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Analysis of Neutron Absorbing Impurities in Nuclear Graphite

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1. Introduction

In a very high temperature reactor (VHTR), nuclear graphite acts as a moderator and reflector as well as a major structural component that may provide channels for the fuel and coolant gas, channels for control and shut down, and thermal and neutron shielding. These application of graphite for a VHTR are largely based on its superior high temperature mechanical properties, chemical stability, high neutron moderating ratio, and a high neutron multiplication factor which are influenced by the impurity contents of the graphite [1].

On the other hand, it is well known that, since the impurity acts not only as an oxidation catalyst but also as an radioactive elements inventory during a decommissioning of a graphite moderating reactor, even a small amount (~ few tenth ppb order) of impurities can have negative effects on these properties. Accordingly, It is important to determine the kinds and exact quantity of the impurities in the selected core structural graphite components. However, comparing to its importance, few studies have been performed. Even the relevant ASTM specifications were published very recently [1][2].

Based on this discussion, in order to provide some information as to the impurities in a recently developed nuclear graphite for a VHTR and as to the impurity measurement and analysis techniques, three different impurity measurement and analysis methods (combinations of prior-specimen treatment methods and impurity measurement technique) were compared based on the results obtained for the PCEA nuclear graphite grade.

2. Experiment

2.1 Materials and preparation of specimen.

Specimens used in the present study were prepared from the PCEA nuclear graphite (Graftech, USA). Table 1 summarizes the characteristics and manufact- urer's impurity data of the grade. The impurity data in Table 1 were obtained by Glow Discharge-Mass Spectroscopy (GDMS) method, and reproduced in Table 3. (GDMS) which can directly ionize the solid sample by glow discharge plasma before injection to mass spectroscopy. Powder specimens were prepared from a coupon (size: 70 x 5 x 200 mm) machined from a block (size: 70 x 240 x 200 mm). After grounding the coupon by using an agate mortar, the powder was divided into 3 portions for analysis.

It is worth noting that all the elements analyzed and compared in the present study were of neutron absorbing impurities as classified in the ASTM D 7219-05 (Table 1, Table 3).

Table 1 Characteristics and manufacturer's impurity data of PCEA nuclear graphite grade.

Source coke	Petroleum Coke
Forming method	Extrusion, Near-isotropic.
Grain size	360 ㎛
Density	1.84(//) /1.82(⊥)
Ash content	Not Detected
B	1.1
Cd	<0.1
Sm	<0.05
Eu	<0.05
Gd	<0.05
Dy	<0.05
W	<0.05

2.2 Prior-treatment and impurity measurements.

Table 2 shows three impurity measurement and analysis methods. It is seen that each method is composed of the impurity measurement method plus prior-treatment method – Micro Wave Digestion (MWD) plus ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy), Acid Boom Digestion (ABD) plus ICP-MS (Inductively Coupled Plasma-Mass Spectroscopy), and Furnace Ash (FA) plus ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy).

Table 2 Prior-treatments and impurity measurements.

Pre – Treatment and Measurement	Details
MWD + ICP-MS	0.1 gram of the powder from the first specimen portion was added to a Teflon vessel containing 6 mL of HNO_3 and 2 mL of $HClO_4$. The vessel was sealed and digested 2 times in a microwave oven to extract impurity contents from the ground powder to solution. Analyzed by ICP-MS (Thermo Elemental, X5, UK).
ABD + ICP-MS	50 mg of the powder from the second specimen was added to a solution composed of 5 mL of H_2SO_4 (98%), 1 mL of HCl (35%) 1 mL of HF (50%) and 1 mL of HNO_3 (70%) in a Teflon vessel. The vessel containing the slurry was sealed with stainless steal jar and heated at 150 ℃ for 1 hour fallowed by heating at 230 ℃ for a day to extract impurity contents. After

	filtration, the digested solution was analyzed by ICP-MS (Thermo Elemental, X7, UK).
FA + ICP-AES	Powder prepared from the third specimen was burnt to ash to remove insoluble carbon contents. The platinum crucible containing 10.15 grams of the graphite powder was burnt in a furnace at 500 ℃ for 1 hour, 750 ℃ for 2 hours, 900 ℃ for 8 hours and 1020 ℃ at 24 hours. The ash containing impurities was dissolved with 5 mL HCl (36%) and prepared a sample volume (10 mL) by adding water. The solution was analyzed by using ICP-AES (Jobin Yvon, Ultima 2, USA).

3. Result

Table 3 summarizes the results obtained by the three different impurity analysis method plus prior-treatment method.

Table3. Analytical results of impurities (ppm).

	ASTM	Graftech (GDMS)	MWD + ICP-MS	FA+ICP -AES	ABD + ICP-MS
B	<1.0	1.1	-	-	0.692
Cd	<0.05	<0.1	<0.5	-	<0.003
Sm	<0.05	<0.05	<0.5	<0.01	<0.003
Eu	<0.05	<0.05	<0.5	<0.01	0.008
Gd	<0.05	<0.05	<0.5	<0.01	0.007
Dy	<0.05	<0.05	<0.5	<0.01	0.001
W	<1.00	<0.05	4.43	<0.02	<0.012

In table 3, the ASTM column shows the maximum allowable limit for each impurity elements by the ASTM [2]. In the present study, comparisons between the three methods were made based on the manufacturer's data, Graftech (GDMS) and ASTM specification.

Table 3 shows that, except MWD + ICP-MS, the results of the other three methods including the Graftech (GDMS) meet the ASTM impurity require- ment (specification) on nuclear graphite. Thus, only the results of MWD + ICP-MS show that the PCEA Grade does not meet the ASTM impurity requirements. Further, the result on Tungsten (W) appears too high while the other three methods reveal the measurement data satisfying the ASTM requirements.

It is worth noting that, of the seven ASTM impurity requirements in Table 3, the FA+ICP-AES method show that the PCEA satisfies partly the five ASTM impurity requirements except B and Cd. The failure of detection on these elements by the FA+ICP-AES method may be attributed to the differences in the specimen pre-treatment method.

Among the four methods, it is seen that the ABD + ICP-MS method shows the lowest level of detection exhibiting that the PCEA meets the ASTM impurity requirements.

In view of the impurity detectability, the present results show that the ABD + ICP-MS method may be better than the other three methods. It is worth noting that the boron (B) was not detected by the other two methods exercised in the present study.

4. Discussion

Comparison of the result between the MWD + ICP-MS and ABD + ICP-MS show that the pre-treatment method of the specimen plays a critical role and determine the detectability of the impurity measurement and analysis method. While it takes more time for measurement and analysis, the ABD + ICP-MS method appears to be an appropriate method applicable for the impurity determination in nuclear graphite. The advantage of the method may be attributed to its higher impurity extractability from graphite due to its dual controllability of time and temperature simultaneously with various acids when the MWD controls only time with limited acid [3].

The FA + ICP-AES method appears to be inappropriate for the analysis of volatile impurities in graphite since the high temperature operation employed in the method may decompose organic impurities in the sample during analysis. One of the other disadvantages of the method may be the large amount of initial specimen mass which takes more time to analyze the impurities in the sample.

5. Conclusion

The neutron absorbing impurities in the PCEA nuclear graphite were analyzed by three methods: MW D-ICP-MS, FA-ICP-AES and ABD-ICP-MS. Of those three methods, the ABD-ICP-MS appeared to be the most appropriate for the impurity analysis in the nuclear graphite for its higher impurity extraction ratio.

All the methods except the FA + ICP-AES show that the PCEA nuclear graphite grade meets the ASTM impurity requirement.

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