previous line for determination of total removal of sample. Time should be added for total time.

Aqua regia = 1 part conc. HNO<sub>3</sub>, 3 parts conc. HCL, 2 parts DI water.

† Hydroxylamine

The following additional notes apply to the above set of experiments:

**#1, #2:** this was an activated section, and it was subsequently concluded that nitric acid was dissolving the base metal at the tube ends.

**#3, #4 :** The results suggest that there is no oxide layer dissolution of any significance.

**#5, #6:** Here microstop was used to prevent dissolving base metal at tube ends, and it was found that after 45 minutes total of decon, 98% of the activity was removed. Microstop is a protective acid resistant coating used in TEM sample preparation techniques.

**#7, #8:** Here after 20 minutes almost 10 times the expected activity was removed, and after closer inspection it was determined that microstop failed by peeling off of the tube, and hence did not protect it. More careful application of microstop gave much less removal after an additional 15 minutes.

**#9:** Since PR1 0-3 was not originally de-scaled to an adequate extent, it was used again, this time with the aqua regia.

These flow-through experiments were early trials which show that much bulk metal dissolution occurs using this method. Trials 3-6 done on unactivated Inconel show that aqua regia can remove all the crud, while nitric acid removes very little. Trial 9 shows that indeed much activity is removed using aqua regia, but most is probably bulk metal. The ultrasonic de-scaling results (section 4.3.1) confirm that in the trials above using activated Inconel, most removal

was indeed bulk metal; an extrapolated crud activity value of about  $12\text{nCi/cm}^2$  is obtained in these trials.

The P.O.D. process was applied to Inconel samples from all four PCCL runs, and can therefore be used for a crud toughness comparison; therefore all P.O.D. results are discussed in section 4.4. A comparison between the P.O.D. process and other chemical methods is made in section 4.4.

### 4.3 Inconel De-scaling Results

Inconel de-scaling is important to computation of a total activity inventory of the PCCL steam generator region. Two methods were investigated, electropolishing and ultrasound. It is desirable to use ultrasound whenever possible due to the insignificant base metal removal by this process for the application period of interest. Note that each run had two steam generator legs: the inlet (hot leg) is labeled 0-180 cm and the outlet (cold leg) is labeled 180-360 cm. This is primarily important when considering the low pH run (PL1) because there is a factor of 10 difference in activities between the two legs, and they may therefore behave differently. All other runs had little difference in activity per unit area between the two steam generator legs.

#### **4.3.1 Ultrasonic De-scaling Results**

A test was performed to verify the absence of significant base metal attack using ultrasound under the desired conditions. As mentioned in section 3.5.2, the optimal conditions for activity removal were:

Ultrasound for 5 minutes at 60°C using 5% nitric acid.

The test involved subjecting a clean new Inconel piece to the above condition for 11 hours and measuring the base metal removal.

initial tube weight: 3.9985 g

final weight: 3.9980 g

Total weight removal: 0.0005 g (= 0.5 mg)

This removal is insignificant since the highest bulk metal activation measured for the Inconel section is 600 nCi/cm<sup>2</sup>. When one considers the tube, 3 cm in length, having a weight of about 4.5 grams, this corresponds to 750 mg/cm<sup>2</sup>. Therefore, the specific activity removed corresponds to approximately 0.8 nCi/mg. Expected crud activities are on the order of 10-20 nCi/cm<sup>2</sup> which is 60-120 nCi/tube. Since the actual application time is only 5 minutes, less base metal will be removed in practice than in this test, and the correction is negligible.

A summary of the different trials performed using ultrasound, before the eventual designation of the final method of choice, is dis-

played in Table 4.3 below. Attention should be given to the temperatures, times, and electrolyte chosen.

Table 4.3 Ultrasound Decontamination Test Results

Sample Tube	Ultrasound electrolyte	Time (min.)	Temp. (°C)	Tube DF
PR1 294-297	Deionized H <sub>2</sub> O	20	60	2.0
PR2 294-297	Deionized H <sub>2</sub> O	20	60	2.2
PR2 136-139	3% Citric acid	35	25	1.4
PR2 139-142	Deionized H <sub>2</sub> O	35	25	1.3
PR2 154-157	5% nitric acid	3	60	>83†
PR1 99-102	5% nitric acid	3	60	>70†
PH1 139-142	5% nitric acid	3	60	>62†
PL1 145-148	5% nitric acid	3	60	2.2
PL1 301-304	5% nitric acid	5	60	26

† These tubes showed no activity after decontamination.

It would seem that temperature can play an important role in decontamination using the same electrolyte. DI water was used at room temperature and at 60°C with significantly different results. The citric acid electrolyte offered no improvement over pure water, but nitric acid showed complete de-scaling (with the exception of PL1 inlet Inconel), so it became the method of choice for Inconel de-scaling, without further investigation of other ultrasound electrolyte/temperature conditions.

Except for inlet PL1 Inconel, all Inconel tubes were subjected to the 5% nitric acid ultrasonic de-scaling procedure described in section 3.5.1. The resulting solutions were diluted to 110 ml and counted. The activity measured has been transformed into activities per unit area using 6 cm<sup>2</sup> per tube. The results for the Co-58 activity are displayed in Table 4.4 below.

Table 4.4 Activated Inconel De-scaled Crud Activities

Steam Generator Inlet		Steam Generator Outlet	
Tube ID	Co-58 (nCi/cm <sup>2</sup> )	Tube ID	Co-58 (nCi/cm <sup>2</sup> )
		PR1 321-324	10.7
PR1 12-15	13.1	PR1 333-336	11.6
PR1 24-27	12.0	PR1 345-348	10.6
PR1 36-39	12.8	PR1 357-360	9.8
PR2 0-3	43.0	PR2 321-324	13.1
PR2 12-15	28.0	PR2 333-336	14.7
PR2 24-27	17.7	PR2 345-348	15.0
PR2 36-39	18.5	PR2 357-360	15.5
		PL1 321-324	12.6
		PL1 333-336	13.3
		PL1 345-348	14.9
		PL1 357-360	14.4
PH1 0-3	11.8	PH1 321-324	11.1
PH1 12-15	9.0	PH1 333-336	11.0
PH1 24-27	8.4	PH1 345-348	11.8
PH1 36-39	8.2	PH1 357-360	10.3

The activity deposition profile for the inlet to the steam generator (hot leg) can now be plotted using the above values for the activated region Inconel. Figure 4.3 below displays these plots using the values from the ultrasound decontamination, together with the next 60 cm of tubing scan data. The two sets of data fit together fairly smoothly.

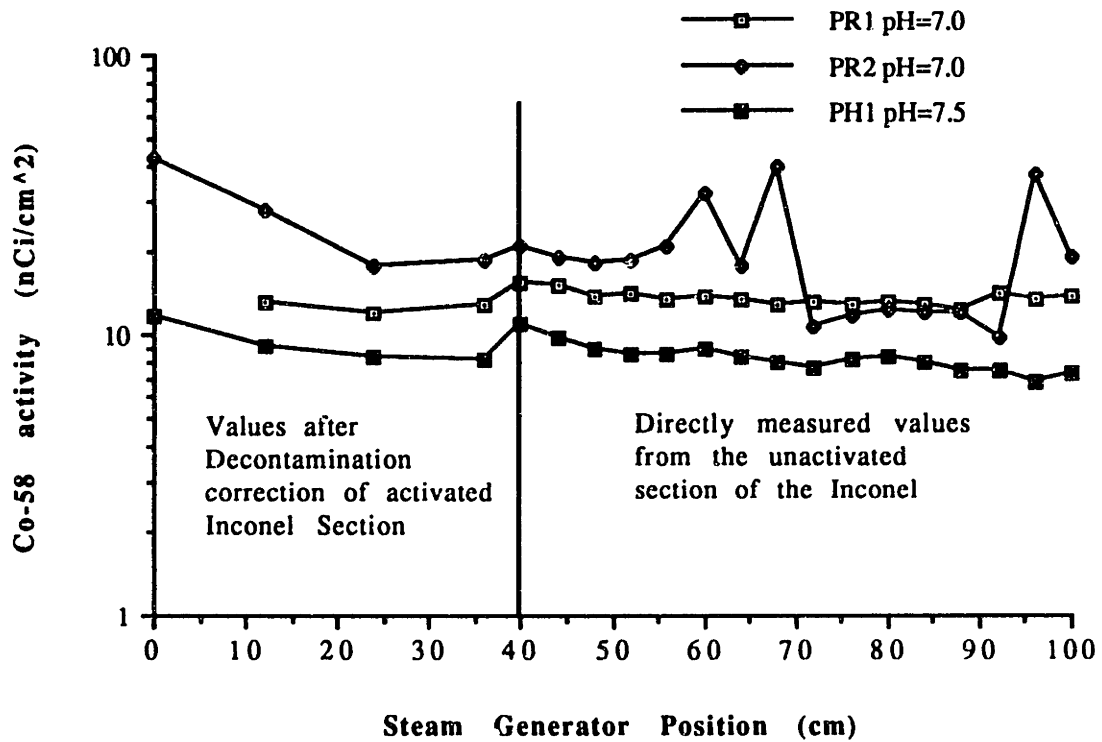


Figure 4.3 Deposition Traverse with Values from Ultrasonic Decontamination of the Activated Inlet Region



The same process was carried out for the steam generator outlet. Figure 4.4 displays the corrected steam generator outlet leg data.

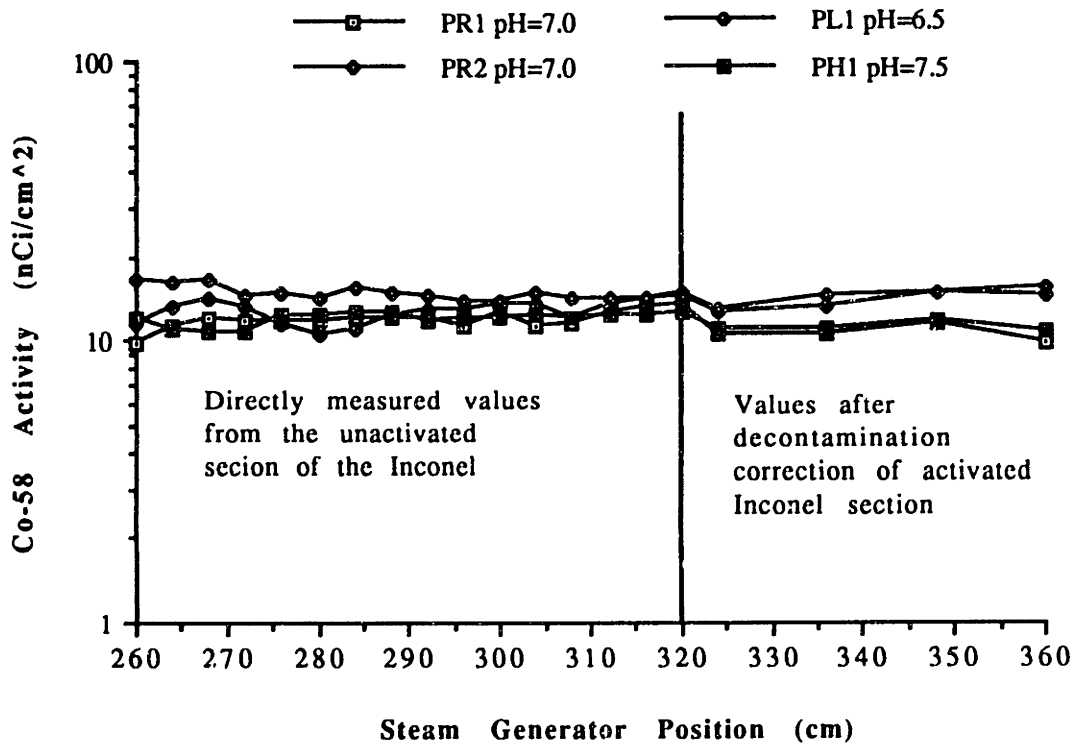


Figure 4.4 Deposition Traverse with Values from Ultrasonic Decontamination of the Activated Outlet Region

The plots clearly show that the deposited crud activity is, as expected, essentially the same in the regions with and without significant bulk metal activation.

### **4.3.2 Electropolishing De-scaling Results**

An investigation of electropolishing was conducted to determine its effectiveness on the PCCL Inconel samples. There were three methods investigated, anodic electrodecontamination, alternating anodic/cathodic electropolishing with a basic electrolyte, and alternating anodic/cathodic electropolishing with electrolytes recommended by Mitsubishi. Further motivation for using electropolishing as an Inconel de-scaling method arises from the unsuccessful de-scaling attempt of the PL1 Inconel using ultrasound.

As is evident from Table 4.3, the inlet steam generator leg of PL1 was much more resistant to ultrasonic de-scaling than tubing from other runs. The outlet leg showed somewhat higher resistance but could nevertheless be adequately de-scaled. An electrolytic de-scaling technique was therefore required to obtain PL1 inlet leg data.

The first electropolishing method tested was anodic electropolishing using a 70% volume phosphoric acid electrolyte at 70°C.

Table 4.5 Anodic Electropolishing Results

Sample Tube	Time (min.)	Co-58 Activity (nCi/cm <sup>2</sup> )		Tube DF
		before	after	
PL1 130-133	2	13	0.15	87
PL1 133-136	3	18	<0.1	>180†
PL1 157-160	2	118	0.50	236
PR2 145-148	2	19	0.86	22

† No detectable Co-58; lower limit displayed with minimum DF attained.

The other two forms of electropolishing investigated both used cathodic/anodic alternation types of electropolishing. A method employed by Mitsubishi for their de-scaling, in which a 0.15N sulfuric acid cathodic step is followed by a 0.1N nitric acid anodic step was investigated. A 1.7M sodium sulfate electrolyte is used for both the cathodic and anodic steps in the other alternating electropolishing method. Results of the two methods are shown in Table 4.6.

Table 4.6 Cathodic/Anodic Alternation Electropolishing Results

Sample Tube	step	Time (min.)	Co-58 Activity (nCi/cm <sup>2</sup> )		Total DF
			before	after	
PL1 139-142 (MHI)	cathodic	5	120	85	1.4
	cathodic	25	85	81	1.5
	anodic	1	81	62	1.9
PR2 130-133 (NaSO <sub>4</sub> )	cathodic	2	17	8	2.1
	anodic	1	8	0.6	28

Note: Method used is noted in parenthesis under tube ID. MHI = Mitsubishi method, using sulfuric acid for cathodic step and nitric acid for anodic step.

The Mitsubishi method achieved a DF of only 2 under the tested conditions. A refinement of operating times needs to be done before this method can be qualified for present applications. This method is designed to differentiate between the “inner oxide” layer and the “outer oxide” layer. It is also designed to follow a 20 minute ultrasonic decontaminatin step of 20 minutes to remove “loose” deposited crud. Further refinement of the process could perhaps lead to better characterizing of the PCCL crud into these categories.

The NaSO<sub>4</sub> alternation electrodecontamination method showed a much better DF, and can be employed as a useful decontamination method. The use of the more basic electrolyte (NaSO<sub>4</sub> ) creates a sludge in the decontamination solution. This sludge makes for easier waste disposal as it can be filtered and dried for solid waste disposal.

While this is a virtue for commercial applications, it is a problem for the present work, due to the desire to assay the solution at the gamma spectroscopy facility (section 3.2.1), where the calibrated geometry of interest is a liquid of 110 ml. Sludge precipitation alters the geometry and introduces a bias into the count rate data.

Both methods have an additional drawback for use in de-scaling of activated sections. Since they alternate cathodic and anodic steps, the bulk metal dissolution rate is unknown. It is less than with just anodic electropolishing but not easily characterizable, hence if a highly activated piece were to be decontaminated, one could not accurately correct for bulk metal dissolution.

For these reasons, the above methods were not further investigated for Inconel de-scaling. Instead, anodic, more readily correctable, electropolishing was used for the inlet steam generator PL1 Inconel. The values obtained from the electropolishing are shown in Table 4.7 below.

Table 4.7 Activated PL1 Inconel Region Results

Tube ID†	Co-58 (nCi/cm <sup>2</sup> )
PL1 12-15	200
PL1 24-27	191
PL1 36-39	160

† PL1 0-3 data contaminated and therefore lost.

From Table 4.7 the values can now be added to Figure 4.3 to make a complete steam generator inlet section plot, as shown in Figure 4.5. Again, a relatively smooth traverse results, with only a small discontinuity in slope which is probably due to inaccuracy in the correction process.

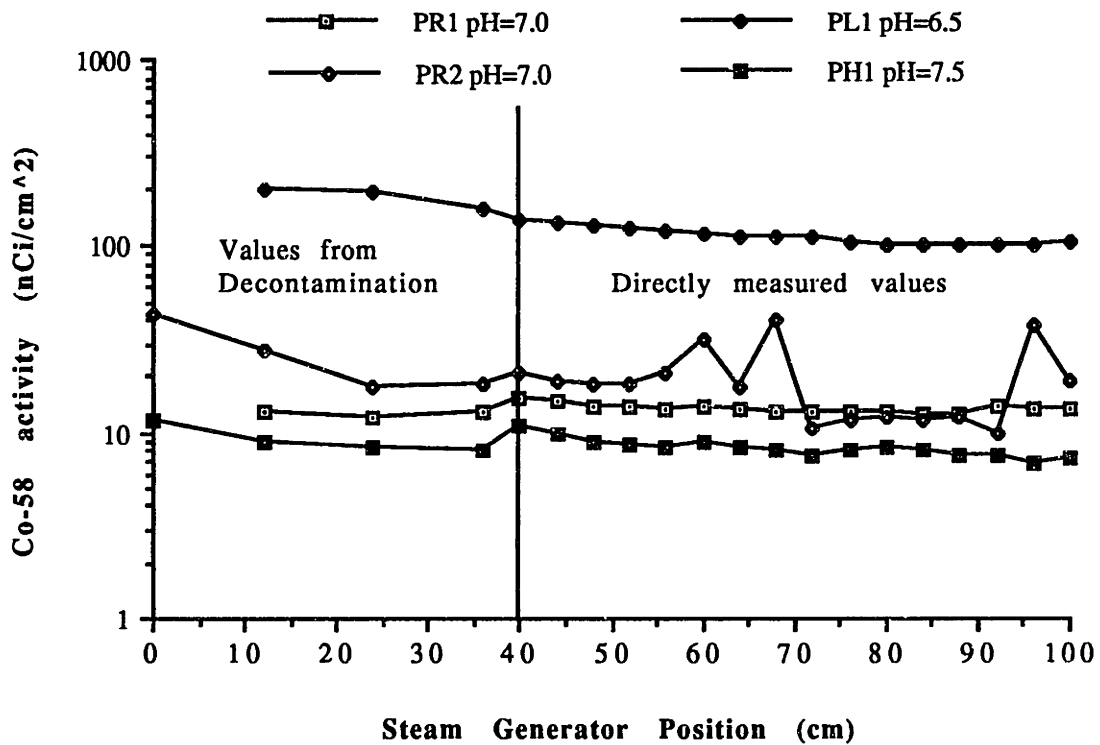


Figure 4.5 Deposition Traverses with Values from Electropolishing and Ultrasonic Decontamination of the Activated Inlet Region.

#### 4.4 Crud Toughness Results

The crud toughness comparison outlined in section 3.3 involved the comparison of DFs as a function of the pH under which the crud layer was created. The two different methods investigated were ultrasonic de-scaling, described in section 3.5.2, and chemical de-scaling using the P.O.D. process as described in section 3.4. All other de-scaling results are described in sections 4.2 and 4.3 for the chemical and ultrasonic procedures, respectively. Here the specific results as they pertain to the crud toughness comparison are outlined.

For the ultrasonic decontamination efforts, two variations were applied, one with deionized water only, and the other with 5% nitric acid. The results for the Inconel samples are shown in Table 4.8.

Table 4.8 Ultrasonic Crud Toughness Test Results

Sample Tube	Ultrasound electrolyte	Time (min.)	Co-58 Activity (nCi/cm <sup>2</sup> ) before	Co-58 Activity (nCi/cm <sup>2</sup> ) after	Tube DF
PR1 294-297	H <sub>2</sub> O	20	12	6.0	2.0
PR2 294-297	H <sub>2</sub> O	20	16	7.3	2.2
PL1 304-307	H <sub>2</sub> O	20	13	5.6	2.3
PL1 142-145	H <sub>2</sub> O	15	120	50	2.4
PH1 294-297	H <sub>2</sub> O	20	12	3.3	3.6
PR2 154-157	5% HNO <sub>3</sub>	3	19	< 0.23*	> 83
PL1 145-148	5% HNO <sub>3</sub>	3	120	55	2.2
PH1 139-142	5% HNO <sub>3</sub>	3	5.6	< 0.09*	> 62
PR1 291-294	5% HNO <sub>3</sub>	5	12	< 0.50*	> 24
PR2 291-294	5% HNO <sub>3</sub>	5	12	< 0.43*	> 24
PL1 301-304	5% HNO <sub>3</sub>	5	14	0.53	26
PH1 291-294	5% HNO <sub>3</sub>	5	12	< 0.15*	> 80
PL1 124-127	5% HNO <sub>3</sub>	40	98	64	1.5

\* These tubes had no measurable activity, minimum detectable activity given.  
 Note: All tests were conducted at 60°C.

The tubes were visually inspected before and after decontamination. When decontamination is successful, the tubes are silver and shiny on the inside, indicating the complete removal of the black oxide, which is visible before decontamination. From the ultrasound results the low pH samples were the most difficult to decontaminate. The reference and high pH samples display similar DFs, with virtually complete removal using the 5% nitric acid reagent. The low pH



sample did have similar “loose” crud using the 20 minute ultrasonic de-scaling in water, but the “fixed” crud is tougher, as demonstrated by the nitric ultrasonic tests, where the other samples have essentially total removal.

There was roughly a decontamination factor of 2.5 for all Inconel samples using 60°C water in the 20 minute ultrasonic de-scaling test. All samples were taken from the middle of one of the steam generator legs, with a piece from each leg of the PL1 run because of the large crud activity difference. It was originally believed that the PL1 sample from the “dirty” leg would demonstrate the best DF since it had the most activity and that the PH1 sample would demonstrate the smallest DF since it was the “cleanest” run. The results demonstrate, however, that the PH1 sample had the best DF, and the PL1 samples have similar DFs to reference pH samples (PR1 and PR2), with deionized water.

Since the samples were all taken from the middle of the steam generator, there is no bulk metal neutron activation and the fixed oxide layed down in prefilming and preconditioning the loops before reactor use are also (obviously) not neutron activated. A 20 minute ultrasound decontamination in water is commonly used to discriminate “loose” deposited crud, from “fixed” crud [P-1]. On this basis, approximately half the crud is “loose” for the reference and low pH runs, compared to almost 75% of the high pH run crud.

The other crud toughness test involved using a chemical decontamination method. The POD process was used on 9 different pieces

taken from three different PCCL post run Inconel steam generator sections. Table 4.9 displays the results of the process on the 9 samples.

Table 4.9 Chemical Decontamination Crud Toughness Test Results

Sample Tube	Oxidation Step(s)	Co-58 Activity (nCi/cm <sup>2</sup> )		Tube DF
		before	after	
PR2 130-133	NP	18	13	1.4
PL1 130-133	NP	100	97	1.0
PH1 130-133	NP	6.1	3.7	1.6
PR1 297-300	AP/NP	12	2.9	4.1
PR2 297-300	AP/NP	13	2.4	5.4
PL1 307-110	AP/NP	14	1.9	7.4
PH1 297-300	AP/NP	11	2.5	4.4
PR2 127-130	AP/NP	18	3.9	4.6
PL1 127-130	AP/NP	92	7.3	13
PH1 127-130	AP/NP	6.2	1.7	3.6

The NP and AP process are nitric permanganate and alkaline (NaOH) permanganate oxidation steps, respectively.

As is demonstrated in Table 4.9, the samples from the low pH run were not the most difficult to decontaminate with AP/NP, contrary to our findings using ultrasound. Without more detailed analysis, a credible explanation for these observations cannot be made without further studies of the crud and oxide films. However, since the low pH oxide was created under a solubility gradient which favored dissolution, it may be more porous, with more accessible deep-

lying sites for radionuclide incorporation. Note also that the NP only version of the process does seem to be least effective in the low pH run samples, consistent with the low removal under ultrasound in nitric acid.

Overall, the POD process gives DFs which are comparable to results cited in the literature [L-2]; and comparing the POD soaks with the previous chemical decontamination soaks (section 4.2), it is concluded that the original chemical soaks were not done under optimal conditions.

#### 4.5 Zircaloy Tube Results

The Zircaloy section of the PCCL is immersed in a lead bath inside a titanium test tube. Approximately 2/3 of the Zircaloy section is in core, and the upper region is just above the MITR-II core, receiving substantially less neutron flux. When the Zircaloy section is removed from the lead bath at the termination of every run, a considerable amount of activated lead adheres to the Zircaloy surface, which presented many problems in cutting and decontaminating the sections.

The Zircaloy tubes were all subjected to a 12 hour decontamination soak in aqua regia, with the exterior protected by heat-shrinkable tubing with a chemical resistant adhesive inner layer (see section 3.6). The following exceptions to the above procedure are noted below.

PR1-Z1 was subjected to a 1 hr 40 minute aqua regia decon in 2 steps and an ammonium bifluoride soak for 10 minutes, removing all crud plus 20% of the base metal. The tube itself was measured before and after decontamination. No shrink tubing was used and the activated lead on the outside of the tube contaminated the results. The results are shown in Table 4.10.

PR1-Z3 was subjected to aqua regia decontamination in three 3 hour steps also without shrink tubing, and consequently also has activated lead contamination in the results. PR1-Z3 was also completely dissolved in approximately 300 ml of ammonium bifluoride ( $\text{NH}_4 \text{HF}_2$ , FW = 57.05) solution (45 grams/liter) to yield a highly concentrated solution of base metal activity from which aliquots were taken for tracer experiments, or on which separation techniques (see sec 3.7) were attempted for qualification.

The above solution was also used to see if base metal impurity concentrations of nickel and cobalt can be determined using an assumed value of the neutron flux (see section 2.8.2). The MCA lower level discriminator was set to reject the zirconium gamma rays and the peak confidence factor for the recognition program was lowered in an attempt to allow recognition of the crud radionuclide activity peaks of interest. However, there was so much pulse pileup and random summing that the background above the zirconium-95 peaks and the region of interest, was still too high to obtain any reasonable impurity concentrations.

As mentioned in section 3.6, 20 ml of the 110 ml aqua regia decontamination sample solution was taken and diluted to 110 ml in a separate bottle. The sample was then taken to the gamma spectroscopy lab (3.2.1) for radionuclide analysis, to serve as both an attempt at absolute measurement, and a baseline for the separation experiments (section 4.6).

It is important to note that all solutions with the exception of PR1-Z1 and PR1-Z3, were counted after the following cooling times for each run:

PR1	10 months
PR2	7 months
PL1	5 months
PH1	4 months

The cooling times are significant for both Co-58 ( $T_{1/2} = 70.8$  days) and Zr-95 ( $T_{1/2} = 64$  days) decay. This is important because the dead times were sometimes very high (20-30%) for PL1 and PH1 samples. This also means that PR2 and PR1 have gone through 3 and 4 Co-58 half lives, respectively. If one were to attempt to measure deposition data for future runs soon after the run completion (1 to 2 months), the Zr-95 activity would be far too high to count samples by diluting a 20 ml aliquot of the decontamination solution, and zirconium separation would be necessary (section 4.6).

Table 4.10 displays the results from the Zircaloy section decontamination using aqua regia.

Table 4.10 Results of Zircaloy Radionuclide Deposition Measurements

Test Piece	Zr-95 nCi/cm <sup>2</sup>	Metal Concentrations, nCi/cm <sup>2</sup>			
		Co-58	Co-60	Fe-59	Mn-54
PR1-Z1†	-	42	-	-	-
PR1-Z3††	1100 ± 69	79 ± 2.3	98 ± 1.4	440 ± 30	280 ± 1.9
PR1-Z5	530 ± 9.9	190 ± 3.3	44 ± 0.72	-	15 ± 0.32
PR1-Z7	3400 ± 85	45 ± 1.9	16 ± 0.35	-	5.1 ± 0.21
PR1-Z8	5000 ± 130	56 ± 2.1	20 ± 0.38	51 ± 17	5.6 ± 0.22
PR1-Z10	610 ± 7.2	48 ± 1.8	14 ± 0.30	-	3.0 ± 0.17
PR1-Z12	990 ± 18	9.3 ± 2.5	11 ± 0.30	-	0.52 ± 0.1
PR1-Z14	26 ± 2.7	55 ± 1.1	0.73 ± 0.10	-	-
PR2-Z1	33 ± 1.1	1.4 ± 0.39	0.42 ± 0.09	-	-
PR2-Z3	4100 ± 1.2	7.1 ± 0.74	3.4 ± 0.17	8.3 ± 3.9	0.94 ± 0.13
PR2-Z5*	4.6E5 ± 8E4	-	21 ± 7.1	-	110 ± 16
PR2-Z7	6000 ± 220	200 ± 2.3	18 ± 0.44	31 ± 5.3	6.0 ± 0.36
PR2-Z8	1900 ± 39	170 ± 2.9	19 ± 0.36	29 ± 9.3	5.0 ± 0.18
PR2-Z10*	2.1E5 ± 1E4	510 ± 31	44 ± 2.9	-	63 ± 6.2
PR2-Z12	2500 ± 61	15 ± 0.74	5.2 ± 0.17	16 ± 3.7	1.1 ± 0.13
PR2-Z14	17 ± 0.81	1.0 ± 0.39	0.44 ± 0.09	-	0.28 ± 0.12
PL1-Z1	45 ± 1.1	3.3 ± 0.28	0.60 ± 0.10	-	0.51 ± 0.09
PL1-Z3	670 ± 12	11 ± 0.66	8.0 ± 0.25	11 ± 2.2	0.8 ± 0.12
PL1-Z5*	2E5 ± 1.5E4	820 ± 56	140 ± 24	-	-
PL1-Z7	2600 ± 130	1100 ± 12	110 ± 2.5	150 ± 19	45 ± 1.5
PL1-Z8	930 ± 32	920 ± 8.8	87 ± 2.0	31 ± 15	49 ± 13
PL1-Z10	4300 ± 110	270 ± 3.1	51 ± 1.2	82 ± 3.9	31 ± 0.62
PL1-Z12	310 ± 4.9	57 ± 0.94	41 ± 0.67	88 ± 3.6	4.9 ± 0.20
PL1-Z14	13 ± 0.55	6.7 ± 0.34	0.86 ± 0.10	-	0.40 ± 0.08
PH1-Z1	14 ± 1.1	2.2 ± 0.46	0.16 ± 0.09	-	0.31 ± 0.06
PH1-Z3*	2.2E5 ± 9E3	-	9.4 ± 2.9	700 ± 78	-
PH1-Z5*	1.7E5 ± 7E3	390 ± 28	37 ± 3.4	890 ± 69	110 ± 11
PH1-Z7	4700 ± 100	144 ± 1.7	0.75 ± 0.17	-	0.80 ± 0.16
PH1-Z8	9600 ± 290	130 ± 2.2	7.9 ± 0.36	200 ± 7.0	24 ± 0.45
PH1-Z10	8000 ± 210	32 ± 0.91	0.56 ± 0.17	16 ± 2.6	1.5 ± 0.21
PH1-Z12	2200 ± 52	-	-	40 ± 8.4	-
PH1-Z14	71 ± 1.1	0.92 ± 0.32	0.30 ± 0.10	-	0.17 ± 0.07

† PR1-Z1 was counted directly before and after decontamination.

†† PR1-Z3 had no heat shrinkable tube cover, and therefore had lead contamination.

\* These pieces require activity correction, see section 2.8.2.

- Indicates that the activity in question was not detected.

The measured activity per cc has been transformed into activity per unit area using  $6 \text{ cm}^2$  per tube.

As we can see, the results are reasonably consistent within each run. Segments Z5 to Z10 are all in-core, Z3 and Z12 are at the top of the core, and Z1 and Z14 are out-of-core. Total crud activity inventories are of interest for the PCCL [S-1] and an average in-core value for each run was therefore determined. The information from Table 4.10 and the post chemical separation (Table 4.16, section 4.6) data were combined to give the following results.

For PR1, the first reference pH run ( $\text{pH} = 7.0$  at  $300^\circ\text{C}$ ), it was determined that the in-core average Co-58 and Co-60 activities were 68 and 31  $\text{nCi/cm}^2$ , respectively. The in-core Zircaloy area is  $250 \text{ cm}^2$ , which yields a total of 17  $\mu\text{Ci}$  of Co-58 and 7.8  $\mu\text{Ci}$  of Co-60 in-core. The total Fe-59 and Mn-54 activities were 7.8  $\mu\text{Ci}$  and 1.5  $\mu\text{Ci}$ , respectively.

For PR2, the second reference pH run ( $\text{pH} = 7.0$  at  $300^\circ\text{C}$ ), the average Co-58 and Co-60 activities deposited on the in-core section of the Zircaloy tubing are 210 and 18  $\text{nCi/cm}^2$ , which yields a total activity of 53 and 4.5  $\mu\text{Ci}$ , respectively. In addition, the total Fe-59 and Mn-54 activity inventories are 31 and 8.2  $\mu\text{Ci}$ , respectively.

PR1 and PR2 should yield the same activities after correction for neutron fluence and decay. The results indicate the differences in these two reference runs which are probably related to the abnormal events during those runs which were unusual and not the

same for PR1 and PR2. Later runs including PL1 and PH1 were carried out with fewer perturbations (see [S-1] for details).

For PL1, the low pH run (pH = 6.5 at 300°C), the average Co-58 and Co-60 activity deposited on the in-pile Zircaloy tubing were 650 and 91 nCi/cm<sup>2</sup>, which yielded a total deposited activity of 160 and 23 μCi, respectively. The total Fe-59 and Mn-54 deposited on the Zircaloy tubing were 57 and 19 μCi, respectively.

For PH1, the high pH run (pH = 7.5 at 300°C), the in-core Co-58 and Co-60 average deposited activities were 120 and 9.6 nCi/cm<sup>2</sup>, respectively. The total Co-58 and Co-60 deposited activities on the in-core Zircaloy tubing are 30 and 2.4 μCi, respectively and the total Fe-59 and Mn-54 deposited activities were 77 and 5.9 μCi, respectively.

It is necessary to find a way to adjust for neutron exposure for decay and hot running time in order to make a more objective comparison of the results for the four runs. Work of this type is in progress using vendor codes such as Cruddsim, Cora, and Pactole.

There were five Zircaloy segments which had anomalously large Zircaloy dissolution for unknown reasons. There is a need to correct for bulk metal dissolution. Using the values from Table 2.5 (section 2.8.2) the following corrections were made:



For PR2-Z5, 460  $\mu\text{Ci}/\text{cm}^2$  of Zr-95 were dissolved which corresponds to the following corrections.

Table 4.11 PR2-Z5 Bulk Metal Dissolution Corrections

Element	Correction (nCi/cm <sup>2</sup> )	Measured (nCi/cm <sup>2</sup> )	Corrected (nCi/cm <sup>2</sup> )
Co-58:	330	380	50
Co-60	64	54	<0
Fe-59	600	440	<0
Mn-54	270	110	<0

For PR2-Z10, 210  $\mu\text{Ci}/\text{cm}^2$  of Zr-95 were dissolved which corresponds to the following corrections.

Table 4.12 PR2-Z10 Bulk Metal Dissolution Corrections

Element	Correction (nCi/cm <sup>2</sup> )	Measured (nCi/cm <sup>2</sup> )	Corrected (nCi/cm <sup>2</sup> )
Co-58:	330	1300	970
Co-60	64	200	130
Fe-59	600	930	330
Mn-54	270	310	40

For PL1-Z5, 460  $\mu\text{Ci}/\text{cm}^2$  of Zr-95 were dissolved which corresponds to the following corrections.

Table 4.13 PL1-Z5 Bulk Metal Dissolution Corrections

Element	Correction (nCi/cm <sup>2</sup> )	Measured (nCi/cm <sup>2</sup> )	Corrected (nCi/cm <sup>2</sup> )
Co-58:	330	1300	970
Co-60	64	200	130
Fe-59	600	930	330
Mn-54	270	310	40

For PH1-Z3, 220  $\mu\text{Ci}/\text{cm}^2$  of Zr-95 were dissolved which corresponds to the following corrections.

Table 4.14 PH-Z3 Bulk Metal Dissolution Corrections

Element	Correction (nCi/cm <sup>2</sup> )	Measured (nCi/cm <sup>2</sup> )	Corrected (nCi/cm <sup>2</sup> )
Co-58:	160	45	<0
Co-60	31	17	<0
Fe-59	290	800	510
Mn-54	130	19	<0

For PH1-Z5, 170  $\mu\text{Ci}/\text{cm}^2$  of Zr-95 were dissolved which corresponds to the following corrections.

Table 4.15 PH1-Z5 Bulk Metal Dissolution Corrections

Element	Correction (nCi/cm <sup>2</sup> )	Measured (nCi/cm <sup>2</sup> )	Corrected (nCi/cm <sup>2</sup> )
Co-58:	120	410	< 0
Co-60	24	35	11
Fe-59	220	910	690
Mn-54	99	120	20

The corrections are very inconsistent. Some appear to be reasonable when compared to other segments within each run, but there is large variation from element to element and tube to tube. It is therefore concluded that the most prudent decision is to exclude the data from these five tubes in the compilation of overall results.

In the future a more accurate correction can be calculated using the actual fluence for each tube, determined, for example, in the manner discussed by Medina [M-3], and improved impurity concentration data. In addition, it may be that there are differences between surface impurities and bulk metal impurities; this possibility should be investigated, possibly by NAA studies.

## 4.6 Separation Experiment Results

The following two sections describe the results obtained from the two different zirconium separation procedures. The chemical separation method, which is the actual method used for the PCCL Zircaloy section decontamination, is described first, showing values obtained, and retention factors for the various elements of interest. The electrolytic separation results are also discussed.

### 4.6.1 Chemical Separation Results

To qualify the method for possible use, two trials using a tracer solution were made to determine zirconium separation factors and transition metal retention factors.

A tracer solution was prepared by taking a 1/100 dilution of the Zircaloy decontamination solution PL1-Z5 #3 (third aqua regia decontamination step of PL1-Z5) which contains both Zr-95 activity and Co-58 activity. This solution was counted at the gamma counting facility and the specific activities of Co-58 and Zr-95 recorded as baseline measurements.

3 ml of  $ZrOCl_2 \cdot 8H_2O$  solution and 3 ml of sodium arsenate solution were added to 50 ml of the tracer solution and allowed to sit for 30 minutes. The resulting solution/precipitate was centrifuged at 2000 rpm for 5 minutes. The liquid was then decanted from the centrifuge tube.

The precipitate was rinsed with 10 ml of wash solution and the solution/precipitate centrifuged again for an additional 5 minutes at 2000 rpm.

The liquid was decanted again. All the liquid was then combined, diluted to 110 ml and counted at the gamma counting facility. The concentrations of Co-58 and Zr-95 were compared with the original assays to establish both a zirconium removal factor and a cobalt retention factor. The retention factor data indicated an average of 95% transition metal retention, with no less than 90% retention on any individual element. The zirconium separation factor was 200, i.e. the Zr-95 activity was reduced by a factor of 200 in the decontamination solution.

For the second trial, slight modifications and additions were made to the procedure followed in the above trial. A new tracer solution was used for this trial. 20 ml of PL1-Z5 #1 solution was placed in each of two 50 ml centrifuge tubes.

Only 2 ml additions of the  $ZrOCl_2 \cdot 8H_2O$  solution and of the sodium arsenate solution were added to each centrifuge tube. The centrifuge times were increased to 15 minutes and the centrifuge speed increased to 3000 rpm. After centrifuging, 10 ml from the top of each of the centrifuge tubes was pipetted and diluted up to 110 ml for gamma spectroscopy. This was done to minimize entrainment of zirconium precipitate into the solution.

The remaining liquid in each centrifuge tube was combined, filtered and diluted to 110 ml for gamma spectroscopy. This step was done to determine the extent of zirconium precipitate carry-over into the decanted solution and also to determine if a concentration gradient of the isotopes of interest is established in the solution during centrifuging. The results were almost identical to the first trial.

PR1-Z1 and PR1-Z3 were the first two pieces handled and were not decontaminated like the rest. PR1-Z1 was directly counted since it was from the out-of-core-region and had decayed 6 months. After some very destructive decontaminations, the tube was recounted and the difference taken as a rough Co-58 concentration.

The first 4 tubes decontaminated using the standardized technique (PL1-Z5, PL1-Z10, PL1-Z7, and PL1-Z8) were prepared by first painting the outside of the tube with (pink) Krylon paint. This was used to inhibit and provide visual indication of exterior base metal dissolution by the aqua regia. A piece of irradiated kynar shrink tubing was then used to cover the Zircaloy tube to further minimize attack on the outside of the tube. The aqua regia solution was prepared as described in section 3.6. They then underwent 3 separate 3 hour soaks in an aqua regia solution.

It is important to note that only the PH1 tubing was decontaminated exactly as described in section 3.6. The main difference is that these precipitations were done with the cobalt chloride carrier

and with 3 wash steps. The first three runs were decontaminated without the cobalt carrier and with only 2 washes.

The separation results of the Zircaloy section decontaminations in aqua regia are presented in Table 4.16. These values are compared with those first obtained in Table 4.10, and retention percentages for the transition metals of interest along with zirconium separation factors are displayed in Table 4.17. Ideally, tables 4.10 and 4.11 should agree for transition metals and Zr-95, activity should be much reduced in table 4.11.

Table 4.16 Zircaloy Radionuclides Determined Using Chemical Separation

Test Piece	Zr-95 nCi/cm <sup>2</sup>	Transition Metal Concentrations in nCi/cm <sup>2</sup>			
		Co-58	Co-60	Fe-59	Mn-54
PR1-Z1†	-	-	-	-	-
PR1-Z3††	-	79 ± 4.9	100 ± 1.6	430 ± 29	280 ± 2.3
PR1-Z5	-	91 ± 2.3	22 ± 0.41	-	11 ± 0.26
PR1-Z7	7.9 ± 1.2	37 ± 1.6	14 ± 0.30	31 ± 9.5	4.8 ± 0.19
PR1-Z8	7.3 ± 1.7	40 ± 1.7	15 ± 0.31	-	4.4 ± 0.19
PR1-Z10	3.2 ± 0.45	25 ± 2.0	9.3 ± 0.23	12 ± 14	2.2 ± 0.15
PR1-Z12	11 ± 2.1	5.0 ± 1.3	6.3 ± 0.19	<17	0.49 ± 0.14
PR1-Z14	7.5 ± 2.0	4.3 ± 1.2	0.63 ± 0.09	<14	0.29 ± 0.09
PR2-Z1	-	1.3 ± 0.54	0.31 ± 0.09	-	0.14 ± 0.08
PR2-Z3	14 ± 1.5	4.1 ± 0.49	2.9 ± 0.13	12 ± 3.1	0.60 ± 0.10
PR2-Z5*	-	380 ± 5.5	54 ± 1.1	440 ± 15	110 ± 1.9
PR2-Z7	14 ± 1.0	200 ± 2.0	17 ± 0.36	33 ± 4.1	5.9 ± 0.18
PR2-Z8	5.2 ± 0.46	160 ± 2.0	19 ± 0.37	26 ± 4.2	4.9 ± 0.17
PR2-Z10*	1200 ± 160	560 ± 5.4	44 ± 0.80	240 ± 18	77 ± 0.77
PR2-Z12	6.1 ± 0.76	16 ± 0.66	4.8 ± 0.16	14 ± 0.33	1.1 ± 0.10
PR2-Z14	-	-	0.21 ± 0.09	-	0.09 ± 0.08
PL1-Z1	1.9 ± 0.30	1.7 ± 0.27	0.50 ± 0.09		0.27 ± 0.07
PL1-Z3	2.0 ± 0.74	5.5 ± 0.80	6.2 ± 0.20	8.9 ± 2.3	0.74 ± 0.09
PL1-Z5*	1200 ± 250	1300 ± 14	200 ± 4.0	930 ± 23	310 ± 2.9
PL1-Z7	15 ± 3.7	1100 ± 12	110 ± 2.5	180 ± 19	45 ± 1.5
PL1-Z8	4.2 ± 0.7	910 ± 1.	79 ± 3.4	34 ± 13	48 ± 1.3
PL1-Z10	53 ± 2.8	620 ± 5.8	120 ± 2.1	180 ± 7.9	60 ± 1.0
PL1-Z12†††	-	-	-	-	-
PL1-Z14	2.0 ± 0.39	2.3 ± 0.27	0.45 ± 0.09	-	0.30 ± 0.07
PH1-Z1	1.8 ± 0.36	2.1 ± 0.24	0.24 ± 0.12	15 ± 1.4	1.5 ± 0.14
PH1-Z3*	280 ± 24	45 ± 1.3	17 ± 0.41	800 ± 14	19 ± 0.33
PH1-Z5*	19 ± .19	410 ± 5.6	35 ± 0.89	910 ± 26	120 ± 2.4
PH1-Z7	20 ± 1.9	150 ± 1.5	0.84 ± 0.14	6.8 ± 1.4	0.96 ± 0.09
PH1-Z8	45 ± 3.5	140 ± 1.7	7.7 ± 0.29	220 ± 5.0	26 ± 0.35
PH1-Z10	63 ± 1.9	37 ± 0.63	0.53 ± 0.12	14 ± 1.4	1.6 ± 0.13
PH1-Z12	100 ± 3.2	2.2 ± 0.27	1.8 ± 0.12	93 ± 3.8	1.4 ± 0.10
PH1-Z14	1.3 ± 0.33	0.62 ± 0.17	0.2 ± 0.09	<0.8	0.05 ± 0.05

- † PR1-Z1 was counted directly with no prior separation done
- †† PR1-Z3 had no shrink tube, and therefore had lead contamination
- ††† PL1-Z12 separation solution was lost in an accident
- \* These pieces require an activity correction, see section 2.8.2
- Indicates that the activity in question was not detected.



Table 4.17 Separation Retention Results

Test Piece	Zr-95 DF	Transition Metal Retention, %			
		Co-58	Co-60	Fe-59	Mn-54
PR1-Z1†	-	-	-	-	-
PR1-Z3††	-	100 ± 7	100 ± 2	98 ± 10	100 ± 1
PR1-Z5	-	48 ± 3	50 ± 2	-	73 ± 3
PR1-Z7	430 ± 66	82 ± 6	88 ± 3	-	94 ± 6
PR1-Z8	640 ± 150	71 ± 6	75 ± 3	-	79 ± 6
PR1-Z10	190 ± 27	52 ± 9	66 ± 3	-	73 ± 9
PR1-Z12	90 ± 19	54 ± 17	57 ± 4	-	94 ± 34
PR1-Z14	3.5 ± 1	78 ± 34	86 ± 14	-	-
PR2-Z1	-	93 ± 50	74 ± 36	-	-
PR2-Z3	290 ± 31	58 ± 16	85 ± 7	100 ± 54	64 ± 22
PR2-Z5*	-	-	100 ± 34	-	91 ± 15
PR2-Z7	430 ± 35	100 ± 2	94 ± 3	100 ± 21	98 ± 7
PR2-Z8	370 ± 34	94 ± 2	100 ± 3	90 ± 36	98 ± 5
PR2-Z10*	175 ± 25	100 ± 6	100 ± 7	-	100 ± 10
PR2-Z12	410 ± 52	100 ± 6	92 ± 5	-	100 ± 14
PR2-Z14	-	-	48 ± 47	-	32 ± 99
PL1-Z1	24 ± 3.8	52 ± 18	83 ± 25	-	53 ± 31
PL1-Z3	335 ± 120	50 ± 16	78 ± 4	81 ± 37	93 ± 19
PL1-Z5*	290 ± 66	100 ± 7	100 ± 17	-	-
PL1-Z7	170 ± 43	100 ± 2	100 ± 2	100 ± 16	100 ± 5
PL1-Z8	220 ± 37	98 ± 1	90 ± 5	100 ± 62	98 ± 27
PL1-Z10	170 ± 5	100 ± 2	100 ± 3	100 ± 8	100 ± 3
PL1-Z12†††	-	-	-	-	-
PL1-Z14	6.5 ± 1.3	31 ± 13	30 ± 23	-	75 ± 31
PH1-Z1	7.8 ± 1.7	95 ± 24	100 ± 75	-	100 ± 21
PH1-Z3*	790 ± 75	-	100 ± 31	100 ± 11	-
PH1-Z5*	8900 ± 960	100 ± 7	95 ± 10	100 ± 8	100 ± 10
PH1-Z7	240 ± 23	100 ± 2	100 ± 28		100 ± 22
PH1-Z8	210 ± 18	100 ± 2	97 ± 6	100 ± 4	100 ± 2
PH1-Z10	130 ± 7.5	100 ± 3	95 ± 38	88 ± 19	100 ± 16
PH1-Z12	22 ± 0.8	-	-	-	-
PH1-Z14	55 ± 3.6	67 ± 44	67 ± 56	-	30 ± 110

† PR1-Z1 was counted directly before and after decontamination

†† PR1-Z3 had no shrink tube and therefore had lead contamination

††† PL1-Z12 separation solution was lost in an accident

\* These values were calculated using uncorrected values.

- Indicates that either the pre or post separation results had no values so no retention factors could be calculated..

In general, the separation results were very good for in-core pieces where there was both higher Zr-95 and higher transition metal activities with retention factors reaching 100% for most samples except for the PR1 Zircaloy. The PR1 Zircaloy had very low activities overall (approximately 1 year decay before assay) and since no cobalt carrier was used, it is assumed that retention suffered from the lower concentrations.

The results for the out-of-core Zircaloy were not as good with the majority of the retention factors less than 70%. The reason is not clear, but overall activities were much lower, and the crud levels were also usually a factor of 10 lower (Table 4.10).

There was much room for uncertainty in the chemical separation procedure. The error in measuring the 20 ml aliquot is about 5%. In the actual separation process, some coprecipitation of transition metals will occur, so that effective washing of the precipitate is very important.

#### 4.6.2 Electrolytic Separation Results

The preliminary tests involving electrolytic separation of transition metals in solution from zirconium were unsuccessful. The trials were limited due to the lack of a clear set of operating procedures for the present conditions: i.e. separation of cobalt and other transition metals from a zirconium laden aqua regia solution containing the transition metals. Table 4.18 displays the results for the electroplating experiments.

Table 4.18 Electrolytic Separation Results

Trial	Solution ID	Applied Voltage	Solution pH	Plating Time (minutes)	Plating Efficiency
1	PR1-Z3 #1	1.0	0	10	0%
2	PR1-Z3 #1	1.0	0	20	0%
3	PL1-Z8 #1	1.0	0	10	0%
4	PL1-Z8 #1	1.0	0	20	0%
5	PL1-Z8 #1	2.0	0	20	0%
6	PL1-Z8 #1	2.0	14	20	0%
7	PL1-Z8 #1	3.0	14	20	0%
8	PL1-Z8 #2	14.0	3.5	20	5%
9	PL1-Z7 #3	9.0	3.5	20	10%

Note: Solution made basic (trials 6 and 7) by adding NaOH  
 Plating efficiency = % Co-58 activity successfully plated.

The possibilities of this approach have by no means been completely tested. The pH levels used here are at extremes, and therefore could have had large influence on the success of electroplating. A very low pH is detrimental because of hydrogen formation at the cathode at low voltages, due to the low electrochemical potential of hydrogen, which prohibits electroplating. A very high pH can be equally detrimental because of the large resistivity of the subsequent solution, that can make it very difficult for the ions to make their way to the cathode for plating. It is not clear whether the voltages applied in our tests contributed to the lack of success. If further

work in electrolytic separation is undertaken, the various relevant parameters will require further study and optimization.

#### 4.7 Peroxide/Boric Acid Addition Results

The experiments for the peroxide/boric acid additions were carried out as described in section 3.8. Four bottles containing 50 ml of the desired coolant were placed in a heated water bath maintained at 90°C. The other four bottles were left open at room temperature for the eight hour duration of the experiment. The results are shown in Table 4.19.

Table 4.19 Test Matrix For Boric Acid/Peroxide Additions

Test Piece†	T °C	Boron (ppm)	Lithium (ppm)	Co-58 (nCi/cm <sup>2</sup> )		DF
				Before	After	
118-121	90	800	1.84	18	16	1.1
115-118	90	2000	1.84	16	16	1.0
121-124	90	2000	5.15	19	17	1.1
124-127††	90	2000	5.15	19	17	1.1
103-106	22	800	1.84	19	18	1.1
106-109	22	2000	1.84	18	18	1.0
109-112	22	2000	5.15	17	16	1.1
112-115††	22	2000	5.15	14	14	1.0

† All sample Inconel Tubes were taken from PR2 at the indicated position.

†† These samples also had 10 ppm hydrogen peroxide added to the coolant.

There does not seem to be much of a difference in DFs for the different runs, and not much activity at all was removed, in general. In fact, one can basically assert that no removal was evident for all the samples. What can be hypothesized from this is that, since in practice there is significant crud removal when boric acid and/or peroxide is injected during plant shutdown, this is not a representative test for the power reactor situation. There was no flow, and the tests were performed months after shutdown, with the Inconel tubing samples being exposed to air the entire time. A true shutdown test must be performed during a clearly-simulated shutdown, while cooldown is occurring.

#### 4.8 Chapter Summary

This chapter summarizes and evaluates all the data obtained during the subject work. Section 4.2 gives the results for the chemically decontaminated Inconel tubes. All trials gave DFs between 1.4 and 2.2, and the results were judged not to be the best achievable. Better results could probably be obtained if conditions were better optimized.

Section 4.3 discussed the results obtained from the descaling experiments on contaminated Inconel tubes. Two different techniques were employed, ultrasonic descaling in the presence of nitric acid and electropolishing using phosphoric acid. The ultrasound with 5% nitric acid successfully de-scaled all but PL1 Inconel tubes. Electropolishing with phosphoric acid removes all crud types. All other electropolishing results and ultrasonic de-scaling results were also presented in this section. The sodium sulfate cathodic/anodic

alternation electropolishing gave a good DF but since a sludge was formed, it became more difficult to analyze. The Mitsubishi method resulted in low DFs as applied but could probably be optimized for higher removal..

Section 4.4 discussed the crud "toughness" comparison results obtained by application of the POD process and the ultrasonic process. The ultrasonic tests showed that PL1 was the most difficult to de-scale; all other samples were completely de-scaled. The POD process was unable to remove all oxide and deposited crud but gave the highest DFs on Inconel tubing samples from the low pH run.

Sections 4.5 and 4.6 discussed the Zircaloy decontamination results. Section 4.5 gave the results for the aqua regia decontaminated pieces including dilute counting of the subsequent solutions. Section 4.6 described the results obtained from the two methods used for zirconium/transition metal separation. Both chemical separation and electrolytic separation were attempted. The chemical separation method was very successful, but the electrolytic separation failed.

The chapter concluded with the results of the post shutdown peroxide/boric acid addition experiments, in section 4.7, which gave inconclusive results relative to the original purpose of these comparisons.

## **5. SUMMARY AND CONCLUSIONS**

### **5.1 Introduction**

An in-pile loop facility to simulate PWR primary coolant system behavior has been constructed at the MIT Nuclear Reactor Laboratory under Electric Power Research Institute (EPRI) and Empire State Electric Energy Research Corporation (ESEERCO) sponsorship [S-1]. A complementary research effort is being conducted under MIT Electric Utility Program auspices; a significant portion of the work described in this thesis was supported under this program. The principal objective of research using the loop, now completing its first campaign and beginning the second, is the optimization of coordinated  $\text{LiOH}/\text{H}_3\text{BO}_3$  pH control to minimize radionuclide deposition on plant surfaces. As a result of this work an inventory of simulated components (Inconel steam generator tubes, Zircaloy fuel surfaces, stainless steel plena) with radionuclide deposits laid down under carefully controlled and prototypic chemistries are being generated.

The work described in this thesis utilizes this inventory for two general categories of activity: testing and evaluation of chemical decontamination methods used in the nuclear industry, and development and qualification of methods for characterizing the activities deposited on PCCL components during irradiation experiments, including a comparison of the decontamination resistance - "toughness" - of crud deposited in various pH environments. A large fraction of the experiments and results reported are concerned with the latter category of activity. In particular, methods for quantitative mea-

surement of surface deposited activities in the presence of activities generated by in-situ activation of the base metal are of interest. The measurements are generally performed at the conclusion of PCCL runs, and degradation of the structural properties of the materials as a result of decontamination is unimportant. In contrast, most decontamination procedures developed by the nuclear industry must be proven to be benign with respect to degradation of material performance and, with the exception of the specialized case of core crud/oxide sampling, are not concerned with activated substrates. The de-scaling processes of interest here are for three sections of the MIT PCCL; the activated section of the Inconel steam generator tubing, the stainless steel plenum, both of which are activated due to leakage of neutrons from the core of the MITR-II reactor, and the heavily activated Zircaloy section, of which 70% is in core.

In order to meet the objectives described above, a number of processes were tested. These included: chemical, ultrasonic and electrolytic decontamination. The problems associated with deposited activity characterization on activated substrates prompted supporting investigations into material impurity characterization (principally by NAA) and chemical separation techniques to remove interfering activities. Methods of correcting for base metal activity contributions to deposited activity measurements were developed and applied where necessary.

A small scoping study of post-shutdown activity transport considerations was also made. An evaluation of temperature, boration, oxygenation, and hydrogen peroxide addition was intended.



## **5.2 Summary of Results**

This section summarizes the results which were obtained in the areas discussed in section 5.1. Particular emphasis is placed on the de-scaling techniques which were used to provide deposited activity data for activated PCCL components.

### **5.2.1 Chemical Decontamination of Inconel**

The trial chemical decontaminations of Inconel tubes (except for those involving the AP/NP POD process) gave DFs between 1.0 and 2.2 which were considered not to be the best achievable. However, better results could probably be obtained if conditions were optimized. The POD process results were much more encouraging, giving DFs ranging from 3.6 to 13. It was also determined that the combination of the AP/NP step was far superior to the NP step alone, which gave DFs of less than 2.

### **5.2.2 Inconel Tube De-scaling for Deposited Activity**

Two different techniques were employed to de-scale activated Inconel tubes: ultrasonic descaling in the presence of nitric acid, and electropolishing using phosphoric acid. The ultrasound with 5% nitric acid successfully de-scaled Inconel tubes from all of the first campaign runs except that at low pH ( $\text{pH}_{300^\circ\text{C}} = 6.5$ ). Electropolishing with phosphoric acid removed crud from all Inconel tube samples.

The sodium sulfate cathodic/anodic alternation electropolishing gave a good DF, but since a sludge was formed, it was more difficult to analyze. The Mitsubishi electrolytic de-scaling method had low DFs as applied in the current work. Optimization of the conditions for PCCL crud is assumed to be necessary.

### 5.2.3 Crud "toughness" Comparison

The crud "toughness" comparison results obtained by application of the POD process and the ultrasonic process yielded interesting results. The ultrasonic tests showed that PL1 tubing (which had crud deposited at  $\text{pH}_{300^\circ\text{C}} = 6.5$ ) was more difficult to de-scale than PR1 and 2 ( $\text{pH}_{300^\circ\text{C}} = 7.0$ ) and PH1 ( $\text{pH}_{300^\circ\text{C}} = 7.5$ ), which were completely de-scaled by ultrasound in 5% nitric acid.. The POD process was unable to remove all oxide and deposited crud but gave better DFs (about 7-13) on PL1 Inconel than on that from the other runs (about 4-5). Unlike what was expected, the crud from the low pH run was the most difficult to completely de-scale. The POD process did, however, display a better DF on the low pH than the high pH, but close inspection of the tube showed that an oxide film remained, and the POD process probably leached out some activity from the oxide.

### 5.2.4 Zircaloy De-scaling and Zirconium Separation

The Zircaloy section de-scaling consisted of soaking the tubes in aqua regia for 12 hours. DFs of about 50-100 were attained. The as-

say was performed on a 20/110 ml dilution of the subsequent decontamination solution. Solutions contained high levels of Zr-95, therefore zirconium separation was desirable.

Both chemical separation and electrolytic separation of zirconium from transition metals were attempted. The chemical separation method was successful: reducing solution Zr-95 activities by on the order of 100-500, while retaining approximately 90-100% of transition metals. The electrolytic separation method failed.

#### **5.2.1 Post-Shutdown Experiments**

The results of the post shutdown peroxide/boric acid addition experiments showed essentially no effect of these chemicals on tubing which had significant exposure to air after removal from the loop.

### **5.3 Conclusions**

A variety of decontamination and de-scaling tests were performed on more than 120 Inconel samples and 32 highly-activated Zircaloy samples. The POD chemical decontamination process has been qualified for use on PCCL samples and appropriate electropolishing and ultrasonic decontamination procedures have been established for the tubing sample geometry used. In the de-scaling of the Zircaloy tubing section, bulk metal and/or  $ZrO_2$  dissolution occurred,

creating solutions containing high Zr-95 activity which made transition metal radionuclide assay difficult.

The success of the ultrasonic de-scaling of the Inconel sections was encouraging, in that with the tubing exposed at reference and high pH, the only pHs currently used in actual PWR practice, virtually all crud and oxide was removed. Another interesting finding was that ultrasonic decontamination using water alone gave decontamination factors of about 2 on unactivated Inconel. This would suggest that about half of the crud is "loose" and can readily participate in transport, while the other half of the deposited activity is chemically bound in an adherent oxide layer.

#### **5.4 Recommendations for Future Work**

Based upon the experience accumulated during the course of the work described in this report, a number of areas deserving of further investigation have been identified, as follows.

(1) As far as continuing the present work, there are several areas which cannot be concluded as completed. One of these areas is ultrasonic de-scaling. Several reagents have been tried in the ultrasound process, but improvements over 5% nitric acid may still be possible.

(2) Better refinement of the Mitsubishi process can lead to better crud characterization in separating "inner" from "outer" oxide layers. Base metal removal using anodic/cathodic alternation electropolish-

ing is described in the literature [B-1] as being much lower than in anodic electropolishing, and hence further investigation is in order.

(3) Another area needing considerable refinement is that of the electrolytic separation of zirconium from transition metals.

(4) The peroxide/boric acid addition experiments were very narrow in scope. Much more elaborate tests of cooldown/shutdown chemistry effects will be necessary, including better simulation of the cooldown process, and prevention of contact with air prior to the tests.

(5) The stainless steel plena of the PCCL loops were not decontaminated during the present work, and the best method to de-scale the plena is not yet clear. It is known that ultrasound attacks stainless steel more strongly than the other PCCL metals, and therefore an evaluation of base metal dissolution needs to be made before the plena can be ultrasonically de-scaled. Electropolishing should also be considered as a potential de-scaling method for the plena, provided that a burr sample is taken at the point where the plenum is to be de-scaled for bulk metal specific activity determination and correction of decontamination solution activity.

(6) Electropolishing of Zircaloy to remove crud deposits for subsequent assay should be attempted. Based on Faraday's law, the base metal removal for a one minute electropolish should be about 12.6 mg, which would correspond to 126  $\mu\text{Ci}$  of Zirconium activity. This would correspond to a cobalt 58 correction of 15  $\text{nCi/cm}^2$  and a cobalt 60 correction of about 3  $\text{nCi/cm}^2$  from the nickel and cobalt

impurities in the Zircaloy. These values are on the order of 1/4 typical activities encountered in the crud deposited on the Zircaloy. If base metal removal could either be reduced or better characterized, then electrolytic de-scaling would be a useful method. It is definitely much quicker than using aqua regia, and one can be better assured that all the crud is removed.

(7) The use of ultrasound in the de-scaling of the Zircaloy section should also be investigated. One could begin by studies on unactivated Zircaloy tubes, and then once a promising method is developed, attempt it on actual activated Zircaloy from one of the PCCL runs, comparing the crud removal results with those of an adjacently cut piece de-scaled using the conventional aqua regia method.

(8) Full system activity transport, decontamination and recontamination experiments should be considered using an out of pile loop containing sections of tubing from a PCCL run. An out of pile loop has already been constructed and is being currently used as a test loop for a canned rotor pump which is a candidate for use in future PCCL runs [E-1]. In particular, this loop can be used for evaluation of post-shutdown chemistry effects, including boron addition and hydrogen peroxide injection at various temperatures.

(9) Crud morphology, weight, and composition are important for determining the true nature of corrosion product deposits. SEM studies and surface analysis using Auger or other electron microprobe techniques should be considered. Chemical and x-ray characterizations of removed crud are also of interest.

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## Appendix A Cobalt in Zircaloy

Several indications from the earlier (see table 2.2) neutron activation analysis results gave rise to concern over the potential importance of cobalt impurity in Zircaloy cladding material, and hence in its surface oxide corrosion film.

This led to a more thorough investigation of this issue. The second NAA of the Zircaloy shown in table 2.3 gave more encouraging results. Table A-1 shows the results of calculations for a representative PWR. As can be seen, if the Zircaloy contains 1 ppm elemental cobalt, potentially releasable Co-60 activities can result, which are about 10% of those in plant corrosion product deposits.

While it is not clear that the cobalt inventory in zirconium oxide is free to participate in crud transport processes, our experience suggests that it may well be in particular circumstances: boiling, whole-core decontamination, and perhaps plant cooldown (during which solubility increases by a factor of on the order of  $10^4$ ).

Table A-1 Calculation of Co-60 in Zircaloy Oxide Layer

<u>Parameter</u>	<u>Value</u>	<u>Reference</u>
Zircaloy surface area	6000 m <sup>2</sup>	[M-1]
ZrO <sub>2</sub> thickness	20 μ	EPRI NP-2789
% theoretical density	90%	EPRI NP-2789
Density of Zr	6.52 g/cc	handbook
Density of ZrO <sub>2</sub>	5.85 g/cc	handbook
ppm Co in Zr	1	see Table 2.3
Cobalt activation rate	40 Ci Co-60/yr g Co	Appendix B
Cycle length	1 full power year	representative
Fuel residence in core	3 full power years	fuel management

Note that during a typical full power year, the average capacity factor for a PWR plant is about 65%.

(2) Computed Inventories (assuming all Co remains in ZrO<sub>2</sub>) for Steady-state Fuel Cycle, linear generation of ZrO<sub>2</sub>, Co-60

		<u>Mid Cycle</u>	<u>End of Cycle</u>
Newest Batch	kg ZrO <sub>2</sub>	35	70
	g Co	0.025	0.05
	Ci Co-60	0.5	2
Middle Batch	kg ZrO <sub>2</sub>	105	140
	g Co:	0.075	0.1
	Ci Co-60	4.5	8
Oldest Batch	kg ZrO <sub>2</sub>	175	210
	g Co	0.125	0.15
	Ci Co-60	12.5	18
Total Core Inventory	kg ZrO <sub>2</sub>	315	420
	g Co	0.225	0.3
	Ci Co-60	17.5	28

(3) Steady State Plant Inventory of Co-60 Assuming all Co-60 in ZrO<sub>2</sub> is released during base metal corrosion (assuming constant corrosion rate)

Release per (one year) cycle from:

	<u>gm Co</u>	<u>Avg Ci/g</u>	<u>Ci Co-60</u>
Newest Batch	0.05	20	1
Middle Batch	0.05	60	3
Oldest Batch	0.05	100	5
Total	0.15		9

Release rate to cooling system = 9 Ci/yr

Steady State Plant Inventory:

$$\frac{9 \text{ Ci}}{\text{yr}} = 9 \left( \frac{5.27}{0.693} \right) = 68 \text{ Ci}$$

This is larger than in part (2) because refueling removes 18 Ci/yr in that case.

(4) Compare to Representative nickel ferrite Crud deposit inventories:

(a) On Core [M1]: ~ 600 Ci Co-60 and 20 g Co

(b) On all ex-core surfaces [B-6] ~ 500 Ci Co-60

As noted, the preceding analysis is based upon a nominal cobalt content of 1 ppm. Values available to date are listed in table 2.3. They show values consistent with about 1 ppm. The comparison shows that 1 ppm cobalt in base metal Zircaloy could increase plant cobalt activities by about 10%; if listed levels of cobalt are higher

than 1 ppm, then the Curie contribution in Table A-1 can be multiplied by the ppm of cobalt present.

Cobalt in Zircaloy may become of greater importance in the future, since it may set a lower limit on current transport reduction strategies, e.g.:

- (a) At high pH, solubility gradients tend to move cobalt from the core to the steam generators.
- (b) There is some indication that high lithium concentrations increase Zircaloy corrosion rates.
- (c) The current trend, in some quarters, to move to 18 or 24 month fuel cycles could lead to 50-100% increases in Zircaloy corrosion, hence cobalt release, and at a higher specific activity.

In any event, this phenomenon appears worthy of further investigation. If nothing else, it can frustrate attempts to test transport models using loop or reactor core crud activity measurements. If it does prove to be an important contributor, then there is some comfort to be taken in the fact that already-built plants can benefit by use of low-cobalt Zircaloy in future core reloads.

### Other Considerations

Zircaloy also contains nickel, hence the  $ZrO_2$  film will also accumulate Co-58, which can contribute to the core and reactor cooling system inventory of that radionuclide. Assay of the PCCL Zy-4 indicates approximately 100 ppm Ni; the resulting inventory is negligible compared to the amount in core crud (~ 3.5 kg).

The question is sometimes raised as to whether  $ZrO_2$  can, by ion exchange or absorption, take up a significant amount of cobalt. At the recent Bournemouth conference, equilibrium constants for specially prepared  $ZrO_2$  high temperature ion exchange media were reported (B-7) for Co-60 at 300°C:

$$K = 1.4 \times 10^3 \frac{\text{ppm Co in } ZrO_2}{\text{ppm Co in } H_2O}$$

Thus, if the circulating coolant contains 0.013 ppb Co [B-8], the cycle-average core  $ZrO_2$  inventory of 315 kg (see Table A-1) might contain as much as 5.7 mg Co – which is negligible compared to the cobalt impurity in the base metal (hence its oxide) or in the surface crud deposits.

## Appendix B Cobalt Activation Rate

In the core of a nuclear reactor, cobalt will be activated at the rate

$$A_{60} = (\lambda) \left( \frac{1}{A} \right) \left( \frac{N_A}{1 \text{ Curie}} \right) (\sigma_{59} \phi) \text{ Ci/g yr}$$

where  $N_A$  is Avogadro's number,  $\lambda$  is the decay constant,  $A$  is the atomic weight,  $\sigma_{59}$  is the cross section, and  $\phi$  is the neutron flux.

Therefore, for Co-60 in a reactor;

$$\begin{aligned} A_{60} &= \left( \frac{0.693}{5.27} \right) \left( \frac{1}{59} \right) \left( \frac{6.023 \times 10^{23}}{3.7 \times 10^{10}} \right) (\sigma_{59} \phi) \text{ Ci/g yr} \\ &= 3.63 \times 10^{10} (\sigma_{59} \phi) \text{ Ci/g yr} \end{aligned}$$

The effective neutron flux can be estimated from the burnup rate of fresh fuel. The grams of U-235 fissioned per year per gram of U-235 loaded is merely:

$$3.16 \times 10^7 \sigma_{25} \phi = \frac{gB}{10^6 X(1+\delta_{28})}$$

where

- $g$  = grams U=235 fissioned per MWd (0.96)
- $B$  = burnup rate of fresh fuel (13,000 MWd/MT per yr)
- $X$  = enrichment of fresh fuel ( $3.5 \times 10^{-2}$ )
- $\delta_{28}$  = ratio of U-238 to U-235 fissions ( $6 \times 10^{-2}$ )

Hence we have

$$\sigma_{25} \phi = 1.06 \times 10^{-8}$$

So that

$$A_{60} = 385 \left( \frac{\sigma_{59}}{\sigma_{25}} \right) \text{ Ci/g yr}$$



The required cross section ratio, considering epithermal reactions is just:

$$\left(\frac{\sigma_{59}}{\sigma_{25}}\right) = \frac{\sigma_{t59} + RI_{59} \left(\frac{\sigma_{t25}}{RI_{25}}\right) \delta_{25}}{\sigma_{25} (1 + \delta_{25})}$$

where

$\sigma_{t59}, \sigma_{t25}$  = thermal maxwellian average cross sections for capture in Co-59 and fission in U-235, respectively (33b, 507b)

$RI_{59}, RI_{25}$  = resonance integrals for capture in Co-59 and fission in U-235, respectively (77b, 282b)

$\delta_{25}$  = ratio of epithermal to thermal U-235 fissions  
(0.2)

Thus, for the above-cited parameters

$$\left(\frac{\sigma_{59}}{\sigma_{25}}\right) = 0.10$$

Finally, then,  $A_{60} \approx \underline{40}$  Ci/g yr,

a value consistent with representative vendor CRUDSIM and PACTOLE computations, which employ 31 and 50 Ci/g yr, respectively.

For long irradiations compared to the half life of Co-60 (5.27 yrs), a saturated level of  $40(5.27/0.693) = 300$  Ci/g would be reached.

## Appendix C Cobalt In-Situ Activity in PCCL Zircaloy

Let's assume at the end of a 21 day PCCL run:

1 ppm Co in Zr

3  $\mu$  Zr corroded

40 Ci/year [Appendix B], x (21 days)/(365 days/year)

= 2.3 Ci/g cobalt activation

This computes out to a Co-60 contamination in the oxide layer of 4.6 nCi/cm<sup>2</sup>. For 5 ppm cobalt (original measured value, table 2.2), this value would be about 23 nCi/cm<sup>2</sup>.

Three microns of Zr corresponds to approximately 200 mg/dm<sup>2</sup>; at 1 ppm Co the surface density of the latter is 0.2  $\mu$ g/dm<sup>2</sup>. This is linear with ppm cobalt.

Compare this to crud: about 1 mg/dm<sup>2</sup> should accumulate (in core) in one month, of which 0.17% is expected to be cobalt, or about 2  $\mu$ g/dm<sup>2</sup>. If cobalt is present to the extent of only 1 ppm in the Zr then it is only about 10% of total cobalt, whereas, if it is 5 ppm, then cobalt in the ZrO<sub>2</sub> corrosion film can be as high as 50% of that in the crud.

Thus in-situ cobalt may be significant compared to crud cobalt. This circumstance greatly complicates the data acquisition and interpretation process, since separating out the two components appears to be a quite difficult task.

## Appendix D Recommended Procedures

This appendix summarizes the final version of all procedures for the work presented in this thesis. Recommendations for changes to each of the procedures are also given.

### Table D1 Inconel Chemical Flow-Through Decontaminations

Cut a 3 cm piece of Inconel tubing from the steam generator section and count it at the gamma spectroscopy (section 3.2.1) facility.

The sample bottle is filled with approximately 90 ml of the desired chemical agent and then placed in the heated water bath where it is heated to approximately 50°C.

The tygon tubing is attached to the Inconel tube by sliding the ends of the tygon tubing over the ends of the Inconel tube. The peristaltic pump is used to flow the chemical through the Inconel tube for 2 hours. The flow comes out of the bottle, through the Inconel tube, and back into the bottle so that the solution is reused. The entire setup is shown in Figure 3.2.

Recommended Changes: 90°C is recommended for the application temperature instead of 50°C, since it is a characteristic chemical decontamination application temperature [W-1].



Heat up ultrasonic bath to 60°C along with beaker containing 70 ml of HNO<sub>3</sub> solution.

Place Inconel tube sample in beaker, inside ultrasonic bath and turn power on for 5 minutes rotating tube sample occasionally.

Visually inspect tube to be sure oxide is removed, otherwise place in solution and ultrasonically clean for another 2 minutes.

Dilute solution with 50% HNO<sub>3</sub> solution to 110 ml and evaluate for radionuclide content.

Recommended Changes: Use a tube holder to suspend tube in the center of the solution and perform ultrasonic de-scaling in five minute steps, visually inspecting tube after each step.

#### Table D4 Anodic Electropolishing

A spring clip connects the positive lead from the power supply to the tube to make it the anode.

The stainless steel shaft located on the tube holder is the negative connection, making it the cathode in the electrolytic cell. The cathode lead is shielded with teflon tubing outside the teflon tube holder, as shown in Fig. 3.4, to prevent unnecessary reaction with the anode clip.

The tube to be decontaminated is placed in the holder and the holder is placed in a small beaker containing about 70 ml of the desired electrolyte.

The anodic step using the tube as the anode with a current density of  $0.1 \text{ A/cm}^2$  for 2 minutes is performed.

An ammeter and voltmeter are used to characterize the operating conditions, along with a thermometer located inside the controlled temperature heated water bath. The entire electropolishing setup is shown in Figure 3.5.

**Recommended Changes:** Employ electrolyte agitation using a stir bar, or a flow system out of the beaker through a peristaltic pump and back into the beaker. Also attempt to keep a more constant amperage.

**Table D5      Sodium Sulfate Cathodic/Anodic Alternation  
Electropolishing**

A  $\text{Na}_2\text{SO}_4$  ( $1.7 \text{ mol/dm}^3$ ) electrolyte is prepared for both the cathodic and anodic steps.

The cathodic step is performed for 1 minute using the centerline electrode of the above described setup (Table D4) as the anode and the test piece as the cathode. The current density required is  $0.3 \text{ A/cm}^2$ .

The anodic step then follows using the tube as the anode with a current density of  $0.3 \text{ A/cm}^2$  for 1 minute..

Recommended Changes: Attempt various cathodic times and anodic step times to optimize procedure for given conditions. Also carefully characterize base metal removal by weight change comparisons.

Table D6 Mitsubishi Cathodic/Anodic Alternation  
Electropolishing

A 0.15 N sulfuric acid (s.g.1.84) electrolyte is prepared for the cathodic step.

The cathodic step is performed for 2 minutes at room temperature using the centerline electrode of the above described setup (Table D4) as the anode and the test piece as the cathode. The current density required is  $0.1 \text{ A/cm}^2$ .

A 0.1 N nitric acid (s.g. 1.42) electrolyte is prepared for the anodic step.

The anodic step then follows using the tube as the anode with a current density of  $0.015 \text{ A/cm}^2$  for 1 minute at room temperature.

Recommended Changes: Attempt various cathodic times and anodic step times to optimize procedure for given conditions. Also carefully characterize base metal removal by weight change comparisons.

## Table D7 Zircaloy Section Aqua Regia Decontamination

The 3 cm pieces are prepared by first applying a piece of heat shrinkable tubing. The tubing is alpha FIT 750 adhesive wall polyolefin tubing (available from electronics supplies catalogues). The inner coating of thermoplastic adhesive melts when tubing is shrunk and completely coats the object. Upon cooling, the material reverts to its solid state and forms a waterproof bond.

Approximately 70 ml of aqua regia (defined in section 3.4) is poured into a 4 oz. standard polyethylene sample bottle.

The sample tube is placed into the bottle for a 12 hour soak.

The tube is removed from the bottle using 12" forceps and placed into a plastic funnel back on the sample bottle.

The sample tube is thoroughly rinsed and then placed into the hot box (section 3.2.3) for storage.

The solution in the sample bottle is diluted to 110 ml from which 20 ml is taken and diluted for gamma spectroscopy (3.2.1) and another 20 ml is taken to be used for zirconium separation (Table D8).

**Recommended Changes:** Soak in heated water bath to reduce total exposure time. Two 20 ml samples for direct dilution for gamma spectroscopy should be taken for comparison.



## Table D8          Zirconium Separation in Aqua Regia

A 1.5 M solution (50 grams/100 ml H<sub>2</sub>O) of sodium arsenate (FW 312.01) is prepared by mixing sodium arsenate in heated water.

A wash solution is prepared by diluting 1 ml of the sodium arsenate solution (above) to 100 ml using 2.4 N hydrochloric acid (HCL s.g. 1.19).

A 0.1 M zirconyl chloride (ZrOCl<sub>2</sub>·8H<sub>2</sub>O, FW 322.262) solution is prepared by mixing 3.22 grams of ZrOCl<sub>2</sub>·8H<sub>2</sub>O in 100 ml of deionized water at about 80°C.

Pipet 20 ml of the sample solution into a 50 ml centrifuge tube and another 20 ml into a 4 oz. bottle, dilute the bottle to 110 ml and count at the gamma counting facility to get baseline measurements.

Pipet 2 ml of the zirconium chloride solution into the centrifuge tube, add a small amount (about 200 mg) of cobalt chloride, and mix well.

Pipet 2 ml of the sodium arsenate solution into the centrifuge tube, mix by vortex agitation, and wait 30 minutes.

Put the centrifuge tube into the centrifuge and centrifuge at 3000 rpm for 15 minutes.

Decant the resulting solution through a standard 9 cm paper filter (Schleicher & Schuell Analytical Paper #595) into a 4 oz. poly bottle.

Add 5 ml of wash solution to the centrifuge tube containing the precipitate, mix by agitation, and centrifuge at 3000 rpm for 8 minutes. Pour off liquid into filter, adding to original filtered liquid.

Repeat above step twice so that a total of three washes are performed.

Dilute liquid in 4 oz. bottle up to 110 ml and count on gamma counting system to determine radionuclide concentration.

Compare post precipitation radionuclide concentrations with baseline measurement to obtain zirconium removal factor and transition metal retention factor.

**Recommended Changes:** Add an additional wash step, so that a total of four are performed. Also take two 20 ml aliquots and perform two independent separations on each Zircaloy decontamination solution for comparison.

#### Table D9 Electrolytic Separation Methods

The Zircaloy decontamination solution is adjusted to desired pH (0, 3.5, and 14) by adding NaOH.

A copper cathode is placed on one side of the solution bottle and a stainless steel 1/8" tube is used as the anode on the opposite side of the bottle. The desired voltage is applied to the system (1, 2, 3, 9, and 14) for 20 minutes.

**Recommended Changes:** Investigate optimal plating voltages and electrolyte pHs for the given setup and attempt longer plating periods. Also evaluate effect of addition of transition metal carriers.

**Table D10 Post Shutdown Boric Acid/Peroxide Additions**

The 3 cm sections of Inconel tube from the reference pH PCCL runs were first counted for specific activity at the gamma spectroscopy facility (section 3.2.1) and then put into 4 oz. bottles containing about 50 ml of the desired coolant. The bottles requiring the 90°C condition were then placed in a heated water bath and kept at 90°C for eight hours of exposure. The other four bottles (room temperature) were just kept on a lab bench, uncovered. After the exposure time, the tubes were recounted and the radionuclide removal and DF were determined.

**Recommended Changes:** Attempt to obtain Inconel tubing samples not exposed to air. Perform all tests in an argon filled glove box and perform aerated tests by bubbling oxygen through desired sample solution outside glove box.