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Review of Technical Methods for Graphite Purification by Reactive Gases

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Document title

Review of Technical Methods for Graphite Purification by Reactive Gases

Executive summary

Graphite purification methods as deployed during industrial manufacture of nuclear graphite and other high purity special graphite grades are described in this technical report. Selected methods are proposed to be applied also for the treatment of irradiated graphite to extract specific radioisotopes. This might allow a reuse of purified i-graphite or a conditioning of graphite waste for easing the final disposal.

Revisions

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1. Objectives of the Report

The Objective of this Report is to give an overview about historical and current methods for purification of graphite used as moderator in gas-cooled nuclear rectors.Impurities have an adverse effect on neutron absorption, in particular boron, which is also difficult to remove. Furthermore, rare earth elements contained in graphite may undergo nuclear fission reactions leading to formation of undesirable radioactive species.

2. Industrial Purification of Nuclear Graphite

2.1 Former practices at SGL

Three basic methods are usable for obtaining graphite of sufficient purity for use in nuclear reactors [SGL1].

a) Selection of extremely pure raw materials, alternatively purification of raw materials by adaption of one of the methods listed below.
b) Thermal purification of formed graphite. Graphitization is performed at sufficiently high temperatures to cause impurities diffuse out of the graphite
c) Chemical purification by use of halogens. Halide-containing gas, introduced directly or produced in-situ from halides in the graphitization process, reacts with impurities and evaporates from graphitizartion vessel.

Since highest-purity raw materials are of limited availability, methods b) and c) were commonly used.
Thermal purification is obtained by temperatures up to 3100 ºC, during Acheson graphitization process. This is facilitated by using relatively pure petroleum coke as packing material rather than metallurgical coke. However, the degree of thermal purification is about one order of magnitude lower than for (thermo-)chemical purification. Reason is that some carbide forming elements, such as vanadium and boron, reside in the lattice.
Chemical purification by the use of halides, circumvents this problem. Halides penetrate the graphite body and lattice, and removes impurities via formation of volatile halide species.
For practical reasons, chemical purification is combined with graphitization treatment. Halide-containing materials suitable for purification are e.g. fluoride salts (NaF, MgF_2), chlorine (Cl_2), or chlorinated/fluorinated hydrocarbons (e.g. Freon-12®).
Early reactor graphites were developed towards an ash level of about 600 ppm, whereas modern nuclear graphite should contain max. 200 ppm ash, with boron content below 1 ppm.

2.3 Actual methods at SGL

Today, all graphites for use as moderator or reflector are thermo-chemically purified, using fluorinated-only compounds, as described in previous paragraph 2.1.. Only by this, purity requirements of current nuclear technologies can be met, also avoiding contamination by chlorine.

3. Residual Impurities after Purification

3.1 Typical impurities in SGL nuclear graphite grades

Typical impurities for reactor graphites from SGL (examples).

	ATR-2E	**NBG-18**
Purification:	thermal	thermo-chemical
Ash (ppm)	560	180
Element's content (ppm)		
Boron	1,3	0.9
Chlorine	8	< 10
Iron	61	15
Nickel	1.4	1.8
Vanadium	6.8	1.8

3.3 Information manufacture of other high-purity graphite grades

For graphite materials used in silicon production for semiconductor applications, e.g. crucibles, also high purity is required. Carbon fiber-reinforced carbon composites (CFRC) used for this purpose are purified in vacuum graphitization furnaces at temperatures up to 2800 °C. Due to the application as structural component, these parts are rather small-sized. Large-size blocks, such as reflector blocks for gas-cooled nuclear reactors cannot be purified in this way, because of the long distance from core to surface, and significant amounts of entrapped air.

The same rationale applies to structural elements from CFRC for future VHTRs, which are under consideration in current nuclear technology developments.

4. Recommendations for Treatment of i-Graphite

From a technical standpoint, the recommended cleaning process is strongly depending on the particle size of the retrieved i-graphite material.

To achieve sufficient purity for re-use in commercial graphite-producing facilities, i.e. with lowest degree of contamination, only a thermo-chemical purification seems viable. For big scale blocks, this would require an Acheson furnace with exhaust gas cleaning facility to condense the vapors leaving the material.

When milled to powder, one can consider also a vacuum graphitization furnace unit, which allows inlet of fluorine- or chlorine-containing gas.

However, both methods described above will not reduce the content of C14. There the methods evaluated in WP4 (water steam oxidation, biological surface treatment, etc.) would be envisaged.

5. References

[SGL1] Nightingale, R.E. ed. 1962. *Nuclear Graphite*. New York and London: Academic Press