Effect of Impurity Adsorption on U Concentration of UO2 Powder in Storage

Haneol Lee*, Hyun Ju Kim, Jung Youn Choi, Hyun Young Kim, Jinho Ryu Korea Institute of Nuclear Non-proliferation and Control (KINAC) Corresponding Author: haneol@kinac.re.kr

*Keywords: Nuclear Safeguards, National Inspection, UO2 powder, U factor, Thermogravimetric Analysis

1. Introduction

Korea Institute of Nuclear Non-proliferation and Control (KINAC) is a part of a state system of accounting for and control (SSAC) of the Republic of Korea (ROK) under the Nuclear Safety and Security Commission (NSSC). The KINAC has been operating a special nuclear material analysis center. The center takes samples from domestic bulk handling facilities, analyzes the samples, and evaluates the facilities' declared information as a part of national safeguards inspection. The attributes of samples to be analyzed are U concentration using thermo-gravimetric analysis (TGA) and ²³⁵U enrichment using thermal ionization mass spectrometry (TIMS).

The U concentration of UO_2 powders has been underestimated since the center operation. Since the samples were stored more than a few months before KINAC analysis, the analysts of KINAC suggested that they originated from additional oxidation or volatile impurity adsorption during UO_2 powder storage. Previous studies suggested the possibility of additional oxidation of UO_2 at room temperature [1, 2]. However, the studies did not suggest a quantitative model for room temperature oxidation. Therefore, this study focused on impurity adsorption.

Since the TGA results indicated all UO_2 samples have a mass decrease while the samples are in the initial heating zone, this study examined the correlation between the mass decrease and U concentration decrease using the TGA results of 60 UO_2 samples. The study identified that the decreased mass and U concentration have high linearity.

This study then established a correlation equation that adjusts the U concentration of UO_2 powders once the decreased mass during TGA analysis is given. The study then adjusted the U concentration of UO_2 powders using the correlation equation and compared it to the declared U concentration. Results indicated that the KINAC's adjusted U concentration and the operator's declared U concentration were consistent for all samples.

2. Impurity Adsorption of UO₂ powder

The KINAC adopted an ASTM standard to analyze the U concentration of U oxide samples using the TGA [3]. The standard process oxidizes U oxide samples, as depicted in Figure 1. The mass profile (orange line) of Figure 1 indicates decreased mass for the initial heating process. Since all U oxides becomes U_3O_8 under

atmospheric pressure, we can identify initial U concentration using the increased mass after oxidation. This study assumed that the mass decrease occurs due to the volatile impurity adsorption during powder storage [4].



Fig. 1. UO₂ powder mass change during the TGA process.

3. Methods

3.1. Adjusted U concentration

This study first examined whether the decreased mass and decreased U concentration correlate. The study assumed that the operator–inspector difference (OID) of U concentration is zero for all samples. The decreased mass ($\Delta f_{U,meas}$) and U concentration (Δm) are defined as equation (1). m_{min} and m_{init} indicate the minimum and initial mass of the sample. $f_{U,insp}$, fU, and $_{op}$ indicate the inspector's and operator's U concentrations, respectively.

$$\begin{cases} \Delta f_{U,meas} = 100 \times (f_{U,insp} - f_{U,op})/f_{U,insp} \\ \Delta m = 100 \times (m_{min} - m_{init})/m_{min} \end{cases}$$
(1)

Figure 2 depicts the linear correlation between the Δm and Δf_U (R² = 0.9104). This study then established a linear correlation equation using the results of Table 1 and the least square method (LSM) (Eq (2) ~ (4)). $\overline{\Delta f_U}$ and $\overline{\Delta m}$ indicate the average of Δf_U and Δm .



Fig. 2. Correlation between Δf_U and Δm

$$\Delta m = a * \Delta f_U + b \tag{2}$$

$$\sum_{\Delta m_i = \overline{\Delta m_i} (\Delta f_{ij} = \overline{\Delta f_{ij}})}$$

$$a = \frac{\sum (\sum i i j - \sum i j) (\sum j - \sum j - j)}{\sum (A f_{ij})^2}$$
(3)

$$b = \overline{\Delta m} - a\overline{\Delta f_U}$$
(4)

3.2. Adjusted Operator-Inspector Difference

This study identified the measurement uncertainty of adjusted $\Delta f_U(u(\Delta f_U))$ of a target sample using equation (5). Δm_i and $\Delta f_{U,m,i}$ indicate the measured decreased mass and U concentration of sample "i" to establish the correlation equation. s^2 and n indicate the sample standard deviation of residual ($\Delta m_i - \Delta m_{i,meas}$) and number of samples to establish the correlation. $u(\Delta m_{meas})$ indicates the measurement uncertainty of Δm for a target sample.

$$u(\Delta f_U) = \sqrt{\frac{s^2}{a^2} \left(\frac{1}{n} + \frac{\left(\Delta f_{U,i} - \overline{\Delta f_U}\right)^2}{\Sigma \left(\Delta f_{U,i} - \overline{\Delta f_U}\right)^2}\right) + \frac{u(\Delta m_{meas})^2}{a^2}}$$
(5)

Then, the adjusted OID (OID_{adj}) and the uncertainty of OID were evaluated using equations (6) ~ (8). The adjusted OID was tested with k = 3.

$$OID_{adj} = f_{U,op} - f_{U,insp,adj}$$
(6)

$$f_{U,insp,adj} = f_{U,insp} \left(1 - \frac{\Delta J_U}{100} \right) \tag{7}$$

$$u(OID_{adj}) = \sqrt{\frac{u(f_{U,op})}{+ (1 - \frac{\Delta f_U}{100})^2 u(f_{U,insp})^2}} (8) + (\frac{f_{U,insp}}{100})^2 u(\Delta f_U)^2$$

4. Results

Table 1 summarizes the decreased mass (Δm) and U concentration ($\Delta f_{U,meas}$) from the TGA experiment results of 60 UO₂ samples. The red-colored samples in Table 1 are the samples with significant OID differences. Equation (9) is the correlation equation to calculate adjusted Δf_U using the Δm in Table 1.

$$\Delta f_U = 0.3807 * \Delta m - 0.0154 \tag{9}$$

Table 1. Δm and Δf_U of 60 samples.

ID	$\Delta f_{U,meas}$ (%)	Δm (%)	ID	$\Delta f_{U,meas}$ (%)	Δm (%)
1	-0.275	-0.1146	31	-1.419	-0.5913
2	-0.225	-0.0895	32	-1.451	-0.6182
3	-0.316	-0.1302	33	-0.157	-0.0594
4	-0.276	-0.1227	34	-0.155	-0.0666
5	-0.769	-0.2589	35	-2.206	-0.8310
6	-0.768	-0.2779	36	-2.208	-0.8584
7	-0.807	-0.3296	37	-0.200	-0.1825
8	-0.823	-0.3533	38	-0.670	-0.2987
9	-0.776	-0.3029	39	-0.153	-0.0651
10	-0.800	-0.2924	40	-0.117	-0.0725
11	-0.796	-0.2755	41	-1.399	-0.5389
12	-0.781	-0.2974	42	-1.420	-0.5703
13	-0.233	-0.0444	43	-0.580	-0.1676
14	-0.198	-0.0477	44	-0.590	-0.1543
15	-0.241	-0.0470	45	-1.945	-0.7930
16	-0.203	-0.0505	46	-0.614	-0.1176
17	-0.626	-0.2090	47	-1.833	-0.7356
18	-0.609	-0.1705	48	-0.247	-0.2041
19	-0.594	-0.1688	49	-0.448	-0.2740
20	-0.610	-0.2007	50	-0.388	-0.2407
21	-1.593	-0.6285	51	-0.518	-0.2513
22	-1.596	-0.6483	52	-0.212	-0.1498
23	-1.591	-0.6145	53	-0.849	-0.0692
24	-1.545	-0.6188	54	-0.724	-0.3249
25	-0.748	-0.1740	55	-0.554	-0.2233
26	-0.566	-0.2502	56	-0.097	-0.1723
27	-1.348	-0.5888	57	-0.115	-0.1519
28	-0.833	-0.3751	58	-0.405	-0.3192
29	-0.602	-0.2286	59	-0.466	-0.2647
30	-0.600	-0.2521	60	-0.276	-0.1250

Table 2 summarizes the adjusted Δf_U , adjusted KINAC's U concentration ($f_{U,insp,adj}$), *OID*, and u(OID) of 60 samples using equations (5) ~ (9). The results indicated that the adjusted U concentration OID of all samples became insignificant.

Table 2. Δf_U , $f_{U,insp,adj}$, OID, and u(OID) of 60 samples.

	e : e ;:::e ; ;:::;			
ID	Δf_U	$f_{U,insp,adj}$	OID	u(01D)
1	-0.261	87.869	0.012	0.092
2	-0.195	87.861	0.026	0.092
3	-0.302	87.787	0.013	0.092
4	-0.282	87.805	-0.005	0.092
5	-0.642	87.239	0.111	0.091
6	-0.692	87.284	0.066	0.091
7	-0.828	87.295	-0.018	0.091
8	-0.891	87.336	-0.059	0.091
9	-0.758	87.305	0.015	0.091
10	-0.730	87.259	0.061	0.091
11	-0.685	87.224	0.096	0.091
12	-0.743	87.287	0.033	0.091
13	-0.076	87.773	0.137	0.092
14	-0.085	87.811	0.099	0.092
15	-0.083	87.772	0.138	0.092
16	-0.092	87.813	0.097	0.092
17	-0.510	87.129	0.101	0.091
18	-0.408	87.056	0.174	0.091
19	-0.404	87.065	0.165	0.091
20	-0.488	87.124	0.106	0.091
21	-1.621	87.254	-0.024	0.091
22	-1.674	87.297	-0.067	0.091
23	-1.584	87.224	0.006	0.091

24	-1.595	87.273	-0.043	0.091
25	-0.417	87.014	0.286	0.091
26	-0.619	87.346	-0.046	0.091
27	-1.515	87.414	-0.144	0.091
28	-0.949	87.370	-0.100	0.091
29	-0.561	87.178	0.035	0.091
30	-0.624	87.234	-0.021	0.091
31	-1.522	87.302	-0.089	0.091
32	-1.594	87.336	-0.123	0.091
33	-0.116	87.879	0.036	0.092
34	-0.135	87.897	0.018	0.092
35	-2.161	87.646	0.039	0.092
36	-2.234	87.708	-0.023	0.092
37	-0.440	87.479	-0.209	0.093
38	-0.747	87.336	-0.066	0.093
39	-0.131	87.755	0.019	0.094
40	-0.150	87.803	-0.029	0.094
41	-1.383	87.256	0.014	0.094
42	-1.466	87.310	-0.040	0.094
43	-0.401	87.053	0.156	0.094
44	-0.366	87.035	0.195	0.094
45	-2.059	87.328	-0.098	0.094
46	-0.269	86.938	0.299	0.097
47	-1.906	87.300	-0.063	0.097
48	-0.497	87.439	-0.217	0.102
49	-0.681	87.425	-0.203	0.103
50	-0.594	87.457	-0.179	0.104
51	-0.621	87.368	-0.090	0.105
52	-0.354	87.382	-0.123	0.106
53	-0.142	87.283	0.617	0.109
54	-0.816	87.324	-0.080	0.109
55	-0.547	87.238	0.006	0.109
56	-0.413	87.310	-0.275	0.110
57	-0.359	87.247	-0.212	0.119
58	-0.801	87.378	-0.343	0.142
59	-0.657	87.415	-0.165	0.158
60	-0.288	87.261	-0.011	0.176

5. Conclusion

The KINAC has analyzed the U concentration and ²³⁵U enrichment of U oxide samples as a part of national safeguards inspection. However, the analysis results indicated a lower U concentration of UO2 powder samples than the declared value. Since every TGA result resulted in a mass decrease in the initial heating process, this study investigated the volatile impurity adsorption during storage, reducing U concentration for UO_2 powder samples. This study identified a linear correlation between the decreased sample mass and decreased U concentration using 60 UO₂ powder samples. Then, the correlation equation between the two parameters was established. It also adjusted the U concentration of UO₂ powder using the correlation and evaluated the significance of the OID. Results indicated that the difference between the adjusted U concentration and operator declared value was not significant for all cases where the OID of 46 cases was significant without adjustment. Through this, the KINAC has strengthened the technical capability of the ROK SSAC.

ACKNOWLEDGEMENT

This work was supported by the Nuclear Safety Research Program through the Korea Foundation Of Nuclear Safety (KoFONS) using the financial resources granted by the Nuclear Safety and Security Commission (NSSC) of the Republic of Korea. (No. 2106015)

REFERENCES

[1] R. J. McEachern and P. Taylor, A review of the oxidation of uranium dioxide at temperatures below 400°C, Journal of Nuclear Materials, Vol. 254, pp. 87-121, 1998.

[2] S. B. Donald et al., Relative impact of H2O and O2 in the oxidation of UO2 powders from 50 to 300° C, Journal of Nuclear Materials, Vol. 496, pp. 353 – 361, 2017

[3] ASTM, Standard Test Method for the Determination of Uranium by Ignition and the Oxygen to Uranium (O/U) Atomic Ratio of Nuclear Grade Uranium Dioxide Powders and Pellets, ASTM C1453-19, 2019.

[4] H. Lee et al., 2024 Annual Report for Establishment and Operation of Analysis Center for the Special Nuclear Material, KINAC/RR-009/2025, 2025.