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**MASTER**

THE REMOVAL OF IRON FROM IMPURE GRAPHITES\*

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ABSTRACT

Iron impregnated and ash rich graphites have been purified by leaching with gaseous  $I_2$  at  $900^\circ C$ . With addition of  $H_2$ , the rate of removal of impurity iron can be markedly increased and becomes comparable to that obtained with  $Cl_2$ .  $I_2$  has an advantage in that it can also volatilize Ca and perhaps Ba and Sr.

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### Introduction

Impurities in nuclear graphite can have deleterious effects on its physical and chemical properties. Of special importance to structural graphites are the effects of impurities, particularly metallic species, have on the manner and rate of gasification by contaminants in the reactor coolant. Catalytic effects may be moderated by addition of inhibitors,<sup>1</sup> but these may prove unsatisfactory as a result of localized effects. Alternatively, the impurities may be removed. In this paper a leaching technique using  $I_2 + H_2$  is discussed and compared with the  $Cl_2$  leaching method.

### Experimental

Cylindrical specimens 1.27 cm diameter x 0.63 cm length were trepanned from H451 graphite (Great Lakes Carbon) and PGX graphite (Union Carbide) production blocks. The former contain <200 ppm total impurities, while the latter contain up to 1% ash, of which Fe is a major constituent. The Fe content was routinely measured via Mössbauer spectroscopy before and after sample treatment; specimens were hydrogenated prior to Mössbauer spectroscopy in order to convert all the iron to the elemental state and thus permit quantitative analysis. Sample treatment was accomplished by blending He with  $Cl_2$ ,  $I_2$  or  $I_2 + H_2$  at a total pressure of 1 atm and flow rate of 50 sccm and passing the mixture through a graphite specimen maintained at 500-950°C. Oxidation rates were measured before and after sample treatment in a Cahn R-1000 microbalance coupled to a Carle gas chromatograph. The specimens were first exposed to  $H_2$  at 850°C for several hours; rates were then measured at 1% burnoff at 750°C in 0.63%  $H_2O + 6.3\% H_2$  in He flowing at 2300 sccm.

Impurity concentrations of as-received and treated PGX graphite specimens were determined by atomic absorption spectrophotometry; specimens were prepared by low temperature ashing and dissolution in aqua regia.

### Results and Discussion

H451 graphite was impregnated with  $Fe(NO_3)_3$ , heated to decompose the nitrate and hydrogenated to give specimens containing ~1500 ppm Fe. Exposure to  $Cl_2$  and  $I_2$  at 700°C and 900°C gave the results shown in Table 1. Greater than 95% of the iron was removed at 900°C by either  $Cl_2$  or  $I_2$ ; at 700°C, however, a significant amount of iron remained after treatment with  $Cl_2$  and no removal was observed after treatment with  $I_2$ . These results are reflected in the measured oxidation rates.

Table 1. H451 Graphite Specimens Impregnated With  $Fe(NO_3)_3$  Solution

Treatment 24 Hr. in He	Reaction Rate Before Treat. Mg/Min	Reaction Rate After Treat. Mg/Min
0.35% $Cl_2$ , 900°C	0.24	0.001
0.35% $Cl_2$ , 700°C	0.225	0.045
0.046% $I_2$ , 900°C	0.14	0.002
0.046% $I_2$ , 700°C	0.20	0.20

PGX graphite containing <40 ppm Fe was ground and sieved to <50  $\mu m$  diameter particles, homogeneously blended with different amounts of reduced iron powder of similar size and pressed into pellets. The specimens were exposed to 0.046%  $I_2$  in He at 750°C for 24 hours; the effect on iron concentration is shown in Table 2. Residual iron was only found in the 10% and 0.2% iron specimens; further treatment at 750°C produced no effect. An unassignable Mössbauer spectrum was clearly observed after treatment of the 0.2% iron specimen, while it was definitely absent in the case of the 40% iron specimen. Formation of a lamellar compound,  $C_nFeI_2$ , is suggested in the former case.  $I_2$  itself probably does not form a lamellar compound with graphite;<sup>2</sup> likewise, no evidence exists for the intercalation of  $FeI_2$  into graphite.<sup>3</sup> Nevertheless, it may be possible to do so under certain conditions. Intercalation of  $FeI_2$  in PGX graphite is currently being attempted with large amounts of  $FeI_2 + I_2$ , in order to obtain a sufficient amount of material for corroborative analysis via X-ray diffraction. In specimens containing very large amounts of iron, the atom ratio C/Fe may be so low (~7 in the above case) as to preclude the C-C bonding necessary to form a lamellar compound of any stage; additionally, removal of iron is facilitated for iron rich specimens as the reaction progresses, due to the open porosity created by removal of the iron.

Table 2. Pelletized Iron/PGX Graphite Specimens

Initial Iron Content, %	Residual Iron Content, %
40	<0.01
10	0.1
0.2	0.1

Specimens of as-received PGX graphite containing >1000 ppm iron were exposed to 0.046%  $I_2$  or 0.046%  $I_2 + H_2$  in He at various temperatures to optimize the rate of removal of iron. Some results are presented in Table 3. Removal of iron by  $I_2$  appears to be favored by high temperature (~850°C) and addition of  $H_2$ . Treatment without  $H_2$  led to formation of an unknown stable compound with the same unassignable Mössbauer spectrum mentioned above. Regeneration of this spectrum after hydrogenation of a specimen could be accomplished by re-exposure to  $I_2$ .

PGX graphite specimens initially containing >1000 ppm Fe were exposed to 0.046%  $I_2$  at 900°C for 20 hours, after which their oxidation rates and impurity distributions were determined. Some results are compared in Table 4 with those from a specimen similarly exposed to  $Cl_2$ . It appears that the  $I_2$  leaching method, especially with added  $H_2$ , can be as efficient as the  $Cl_2$  method at removing Fe and is much better at removing Ca. Similar but inconclusive results have been obtained for Ba and Sr. At 900°C the chlorides of Ca, Ba and Sr are relatively non-volatile, whereas the iodides are volatile. Purification of contaminated graphite was carried out in the Dragon Project by heating to 900°C in  $Cl_2$ : Al, Fe, Mg, Si, Ti and V were re-

duced to <1 ppm, but Ca, Ba and Sr were not removed.<sup>4</sup> Iodide formation is less favorable thermodynamically than chloride formation; the observation that impurity calcium was removed indicates that it, at least, is present in a chemical form from which iodide formation is thermodynamically feasible.

A large fraction of the  $I_2$  in these experiments is in the form of atomic iodine (e.g. at 727°C  $P_I/P_{I_2} = 4.7$ ); in the presence of  $H_2$ , however,  $HI$  is the overwhelmingly favored species. Addition of  $H_2$  may serve to enhance the rates of impurity removal in two ways: (a) provision of a faster pathway to metal iodide formation, and (b) reduction of metal oxides, which generally makes iodide formation more feasible thermodynamically.

### Conclusion

Impurities, including Fe and Ca, can be removed from graphites by leaching with gaseous  $I_2$  at 900°C. The efficiency of Fe removal can be markedly increased by addition of  $H_2$ .

Table 4. PGX Graphite Specimens With  $\geq 1000$  ppm Fe

Specimen	Treatment	Reaction Rate Mg/Min	Impurity Conc., ppm	
			Ca	Fe
2-1	$I_2$	0.05	78	328
2-2	—	0.15	230	1100
2-4	$Cl_2$	0.084	153	112
2-5	—	0.25	226	1020
2-6	$I_2/H_2$	0.076	30	150

### References

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Table 3. Effect of Temperature and Gas Composition on the Removal of Iron

