Determination Method of Gd_2O_3 Content in Gadolinium Fuel Pellets by Measurements of Gadolinium and Uranium Elements

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1. Introduction

KEPCO-NF, short for KEPCO Nuclear Fuel Cycle Company, developed a new method to determine Gd_2O_3 content contained in gadolinium fuel pellets in 2006 and, at present, the method is practically being used for quality control. The newly developed method is based on the fact that Gd_2O_3 content in gadolinium fuel pellets can be determined by measurements of gadolinium and uranium element concentrations in nitric solution in which a small quantity of gadolinium pellet sample is dissolved. This method is very simple and the time needed for sample preparation and measurement is very short. Moreover, the Gd_2O_3 content determined by this method is accurate and precise, because sample weighing and pipette operation do not affect the accuracy and precision of Gd_2O_3 content determination by this method.

2. Principle and Procedure

The principle of the new method which was developed by KEPCO-NF is based on the fact that if gadolinium and uranium elements and O/M ratio (oxygen to metal ratio) of gadolinium fuel pellet are measured or determined, the Gd_2O_3 content in that pellet can be determined by stoichiometric calculation using the three measured or determined values. (The principle of this method is completely different from the ones of other methods such as X-ray fluorescence method and comparison method.)

2.1Determination of Preliminary Gd_2O_3 Content

A very small quantity of sample is taken from the gadolinium fuel pellet and dissolved in 1:1 nitric acid so that the uranium element concentration in the nitric solution is approximately 100 ppm. In this case, the gadolinium element concentration will be in the range of several ppm. Then, gadolinium and uranium element contents are measured by ICP-AES. Preliminary Gd_2O_3 content is obtained by equation (1) below;

Preliminary Gd_2O_3 content A (%)
$= (100 \cdot 362.498 \cdot Z)/\{2 \cdot (1-Z) \cdot 270.03 + 362.498 \cdot Z\}$ (1)

where, $Z = (X/157.25)/(X/157.25+Y/238.03)$

X: gadolinium element content in the solution, ppm

Y: uranium element content in the solution, ppm

2.2 Determination of O/M Ratio

O/M ratio (oxygen to metal ratio) of gadolinium fuel pellet is measured by 4-hour atmospheric equilibration method at a high temperature of 800 ℃ under nitrogen (or argon) 96% and hydrogen 4% mixed gas atmosphere. The oxygen to metal ratio is determined by equation (2) below;

O/M ratio B
$= 2.00 - (W_2-W_1)/\{W_2 \cdot [0.0593+(0.00026 \cdot A)]\}$ ---- (2)

where, W_1: gadolinium fuel pellet weight, g, before atmospheric equilibration
W_2: gadolinium fuel pellet weight, g, after atmospheric equilibration
A: the preliminary Gd_2O_3 content previously obtained from equation (1), %,

2.3 Final Determination of Gd_2O_3Content

The Gd_2O_3 content of the gadolinium fuel pellet is finally determined by the following equation (3);

Final Gd_2O_3 content C (%)
$= (0.5 \cdot 100 \cdot 2.3052 \cdot X)/[X+Y+B \cdot (0.1017 \cdot X+0.0672 \cdot Y)]$
----------(3)

where, the same X and Y values as applied in equation (1) are used, and B is the O/M ratio previously obtained from equation (2).

3. Experiment and Uncertainty Evaluation

3.1 Experiment

Using a gadolinium fuel pellet with 6% of nominal Gd_2O_3 content, an experiment for evaluation of the uncertainty of Gd_2O_3 content determined by the KEPCO-NF method was performed. A very small quantity of sample was taken from that pellet and the sample was dissolved in 1:1 nitric acid. Each of gadolinium element content and uranium element content contained in the solution was repeatedly measured 6 times by ICP-AES. The data obtained from the experiment can be seen in Table I: Experimental Measurement Results.

Table I: Experimental Measurement Results

Measurements	X, Gd content (ppm)	Y, U content (ppm)
1st measurement	5.32	85.74
2nd measurement	5.38	85.46
3rd measurement	5.33	85.49
4th measurement	5.36	85.52
5th measurement	5.36	85.55
6th measurement	5.37	85.41
Mean Value	5.353	85.528
Standard Deviation	0.023	0.114

By applying the average Gd content value 5.353 ppm, the average U content value 85.528 ppm and nominal O/M ratio 2.00 in equation (3), the Gd_2O_3 content of the sample pellet could be determined at 5.963%.

3.2 Uncertainty Evaluation

By applying error propagation theory to equation (3), the combined uncertainty was calculated as follows;

(Combined uncertainty)² = (∂C/∂X)²•(Gadolinium measurement uncertainty)²+(∂C/∂Y)²•(Uranium measurement uncertainty)²+(∂C/∂B)²•(O/M ratio determination uncertainty)²
= 0.000146
∴ Combined uncertainty = 0.012% absolute as one standard deviation

4. Conclusions

An experiment for uncertainty evaluation of Gd_2O_3 content determined by the KEPCO-NF method was performed using a gadolinium fuel pellet with nominal Gd_2O_3 content of 6%. As a result of the experiment, the combined uncertainty was evaluated to be 0.012% absolute as one standard deviation. This combined uncertainty is very small. In conclusion, this newly developed method is excellent and very useful for Gd_2O_3 content determination contained in gadolinium fuel pellets, and even industrially cost effective. From all the aspects of measurement efficiency, accuracy and precision including measurement cost, this method can replace other methods such as X-ray fluorescence method and comparison method.

REFERENCES

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