CHLORINATION PROCESS DEVELOPMENT FOR ZIRCONIUM RECOVERY FROM USED FUEL CLADDING

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Development of a process for recovery and recycle of zirconium from used nuclear fuel (UNF) cladding was continued in 2014. New studies were done with non-radioactive cladding to determine (1) the quantitative effects of an anhydrous oxide coating layer on the subsequent chlorination reaction, (2) the effects of varying chlorination process parameters, and (3) scaling up the amount of cladding from 15 to 500 g. The larger amount produced greater than 1 kg of $ZrCl_4$ salt product.

I. INTRODUCTION

The second largest mass (~25%) in used nuclear fuel (UNF) is the zirconium in the cladding. In current practice, the cladding requires disposal in a geologic repository. Therefore, process development studies are being conducted to recover, decontaminate, and possibly recycle the valuable hafnium-free zirconium while keeping costs of the recovery process below those for current compaction treatment and disposal. The recovered product must contain lowered impurity concentration that would allow disposal as low-level waste or would be inconsequential to use in future nuclear applications, recognizing that the recovered zirconium will inherently contain ^{93}Zr (half-life = 1.5 million years and a weak beta radiation emitter). Radioactive impurities include uranium, transuranium elements, fission products, and activation products other than ^{93}Zr. Chemical impurities include tin, niobium, iron, nickel, chromium, nitrogen, oxygen, and carbon. Alternatively, the recovered zirconium must at least meet specifications for disposal as low-level waste.

Earlier developmental studies demonstrated that impurities can be removed from UNF cladding in a process that produces recovered zirconium which can be handled without shielding or significant dose.[1,2] However, the earlier feasibility tests with actual UNF cladding also showed that the presence of an apparent oxide layer on the cladding surface can cause an initial incubation period in the reaction of chlorine with the zirconium. Therefore, a series of nonradioactive tests were made in 2014 to determine, quantitatively, the reduction of chlorination reaction rate due to thickness of an anhydrous layer of zirconium oxide applied as a result of prior oxidation in air at 600°C for varying lengths of time and the succeeding mitigation of the reduced chlorination reaction rate by various prewashings with acidic or alkaline liquids or by dry treatment at elevated temperatures with argon gas saturated with carbon tetrachloride.

Further studies of the chlorination were done in 2014 to determine the effects of reactor temperature and chlorine concentration on the reaction rate. Finally, a series of tests were made to determine the effects of increasing the amount of cladding from 15 to 500 g per batch and to determine the heat removal requirements due to the exothermic heat of reaction in order to maintain the reactor temperature in the range of 350 to 400°C. In addition, product purification needs were assessed to determine experimental and analytical needs for future process development. For these studies, the glassware equipment configuration included a horizontal reactor and a vertical condenser (Fig. 1). The glass reactor was designed and built to fit a horizontal clam-shell furnace, thus enabling visual observation of zirconium alloy cladding tubes during chlorination. The vertical condenser was modified to include rotating wiper blades to prevent the condensed $ZrCl_4$ salt powder from collecting on the walls of the condenser and to promote movement into the collection bottle.
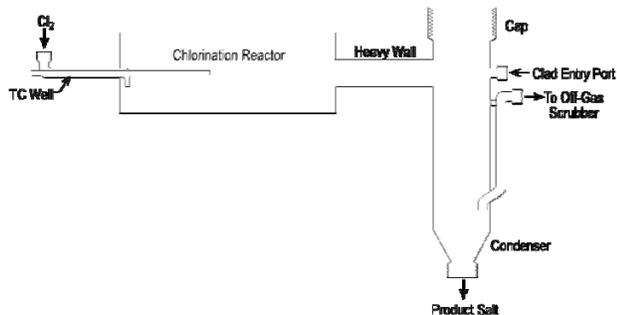
Fig. 1. Glass equipment configuration used for tests.

I.A. Oxide Layer Effects Tests

In 2014, a study was done using ~100 g samples of unirradiated cladding tubes to determine the effects of anhydrous oxide layers of varying thicknesses on the chlorination reaction rate and Cl_2 utilization efficiency, and to investigate various methods of chemical pretreatment prior to chlorination to mitigate the oxide layer effects. Dry oxidations of Zircaloy-Z-4 cladding tubes were made in air at $600^{\circ}C$ for 6, 12, and 72 hours, and dry oxidation of Zircaloy-2 cladding tubes in NO_2 at $350^{\circ}C$ for 12 hours. The weight gains and oxide layer thicknesses resulting from dry oxidations in air were initially linear, but decreased significantly during the 72-hour oxidation, likely because of the thick oxide layer deposited. Measurement results are shown in Table 1.

TABLE 1. Weight Gain and Oxide Thickness Measurements

	Weight gain, %	Avg. Rate, %/hour	Oxide Thickness, μm
6 hours in air at $600^{\circ}C$	0.67	0.11	~5
12 hours in air at $600^{\circ}C$	1.22	0.10	~11
72 hours in air at $600^{\circ}C$	6.7	0.093	~60
And in comparison			
12 hours in NO_2 at $350^{\circ}C$	0.056	0.0047	<1

Scanning electron microscopy and energy dispersive X-ray spectroscopy (EDS) analyses were made on the oxidized cladding to measure oxide layer thickness (Table 1) and the oxide species. The EDS analyses indicated species were a lower oxidation state than ZrO_2, the expected species, but this may have been due to a mixture of ZrO_2 and Zr metal in the analysis.

Mitigation methods tested included washing in concentrated nitric acid at 70°C, washing in nitric-oxalic acid mixture at $70^{\circ}C$, washing in alkaline peroxide at 20°C, and treatment with CCl_4-saturated argon at 550°C.

Results of the oxide layer thickness effects and mitigation pretreatment tests are shown in Table 2. Although the results did not show exactly proportionate comparisons, they did generally indicate increasing resistance to chlorination with increased oxidation time and oxide layer thickness. The results also indicate beneficial effects of pretreatment from both nitric acid washing and nitric-oxalic acid washing, with relatively greater benefits to the cladding with a thicker oxide layer (the 72-hour oxidized cladding).

TABLE 2. Comparison of Oxide Coating Thickness Effects on Chlorination Reaction

Cl_2 Chlorination	No Pretreatment	8M HNO_3 Wash	HNO_3 Oxalic Acid Wash
Unoxidized (no oxide)			
% Reacted	~ 100		
Average Rate % hour	32		
Cl_2 Utilization, %	~ 100		
6-hour air oxidation at 600°C			
% Reacted	86	~100	~100
Average Rate % hour	11	22	25
Cl_2 Utilization, %	47	70	70
12-hour air oxidation 600°C			
% Reacted	51[*]	77	79
Average Rate % hour	6.3[*]	9.6	9.9
Cl_2 Utilization, %	38[*]	52	51
72-hour air oxidation at 600°C			
% Reacted	15[*]	33[*]	70
Average Rate % hour	4.4[*]	4.9[*]	9
Cl_2 Utilization, %	19[*]	29[*]	50

[*]Observed incubation period before reaction started.

Since the thickest oxide layer was deposited during the 72-hour oxidation, that oxidized cladding was used for an expanded set of tests to compare the effectiveness of various mitigation methods of pretreatment on the subsequent chlorination reaction. The pretreatment with CCl_4-saturated argon was the most effective (Table 3). However, that process would require precise control since it can also chlorinate uranium and other fuel component oxides that may be present. Among the other pretreatment methods, prewashing with the mixture of nitric and oxalic acids was most effective. Optimization of that method would be worthwhile.

TABLE 3. Comparison of Effectiveness of
Pretreatment Methods of 72-hour Oxidized
Zircaloy-4 Cladding Tubes

Cl_2 Chlorination	No Oxide Layer	Oxide layer from 72-hour air oxidation at 600°C					
		No Pretreatment	8M HNO_3	Alkaline H_2O_2	Wire Brush	HNO_3-Oxalic Acid	CCl_4
% Reacted	~100	15*	33*	46	51	70	~100
Average Rate, % hour	32	4.4*	4.9*	6	6	9	13
Cl_2 Utilization, %	~100	19*	29*	32	39	50	70

* Observed incubation period before reaction started.

Table 4 compares chlorination results of 100 g samples of cladding oxidized in air at 600°C with cladding oxidized in NO_2 at 350°C. Both samples are compared to unoxidized cladding chlorination. The substantial increase in chlorination performance of the NO_2-oxidized material versus the air oxidized cladding may be due to the lower temperature and/or to the oxidation atmosphere, but the temperature levels have been shown to be optimum for the atmosphere used. The chlorination performance on NO_2 oxidized cladding is about 80% of the performance obtained on unoxidized cladding.

TABLE 4. Comparison of Oxide Layer Effects
from NO_2 Oxidation at 350°C

Oxidation Conditions Alloy type	12 hours in air at 600°C Zircaloy-4	12 hours in NO_2 at 350°C Zircaloy-2	Unoxidized Zircaloy-4
% Reacted	51*	~ 100	~ 100
Average Rate, %/hour	6.3*	26	32
Cl_2 Utilization, %	38*	83	~ 100

*Observed incubation period before reaction started.

In summary, the oxide layer and mitigation tests and analyses have shown, quantitatively, the increasing resistance to chlorination caused by increasing oxide layer thickness and the substantial benefit of pretreatment by acid washing of the oxidized cladding. While these results represent only the anhydrous oxide layers incorporated by dry oxidation, the indications may be similar for the hydrous oxide layers deposited by irradiations in light water reactors, particularly for longer irradiated and higher burn up used fuel cladding.

1.B. Process Parameter Tests

The results of the process parameter tests are summarized in Table 5. As indicated, the highest average reaction rates (31–32%/h) and chlorination utilization (77–100%) were obtained with 100% Cl_2 in the feed gas.

The decrease in effective reaction rate using a feed gas of Cl_2 diluted in argon was ~31% at 350°C (from 32%/h to 22%/h) and ~16% at 400°C (from 31%/h to 26%/h). These decreases are not considered too appreciable because the average reaction rate was still in the range of 22 to 27%/h.

TABLE 5. Effect of Cl_2/Ar
Ratio and Chlorination Temperature

Cl_2/Ar Ratio	100/0	75/25	33/67
Unoxidized Zircaloy-4 Chlorinated @ 350°C			
Average Rate, %/hr.	32	22	24
Cl_2 Utilization, %	~100	79	70
NO_2 Oxidized Zircaloy-2 Chlorinated @ 350°C			
Average Rate, %/hr.	26	22	
Cl_2 Utilization, %	83	78	
Unoxidized Zircaloy-4 Chlorinated @ 400°C			
Average Rate, %/hr.	31	26	27
Cl_2 Utilization, %	77	66	65

More surprising is that no significant difference in reaction rate was observed between feed gas containing 75% and 33% Cl_2. Even though the diluted gas flow velocity was still in the range of laminar flow (Reynolds number <<2000), the increased flow velocity in the reaction zone apparently countered the expected decrease in reaction rate due to Cl_2 dilution by increasing the area of the reaction zone.

The reactor temperatures of 350°C and 400°C produced increased reaction rates of <20%, certainly not the increase that is typical of Arrhenius law behavior. That type of behavior has been observed and analyzed in a previous study[3,4] in which excess reactant gas (HCl) was present.

However, in the current process, Cl_2 feed gas is controlled at a rate sufficient to dissipate the reaction heat and maintain reactor temperature at the desired constant level; thus, in this case, the potential increase in reaction rate is not allowed.

1.C. Scale-up Tests and Process Equipment Design

All previous feasibility tests were made using ~15 g of cladding feed. During FY 2014, scale-up tests were made using 100% Cl_2 and results are shown in Table 6.

TABLE 6. Zirconium Chlorination Scale-up Tests

Clad Feed, g	58.6	102[a]	259	502
Reaction time, minutes	210	190	340	380
% Reacted	93	~100	95	97
Avg. Rate, %/hr.	27	32	17	12
Cl_2 Utilization, %	~80	~100	88	100/64[b]
Salt Product, g	126	226	629	1208
% in product collector	80	88	90	96

(a) *100% Zr-4; all others 87–91% Zr-4—Hi Nb.*
(b) *Utilization ~100% until the first 1000 kg of salt collected; 64% for the remaining salt.*

The kilogram-scale (salt production) test exhibited the first indication of inadequate heat removal, resulting in reactor temperatures of 450–490°C. Late in the test, red-hot spots were observed on the cladding. These observations imply that heat removal capacity must be provided in the reactor design to completely remove the heat of reaction at rates commensurate with the chlorination reaction.

During the process of scale-up, several reactor-condenser configurations were tested to determine the design for use in future kilogram-scale tests with actual UNF cladding, either in the form of empty cladding hulls or segmented fuel rods.

II. SUMMARY AND FUTURE PLANS

The initial emphasis of the process development tests has been on equipment design, reactor temperature control for the exothermic reaction of zirconium and chlorine, chlorination reaction rates and chlorine utilization efficiency as affected by oxide layer thickness, reactor temperature, and chlorine concentration. Less emphasis has been placed on product purity because it is assumed that a secondary purification step will be needed to meet specifications for recycle and reuse of the recovered zirconium. Limited analyses of the test product salt ($ZrCl_4$) and observations of product color were combined with chemical thermodynamic analyses to determine likely impurity chloride species. Assessment of the need for further purification will aid in developing future plans and experimental tests. All of the previous analyses indicate that the most likely impurities requiring further removal from the product salt are iron and niobium, plus radioactive cesium-137 and antimony-125.

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