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Review of Methods for Graphite Purification

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Review of Technical Methods for Graphite Purification

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

Even after graphitization at temperatures near 3000°C, most bulk commercial graphite materials contain small amounts of metallic impurities. These impurities originate in the raw material calcined cokes, recycled graphite, and coal tar and petroleum based pitches. The total impurities may equate to as much as 3000 ppm as measured by combustion ash. The ash levels will be higher if inorganic compounds were used in the processing of the graphite material to control certain other chemistries that occur throughout the processing of certain raw materials.

In the carbon-rich environment, many of the metal species are present as carbides, many of which are extremely stable. Scanning electron microscopy imaging reveals that high concentrations of some metals can be present in the final graphite as micron-sized pools of apparently complex alloys.

The use of graphite as a moderator for thermal neutrons in gas-cooled nuclear fission reactors requires material of high-purity. As such, most impurities require removal because they have a high affinity for neutron absorbtion. Subsequently, these impurities have a tendency to form long lived radionucleotides which may present an issue in the further handling of the material, and in waste disposal.

The following report will discuss the types of impurities present in most graphite material, and industrial routes for purification of bulk graphite that are well-known in the field. Due to the sensitive business nature of this type of processing, the information found herein will be limited to material published in the public domain.

2. Typical Impurities found in Manufactured Graphite

Table 1 illustrates the typical metallic carbides that can be found in some manufactured graphites. The levels of each of these compounds may vary significantly based on the raw material selection for any particular grade of graphite. Concentrations of each of these potential impurities can be reduced by selection of premium raw materials, however, in many cases, purification of the graphite may still be required for nuclear applications.

Table 1 : Table showing the common metallic impurities in graphite, the associated carbide form, chemical formula, molecular weight and respective melting point.

Metal	Compound	Formula	Molecular Weight	Melting Point (°C)
Aluminium	Aluminium Carbide	Al_4C_3	143.91	2100
Barium	Barium Carbide	BaC_2	161.35	1780
Boron	Boron Carbide	B_4C	55.29	2350
Calcium	Calcium Carbide	CaC_2	64.1	2300
Chromium	Tri-chromium Di-carbide	Cr_3C_2	180.01	1980
	Chromium Mono-carbide	CrC	64.02	1550
Iron	Iron Carbide	Fe_3C	179.55	1227
Manganese	Manganese Carbide	Mn_3C	176.83	1520
Molybdenum	Molybdenum Carbide	MoC	107.95	2692

	Molybdenum Di-Carbide	Mo_2C	203.89	2687
Silicon	Silicon Carbide	SiC	40.07	2700 (sublimes)
Sodium	Sodium Carbide	Na_2C_2	70	700
Strontium	Strontium Carbide	SrC_2	111.64	1950
Titanium	Titanium Carbide	TiC	59.89	3140
Vanadium	Vanadium Carbide	VC	62.95	2810
Zirconium	Zirconium Carbide	ZrC	103.23	3540

3. Industrial Routes for Purification of Bulk Graphite

Purification processes involving halogen gas purges, developed for the production of spectroscopic grade electrodes for chemical analysis, were enhanced in the 1940's to cope with the purification requirements for monolithic nuclear graphite blocks. The addition of chlorine gas at high temperatures is effective at removing most impurities commonly found in graphite, with the exception of boron, which is most efficiently removed with fluorine containing gas.

Large monolithic blocks of high purity graphite can be produced today either during or after the graphitization process that converts 2 dimensional carbon to 3 dimensional graphite. For high temperature purification that utilizes gaseous inlet of halogens (either chlorine or fluorine), purification can be completed either before or after the appropriate machining of required parts. In order to reduce processing time, other methods allow for the purification of large monolithic billets in-situ, during the graphitization process. These methods have been found to be equally effective at producing large graphite forms that meet the ASTM standard specification for High Purity (HP) nuclear graphite, which limits the total boron equivalence to 2 ppm as defined in ASTM document C781.

All of the discussed purification methods have different advantages. Although concerns regarding the presence of residual chlorine following high temperature thermal purification have been expressed, this can be easily mitigated during the gas/purge cycle to allow for the effective thermal desorption of any absorbed chlorine. In addition, it is mindful to consider the environmental concerns that may present themselves with the use of either chlorine or fluorine purification. Appropriate handling systems, including gas scrubber systems, must be utilized in accordance with the local regulatory agency that may require significant permitting and control of any hazardous waste stream.

When considering the likely effectiveness of any method of purification, it is helpful to review the volatility of chlorides and fluorides, shown below in Tables 2 and 3, respectively. This data can be used to help determine the thermodynamic capability of purification with either chlorine or fluorine.

Table 2 : Molecular weight, melting points and boiling points of metal chlorides commonly produced during purification of graphite with chlorine gas.

Metal	Compound Name	Chemical Formula	Molecular Weight	Melting Point, °C	Boiling Point, °C
Aluminum	Aluminum Chloride	$AlCl_3$	133.3	-	262 (decomposes)
Barium	Barium Chloride	$BaCl_2$	208.3	963	1560
Boron	Diboron	B_2Cl_4	163.5	-92.6	Various

	tetrachloride				
	Boron trichloride	BCl_3	117.2	-107	12.5
Calcium	Calcium chloride	$CaCl_2$	110.9	772	>1600
Chromium	Chromous chloride	$CrCl_2$	123	824	-
	Chromic chloride	$CrCl_3$	158.4	1152	>1300 (dissociates)
Copper	Cuprous chloride	CuCl	99	430	1490
	Cupric chloride	$CuCl_2$	134.5	-	-
Iron	Ferrous chloride	$FeCl_2$	126.8	674	1023
	Ferric chloride	$FeCl_3$	162.2	300	316
Magnesium	Magnesium chloride	$MgCl_2$	95.2	712	1412
Manganese	Manganese chloride	$MnCl_2$	125.8	58	***
	Manganese trichloride	$MnCl_3$	161.3	-	-
Molybdenum	Molybdenum dichloride	$MoCl_2$	166.8	decomposes	-
	Molybdenum trichloride	$MoCl_3$	202.3	decomposes	-
	Molybdenum tetrachloride	$MoCl_4$	237.8	decomposes	volatile
	Molybdenum pentachloride	$MoCl_5$	273.2	194	268
Nickel	Nickel chloride	$NiCl_2$	129.6	1001	973 (sublimes)
Potassium	Potassium chloride	KCl	74.6	773	1500
Silicon	Silicon tetrachloride	$SiCl_4$	169.9	70	59
Sodium	Sodium chloride	NaCl	58.5	804	1413
Strontium	Strontium chloride	$SrCl_2$	158.5	875	1250
Titanium	Titanium dichloride	$TiCl_2$	118.8	1035	-
	Titanium trichloride	$TiCl_3$	153.3	550 (decomposes)	-
	Titanium trichloride	$TiCl_4$	189.7	-24.1	136.4
Vanadium	Vanadium dichloride	VCl_2	121.85	-	-
	Vanadium trichloride	VCl_3	157.3	decomposes	-
	Vanadium tetrachloride	VCl_4	192.8	-28	148.5
Zinc	Zinc chloride	$ZnCl_2$	136.3	290	732
Zirconium	Zirconium dichloride	$ZrCl_2$	162.1	350 (decomposes)	-
	Zirconium trichloride	$ZrCl_3$	197.6	350 (decomposes)	-

	Zirconium tetrachloride	$ZrCl_4$	233.0	437	331 (sublimes)

Table 3 : Molecular weight, melting points and boiling points of metal fluorides commonly produced during purification of graphite with fluorine or fluorine containing gas.

Metal	Compound Name	Chemical Formula	Molecular Weight	Melting Point, °C	Boiling Point, °C
Aluminum	Aluminum fluoride	AlF_3	83.9		1272 (sublimes)
Barium	Barium fluoride	BaF_2	175.4	1353	2260
Boron	Diboron trifluoride	BF_3	67.8	-127	-
Calcium	Calcium fluoride	CaF_2	78.1	1403	2500
Chromium	Chromous fluoride	CrF_2	90.0	894	-
	Chromic fluoride	CrF_3	109.0	1100	1100-1200 (sublimes)
	Chromic tetrafluoride	CrF_4	128.0	277 (estimate)	~400
Copper	Cuprous fluoride	CuF	82.5	980	1100 (sublimes)
	Cupric fluoride	CuF_2	101.5	950 (decomposes)	-
Iron	Ferrous fluoride	FeF_2	93.85	-	>1100 (sublimes)
	Ferric fluoride	FeF_3	112.9	-	>1000 (sublimes)
Magnesium	Magnesium fluoride	MgF_2	62.3	1248	2260
Manganese	Manganese difluoride	MnF_2	92.9	856	-
	Manganese trifluoride	MnF_3	111.9	600 (decomposes)	-
Molybdenum	Molybdenum hexafluoride	MoF_6	209.9	17.5	35
Nickel	Nickel fluoride	NiF_2	96.7	-	>1000 (sublimes)
Potassium	Potassium fluoride	KF	58.1	860	1505
Silicon	Silicon tetrafluoride	SiF_4	104.1	-90	-96 (sublimes)
Sodium	Sodium fluoride	NaF	42	993	1705
Strontium	Strontium fluoride	$SrCl_2$	125.6	1400	2460
Titanium	Titanium trifluoride	TiF_3	104.9	1200	1400
	Titanium trifluoride	TiF_4	123.9	>~300 (sublimes)	-
Vanadium	Vanadium trifluoride	VF_3	107.9	>800 (sublimes)	-
	Vanadium tetrafluoride	VF_4	126.9		>325 (decomposes)
	Vanadium pentafluoride	VF_5	145.9	19.5	47.9

Zinc	Zinc fluoride	ZnF_2	103.4	872	1500
Zirconium	Zirconium fluoride	ZrF_4	167.22	>600 (sublimes)	-

4. Conclusions and Recommendations

As discussed above, many industrially viable methods exist for purification of large monolithic blocks of nuclear grade graphite. These processes range in efficiency, cost, and processing ease. However, each of the methods discussed are sufficient to chemically purify to the required specifications for High Purity (HP) nuclear graphite.

Regarding the possibility of reuse of previously irradiated graphite waste, there are many factors to consider. Obviously, the quantity of long lived radionucleotides, depending on residual impurity concentration prior to irradiation, and the form in which the graphite will exist after irradiation are key variables that will determine the final route for reuse or recycle of the graphite. In previous work, GrafTech International has shown success in the production of new graphite billets from simulated waste materials. This graphite has shown excellent strength and thermal characteristics, and may open the possibility of utilizing graphite waste into a completely new graphite artifact. Of course, the possibility of using this route for recycle is dependent on the particle sizing and robustness of the waste material itself.

As part of the Carbowaste programme, GrafTech International is also investigating the use of a fine carbon additive (stimulant waste form) as a filler portion in a newly developed material. This material will have advantages over traditionally processed graphite because it can be made in days, rather than months, thus significantly reducing handling time of the potentially radioactive material. This work will be presented under a separate work package later in 2010.

5. References

1) CRC Handbook of Chemistry and Physics, 75th edition, 1994.

2) Merck Index, 11th edition, 1989.

3) Shaffer, Handbook of High-Temperature Materials, Plenum Press, 1964.