Perform Tests and Document Results and Analysis of Oxide Layer Effects and Comparisons

Fuel Cycle Research & Development

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SUMMARY

Previous tests have shown that an oxide layer is deposited on used nuclear fuel cladding both during irradiation in a water medium and by dry oxidation pretreatment to remove tritium. This study was made to determine the effects of anhydrous oxide layer thickness on the subsequent chlorination reaction to recover volatile $ZrCl_4$. Results showed quantitatively the increasing resistance to chlorination caused by increasing oxide layer thickness, and the subsequent benefit of pretreating the oxidized cladding by acid washing.

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ACRONYMS

EDS	energy dispersive X-ray spectroscopy
IDIQ	Indefinite Delivery, Indefinite Quantity
KAERI	Korea Atomic Energy Research Institute
LWRs	light water reactors
ORNL	Oak Ridge National Laboratory
SEM	scanning electron microscopy
UNF	used nuclear fuel

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1. Introduction

During the initial feasibility test using actual used nuclear fuel (UNF) cladding in FY 2012, an incubation period of 30–45 minutes was observed in the initial dry chlorination. The cladding hull used in the test had been previously oxidized in a dry air oxidation pretreatment prior to removal of the fuel. The cause of this incubation period was attributed to the resistance to chlorination of an oxide layer imparted by the dry oxidation pretreatment on the cladding. Subsequently in 2013, researchers at the Korea Atomic Energy Institute (KAERI) reported on their chlorination study [R1] on ~9-gram samples of unirradiated Zirlo^{TM} cladding tubes that had been previously oxidized in air at 500^{o}C for various time periods to impart oxide layers of varying thickness. In early 2014, discussions with Indefinite Delivery, Indefinite Quantity (IDIQ) contracted technical consultants from Westinghouse described their previous development (and patents) [R2] on methods of chemical washing to remove some or all of the hydrous oxide layer imparted on UNF cladding during irradiation in light water reactors (LWRs) . Thus, the Oak Ridge National Laboratory (ORNL) study, described herein, was planned to extend the KAERI study on the effects of anhydrous oxide layers, but on larger ~100-gram samples of unirradiated zirconium alloy cladding tubes, and to investigate the effects of various methods of chemical pretreatment prior to chlorination with 100% chlorine on the average reaction rates and Cl_2 usage efficiencies.

2. Description of ORNL Tests

Dry oxidations of Zircaloy-4 cladding tubes were made in air at 600^{o}C for 6, 12, and 72 hours, and Zircaloy-2 cladding tubes were oxidized in NO_2 at 350^{o}C for 12 hours. The earlier KAERI study had oxidized Zirlo^{TM} cladding tubes in air at 500^{o}C for 24, 72, and 168 hours. Both studies compared the chlorination results with unoxidized cladding. However, the KAERI study did not include pretreatments to mitigate the oxide layer effects, whereas the ORNL study compared batch pretreatment with

(1) 8 M HNO_3 washing at 70^{o}C for 1 hour;

(2) 10% wt. HNO_3–2.5% wt. oxalic acid at 70^{o}C for 1 hour;

(3) 10% wt. H_2O_2–3% wt. Na_2SiO_3 – 1.2% wt. $Mg(NO_3)_3$ for 1 hour at room temperature; and

(4) CCl_4-saturated argon gas at 350^{o}C for 0.5 hour.

3. Results and Analyses

The weight gains and oxide layer thicknesses resulting from dry oxidations in air were essentially a linear but slightly decreasing function of the oxidation time. 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°C	0.67	0.11	~5
12 hours in air at 600°C	1.22	0.10	~11
72 hours in air at 600°C	6.7	0.093	~60
And in comparison, 12 hours in NO_2 at 350°C	0.056	0.0047	<1

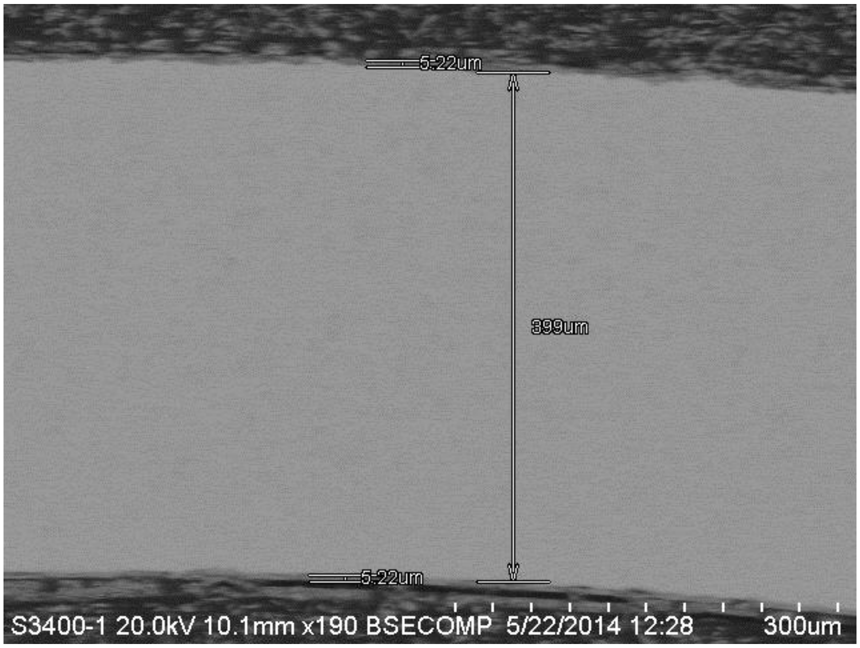
As shown in Fig. 1, after 72 hours of oxidation in air at 600°C, the Zircaloy-4 cladding tubes developed a heavy tan, flaky oxide coating and were bent, whereas the tubes after 12 hours oxidation remained light gray in color and straight. In comparison, the Zircaloy-2 tubes oxidized for 12 hours in NO_2 at 350°C developed multi-colored green-brown-gray hues.

72-hour air-oxidized Zircaloy-4 tubes.

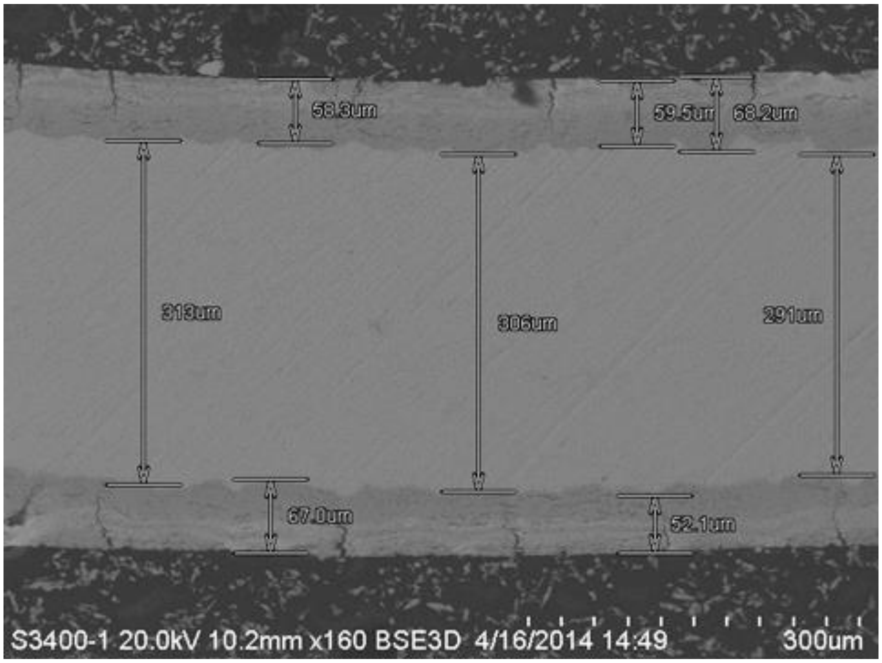
12-hour air-oxidized Zircaloy-4 tubes **12-hour NO_2-oxidized Zircaloy-2 tubes**

Fig. 1. Appearance of oxidized cladding tubes.

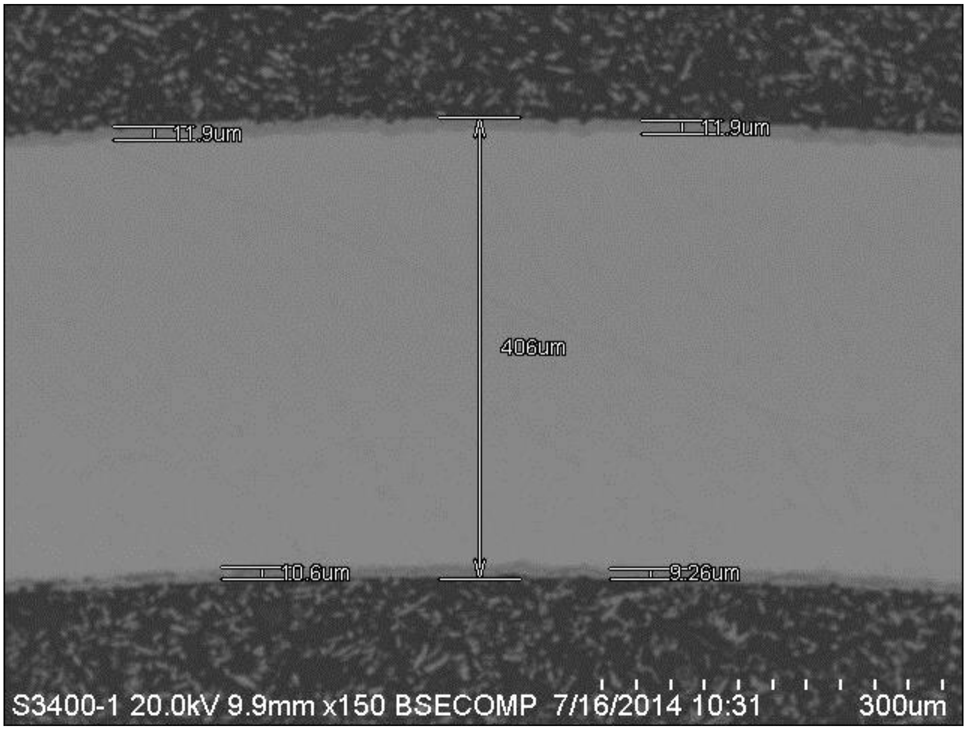
Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analyses were made on the oxidized cladding to measure oxide layer thickness and the oxide species. The thickness measurements are shown in Fig. 2. EDS analyses indicated the oxide species were predominantly anhydrous sesquioxide, Zr_2O_3, with smaller amounts of dioxide, ZrO_2, and monoxide, ZrO. KAERI studies [R3] reported that a non-stoichiometric zirconium suboxide, such as Zr_2O_3, was found to be formed at the surface after air oxidation at 500°C, regardless of the oxidation time.



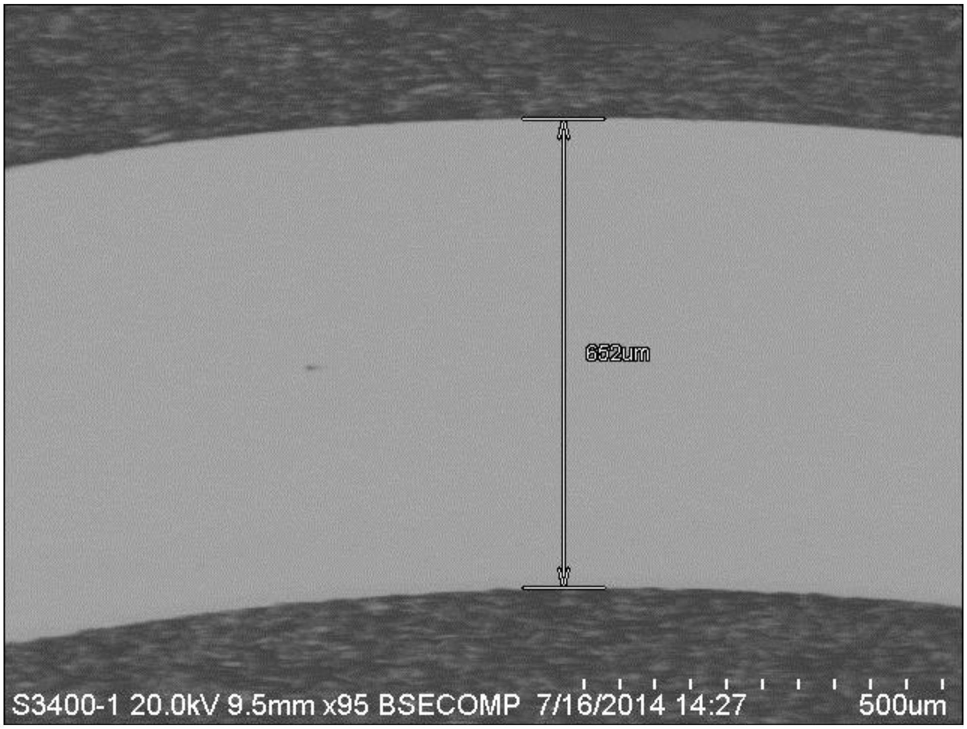
6-hour air oxidation-Zircaloy 4 tube



72-hour air oxidation-Zircaloy 4 tube



12-hour air oxidation-Zircaloy 4 tube



12-hour NO_2 oxidation-Zircaloy 2 tube

Fig. 2. SEM of oxide layers on Zircaloy-4 (air oxidation) and Zircaloy-2 (NO_2 oxidation) cladding.

Since the thickest oxide layer was imparted during the 72-hour oxidation, that oxidized cladding was used for an extensive set of pretreatment tests to compare the pretreatment effectiveness on the subsequent chlorination reaction. Results are shown in Table 2 and indicate that the pretreatment with CCl_4-saturated argon was the most effective. However, that process would require precise control since it can also chlorinate uranium and other fuel component oxides that may be present. Of the other pretreatment methods, pre-washing with the mixture of nitric and oxalic acids was most effective. This method had been suggested by consultants from Westinghouse. Optimization of that method will be worthwhile.

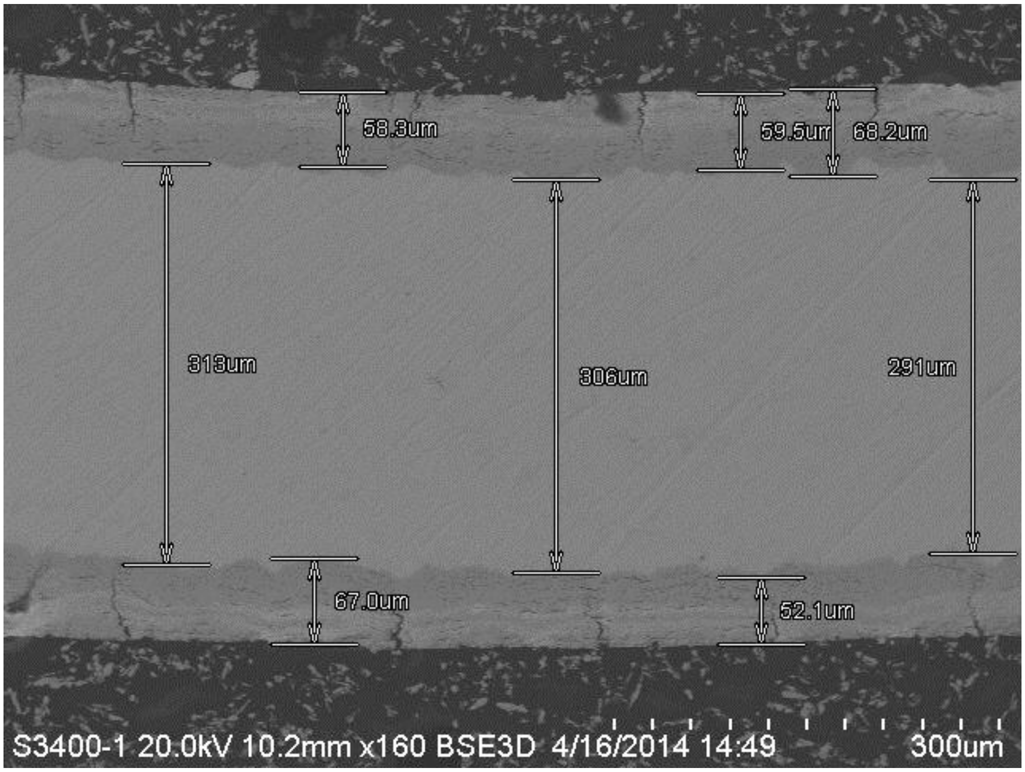
Table 2. Comparison of Effectiveness of Pretreatment Methods of 72-hour Oxidized Zircaloy – 4 Cladding Tubes

		Oxide layer from 72-hour air oxidation at 600°C					
Cl_2 Chlorination	No Oxide Layer	No Pretreatment	8 M 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	2.3*	5*	6	6	9	13
Cl_2 Utilization, %	~100	19*	29*	32	39	50	70

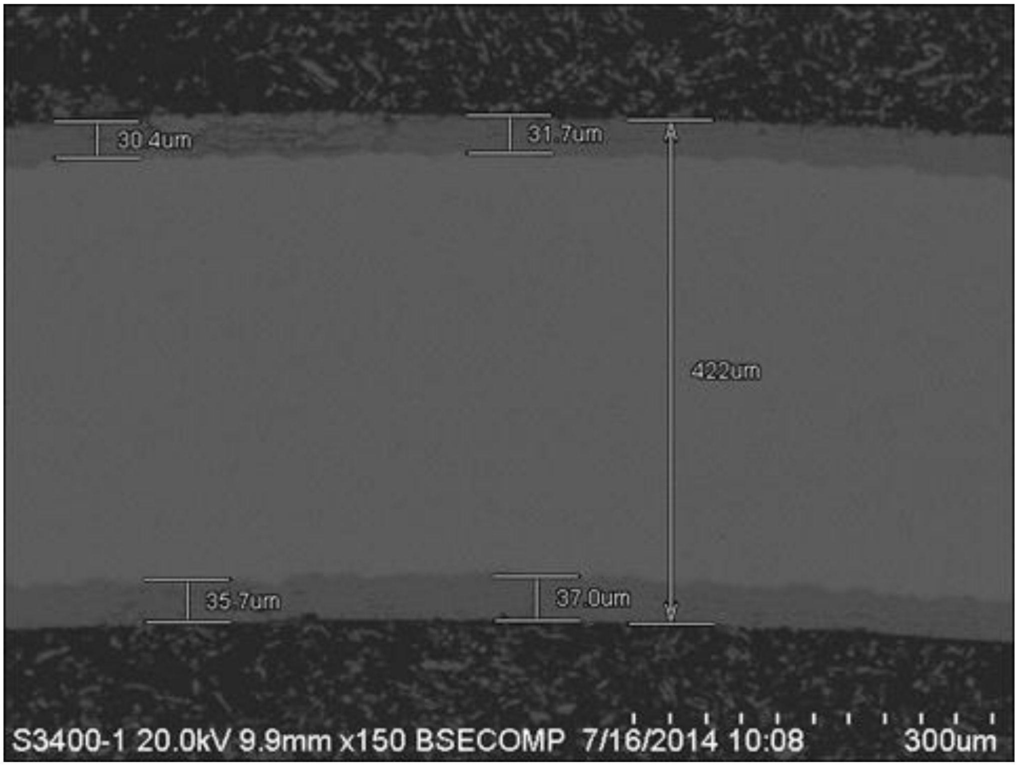
* Observed incubation period before reaction started.

The SEM analyses in Fig. 3 show the measured oxide layer thickness before and after pretreatment with the mixture of nitric and oxalic acids for cladding that had been oxidized for 12 and 72 hours.

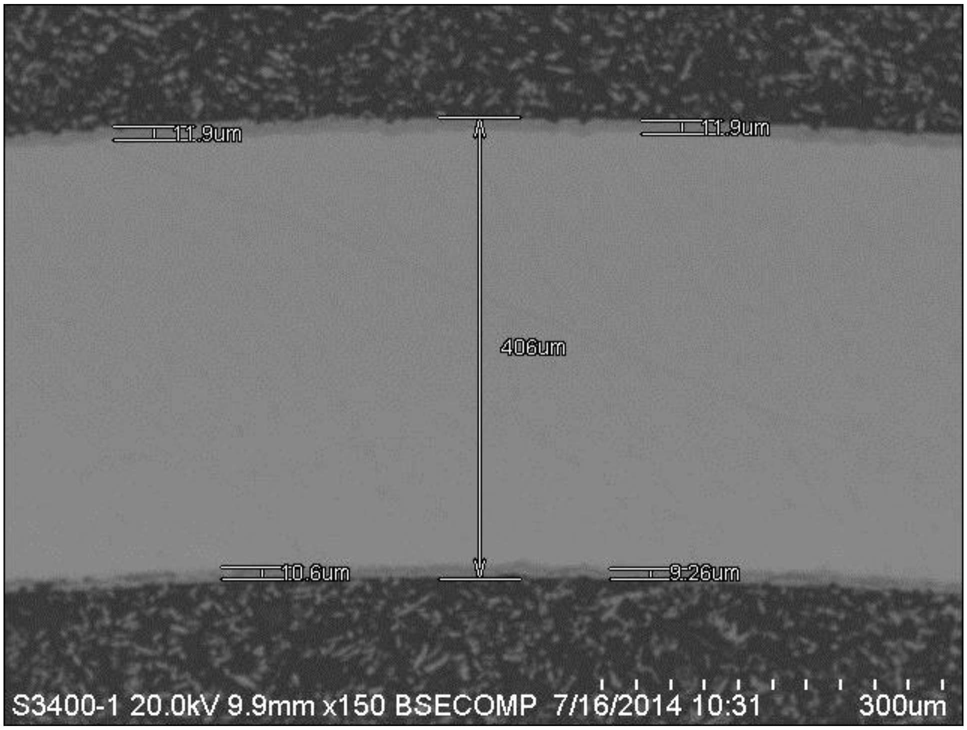
The overall wall plus oxide thickness is an insignificant measurement for the SEM analyses because of variations in the type of Zircaloy tube (Zircaloy-4 or Zircaloy-2) and the flaky oxide layer deposited during the 72-hour air oxidation. A significant reduction in oxide layer thickness from ~60 µm to 30–37 µm was evident for the greater thickness layer imparted during the 72-hour oxidation. A similar reduction was not evident with the 12-hour oxidized cladding sample, perhaps because of the much smaller oxide layer thickness. However, in subsequent chlorination tests shown in Table 3, a significant beneficial effect of the pretreatment was indicated.



72-hour air oxidized; no pretreatment



72-hour air oxidized; pretreatment with nitric-oxalic acid wash



12-hour air oxidized; no pretreatment

12-hour air oxidized; pretreatment with nitric-oxalic acid wash

Fig. 3. Comparison of oxide layer thickness effects of pretreating with nitric-oxalic acid washing.

Table 3. Comparison of Oxide Coating Thickness Effects on Chlorination Reaction

Cl_2 Chlorination	No Oxide Layer	No Pretreatment	8 M HNO_3 Wash	HNO_3-Oxalic Acid Wash
Unoxidized				
% 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		2.3^*	5^*	9
Cl_2 Utilization, %		19^*	29^*	50

*Observed incubation period before reaction started.

In general, the results shown in Table 3 indicate increasing resistance to chlorination with increased oxidation time and oxide layer thickness. The results also indicate the beneficial effects of pretreatment from both nitric acid washing and nitric-oxalic acid washing, with relatively greater benefits to the cladding with thicker oxide layer (the 72-hour oxidized cladding). However, the KAERI study [R1] indicated no chlorination reaction at all with 50% Cl_2 50% Ar on 72-hour oxidized cladding.

Table 4 compares chlorination results of cladding oxidized in air at 600°C with cladding oxidized in NO_2 at 350°C. Both 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 selected have been shown to be optimum for fuel oxidation in the atmosphere used. This is another reason why NO_2 fuel oxidation is preferred. The chlorination performance on NO_2 oxidized cladding is only slightly less than that obtained on unoxidized cladding.

Table 4. Comparison of Oxide Layer Effects in Air at 600°C and NO_2 Oxidation at 350°C
(chlorination of ~100-g clad samples)

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

4. Conclusions

Results of this series of 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, indications are that results for hydrous oxide layers imported by irradiations in light water reactors will be similar, particularly for longer irradiated and higher burnup used fuel cladding. Clarifying this phenomenon will be a major objective of future tests of actual UNF cladding.

5. References

1. M. K. Jeon, Y, T, Choi, C. H. Lee, Y. L. Lee, K. H. Kang, and G. I. Porte, "Effect of Oxidation Process on the Reaction Kinetics of Zirlo Reaction," Translations of the 2013 Annual Meeting of the American Nuclear Society (June 2013).
2. D. F. McLaughlin, "Removal of Niobium Second Phase Particle Deposits from Pickeled Zirconium Niobium Alloys," U.S. Patent 7, 468, 106, 106, Westinghouse Electric Co., LLC (December 2008).
3. C. H. Lee, Y. L. Lee, M. K. Jeon, H. H. Kang, and G. I. Porte, "Zr Electrorefining Process for the treatment of Cladding Hull Waste in LiCl-KCl Molten Salts," Proceedings for Global 2-13 Conference (October 2013).