2005

Development, Fabrication and Study of Fullerene-Containing Carbon Material (FCC) for Immobilization of Iodine: Final report 2005

Michael Savopulo
V.G. Khlopin Radium Institute – Research-Industrial Enterprise

Boris E. Burakov
V.G. Khlopin Radium Institute – Research-Industrial Enterprise

Repository Citation

Research-Industrial Enterprise "KIRSI", branch of the V.G. Khlopin Radium Institute (KRI)

UNLV – KRI-KIRSI Agreement 280203-1

Development, Fabrication and Study of Fullerene-Containing Carbon Material (FCC) for Immobilization of Iodine

Final Report #280203-1

Saint-Petersburg – 2005

1. Introduction

Immobilization of highly radioactive and long-lived isotope of ^{129}I, which is a fission product in spent nuclear fuel, requires development of new durable host-materials. Such materials should be characterized with the following principal features:

- high loading capacity to iodine incorporation;
- chemical durability and radiation resistance in order to prevent iodine release over long time (higher than 10^5 years) storage under conditions of underground repository of radioactive wastes;
- possibility to use iodine-doped material as a target for iodine transmutation.

Iodine is a very volatile chemical element, and even its chemically strong compounds such as AgI and CuI are not stable under ultraviolet irradiation or oxidizing conditions. Therefore, development of host materials for iodine immobilization is based on unusual approach – the search and testing of new compounds which were not studied before in respect of iodine sorption and strong fixation.

Laboratory of Applied Mineralogy and Radiogeochemistry of the V.G. Khlopin Radium Institute carries out investigation of prospective materials for iodine immobilization including transmutation since 1994 year. Recently, a family of new discovered carbon molecules – fullerenes – was suggested for incorporation and strong fixation of highly radioactive elements. It was found that pure crystalline fullerenes were not effective for the iodine incorporation. However, fullerene-containing carbon material (FCC) which is used as starting precursor for fullerene extraction was characterized by high capacity to iodine sorption (higher than 450 mg iodine per gram FCC). This powder consists of three carbon forms: graphite, fullerenes and amorphous carbon, which associate with each other by well not studied bonds.

Although FCC material demonstrated high loading capacity to iodine sorption it is necessary to take into account that FCC itself is not a final form of ^{129}I immobilization. Either for disposal in geological formation or iodine transmutation in nuclear reactors the FCC should be converted into more chemically and mechanically durable material. In case of transmutation it is necessary to provide, also, an acceptable «transparency» of final material to neutron fluxes. Therefore, we decided to consider two main groups of durable compounds: silicon carbides and carbon nitrides (of fullerene structure) as possible targets of FCC conversion. It was assumed that synthesis of Si_xC_y might be carried out at relatively low temperature as a result of chemical reaction between FCC and Si-organic chemicals. Successful synthesis of C_xN_y of fullerene-like structure might be carried out using N-ion bombardment of carbon material.

In the framework of first year ("KRI-KIRSI"-HRC Agreement 280203) we have studied optimal synthesis conditions and principal features of FCC. The preliminary results have been obtained from precise XRD analyses of iodine-doped and pure FCC samples before and after gamma-irradiation. It was found that iodine doping and irradiation caused principal changes in phase composition of FCC such as substituting of crystalline fullerene C_{60} (formed by benzene-like carbon rings) for crystalline chaoite phase (formed by carbyne carbon chains). It was decided to continue these experiments during second (current) year ("KRI-KIRSI"-HRC Agreement 280203-1) in comparison with study of activated carbon. In our experiments we decided to use samples of activated carbon SKT-3S that is widely used in Russian nuclear industry for different purposes including sorption of ^{129}I.

2. Synthesis of FCC samples, iodine doping of FCC and activated carbon

The graphite of high purity was used as starting material for the synthesis of FCC. Highly disperse powder of FCC was obtained by electric-arc method under conditions of glove box in helium atmosphere (Fig. 1).
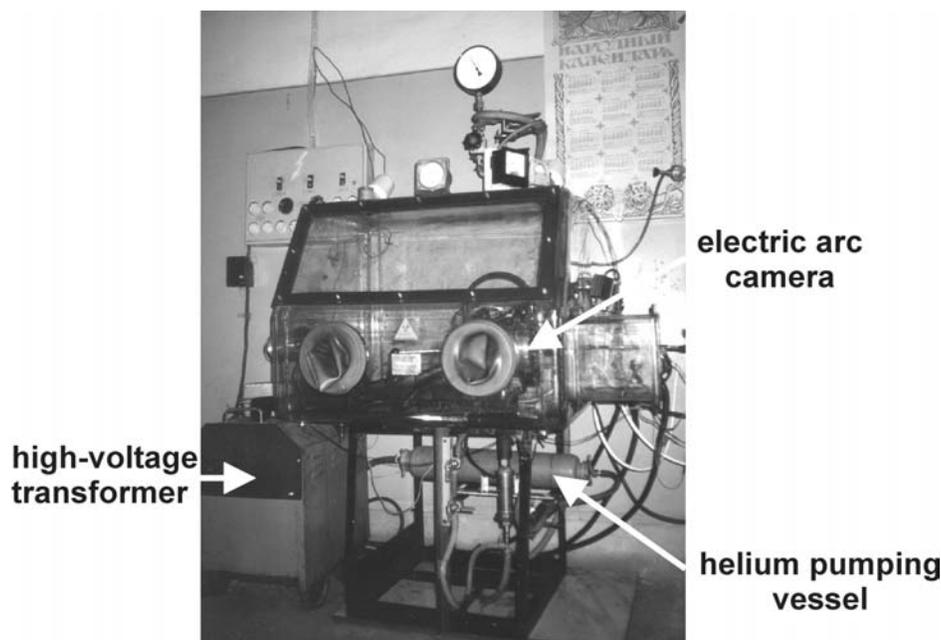

Figure 1. Electric-arc equipment installed into glove box for the synthesis of FCC material.

The samples of FCC and activated carbon SKT-3S were dried at 105-110°C up to constant weight, and then placed in glass ampoules. The crystalline iodine was put into the extension of the same ampoules. Then the atmosphere in the ampoule was replaced on high purity nitrogen and the ampoules were sealed. Then the ampoules were placed in a furnace and maintained at 300°C for 8 hours. After the exposure the unreacted iodine was re-crystallized into the extension and the ampoules were cooled to room temperature.

3. Irradiation of FCC and activated carbon

In order to obtain ceramic based on C_xN_y with fullerene structure we decided to carry out gamma-irradiation of iodine doped samples in nitrogen atmosphere. Parts of initial and iodine-doped samples of FCC and activated carbon were sealed in glass ampoules in nitrogen atmosphere (0.7 atm. N_2) and then irradiated by gamma-source (^{60}Co).

4. Conversion of FCC and activated carbon into ceramic-like Si_xC_y

Similar method from previous study was used to convert FCC and activated carbon into ceramic-like Si_xC_y material. Cold pressed granules of iodine-doped FCC and activated carbon

were rinsed in water-ethanol solution of tetraethoxysilane (TEOS), $Si(OC_2H_5)_4$, with the following proportions: 130 ml TEOS, 60 ml ethanol and 290 ml distilled water. Then granules were dried at 60°C for 6-8 hours or under infra-red lamp for 1 hour and calcined in air at different temperature: 300; 400; 420 and 800°C for 10 min or 30 min in order to provide formation of Si_xC_y phase.

5. Samples obtained

The following samples have been obtained:

FCC and activated carbon used for irradiation

1) Initial undoped FCC with fullerene (mainly C_{60}) content 6.2 wt.%;
2) Iodine doped FCC with iodine content 683 mg/g;
3) Undoped FCC after gamma-irradiation for 3.63×10^8 Rad in nitrogen atmosphere;
4) Iodine-doped FCC (683 mg/g) after gamma-irradiation for 3.63×10^8 Rad in nitrogen atmosphere;
5) Initial undoped activated carbon SKT-3S containing admixtures of sulfur and calcite;
6) Iodine doped activated carbon SKT-3S with iodine content 571 mg/g.
7) Iodine doped (432 mg/g) activated carbon (pure) after gamma-irradiation in nitrogen atmosphere for 2.1×10^7 Rad;
8) Iodine doped (432 mg/g) activated carbon (pure) after gamma-irradiation in nitrogen atmosphere for 3.3×10^7 Rad.

Samples used for the synthesis of Si_xC_y

FCC
1) Initial FCC containing 6.2 wt.% fullerenes. This material was used for all other experiments.
2) FCC + TEOS dried under infra-red lamp in air for 1 hour.
3) Sample #2 after sintering in vacuum at 800 °C for 30 minutes.
4) Sample #2 after affecting by laser (with beam diameter 1 mm and energy 10 joules) at both pellet sides.
5) FCC doped with iodine (252 mg/g).
6) Iodine doped FCC (sample #5) + TEOS dried under infra-red lamp in air for 1 hour.
7) Samples #6 after sintering in vacuum at 400 °C for 30 minutes.
8) Samples #6 after affecting by laser (with beam diameter 1 mm and energy 10 joules) at both pellet sides.

Activated carbon
1) Initial activated carbon SKT-3S using as an absorbent in Russian nuclear industry.
2) Activated carbon + TEOS dried under infra-red lamp in air for 1 hour.
3) Sample #2 after sintering in vacuum at 800 °C for 30 minutes.
4) Activated carbon SKT-3S doped with iodine (57 mg/g).
5) Iodine doped activated carbon (sample #4) + TEOS dried under infra-red lamp in air for 1 hour.
6) Sample #5 after sintering in vacuum at 400 °C for 30 minutes.

6. XRD analyses of initial and irradiated samples

Results of precise XRD analyses confirmed previous data that initial FCC consisted of three main carbon phases: graphite; fullerene (mainly C_{60}) and amorphous carbon (Fig.2, spectrum #1, Fig.4, spectrum #1). Iodine doping caused essential decrease of graphite content and substitution of C_{60} for chaoite phase (Fig.2, spectrum #2, Fig.4, spectrum #5). High iodine doping (683 mg/g) causes complete fullerene destruction and decrease of graphite content up to two times.

Activated carbon SKT-3S does not contain crystalline carbon forms such as graphite and fullerenes (Fig.3, spectrum #1). Admixtures of calcite ($CaCO_3$) and sulfur, which are particular additives in this type of industrial activated carbon, caused formation of anhydride ($CaSO_4$) during iodine doping at 300°C (Fig.3, spectrum #2). However, no evidences of interaction between iodine and calcite were observed. It is important to note that XRD patterns of activated carbon (initial and iodine doped) in low angle area (before 20° of 2 theta) are very similar to ones of FCC (Fig. 2). This is indirect evidence that iodine doping of activated carbon might cause similar conversion of carbon rings into carbyne carbon chains. However, it requires confirmation by TEM study.

Gamma-irradiation of undoped FCC (in nitrogen atmosphere) causes partial destruction of fullerenes but increase of contents of amorphous carbon and graphite (Fig. 1, spectrum #2). Similar effect of gamma-irradiation was observed in FCC with low iodine doping level (145 mg/g): increase of graphite content (depending on cumulative dose), accompanied with an additional partial destruction of fullerenes (Fig. 1, spectra #3 and #4). However, at high iodine doping level (683 mg/g) irradiation causes an additional decrease of graphite content (Fig. 1, spectra #5 and #6).

Gamma-irradiation of undoped activated carbon SKT-3S did not cause any effect identified by XRD. In order to obtain clear results from irradiation of iodine doped activated carbon we decided to use sample of other trademark without admixtures of sulfur and calcite. No essential effect of gamma-irradiation at 2.1×10^7 and 3.3×10^7 Rad has been observed (Fig. 5).

It is important to note that the use even precise XRD analysis does not allow identifying formation of C_xN_y phase of fullerene structure in the matrix of FCC or activated carbon. Further analyses of obtained samples are needed applying method of high resolution transmission electron microscopy (HRTEM).
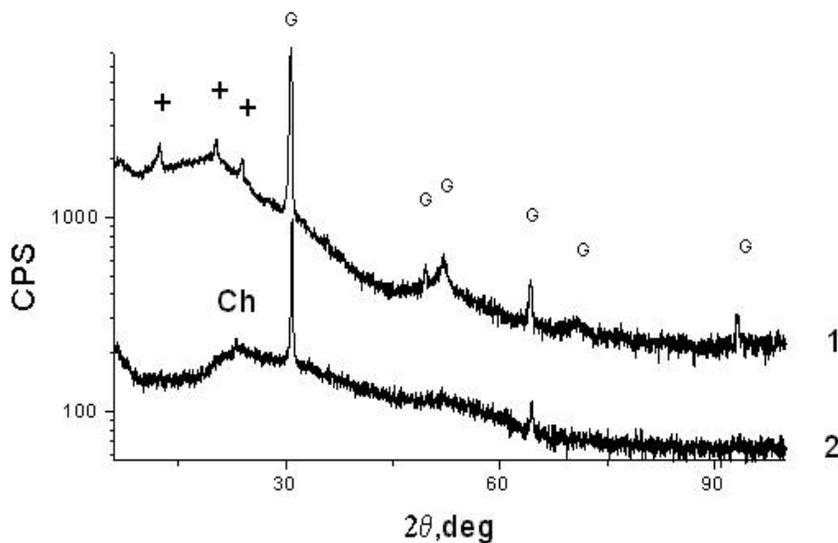
Figure 2. XRD patterns of FCC: 1) initial undoped with fullerene content 6.2 wt.%; 2) iodine-doped (683 mg/g). The following peaks are marked: "**G**" – graphite; "**+**" – C_{60}; "**Ch**" – chaoite.
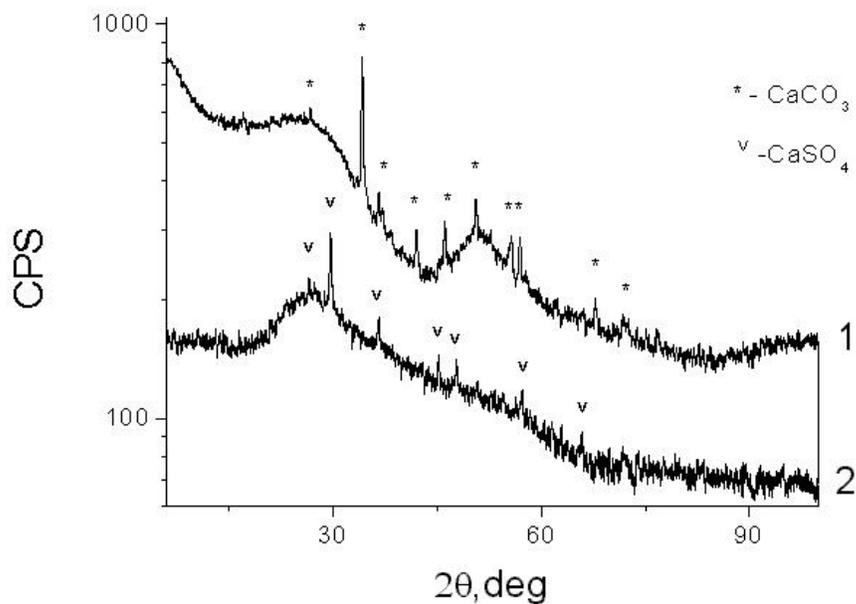

Figure 3. XRD patterns of activated carbon SKT-3S: 1) initial undoped; 2) iodine-doped (571 mg/g). There are no crystalline carbon phases in both samples. Type of activated carbon SKT-3S contains admixtures of calcite ($CaCO_3$) and elemental sulfur that causes formation of anhydride ($CaSO_4$) during process of iodine doping at 300°C.
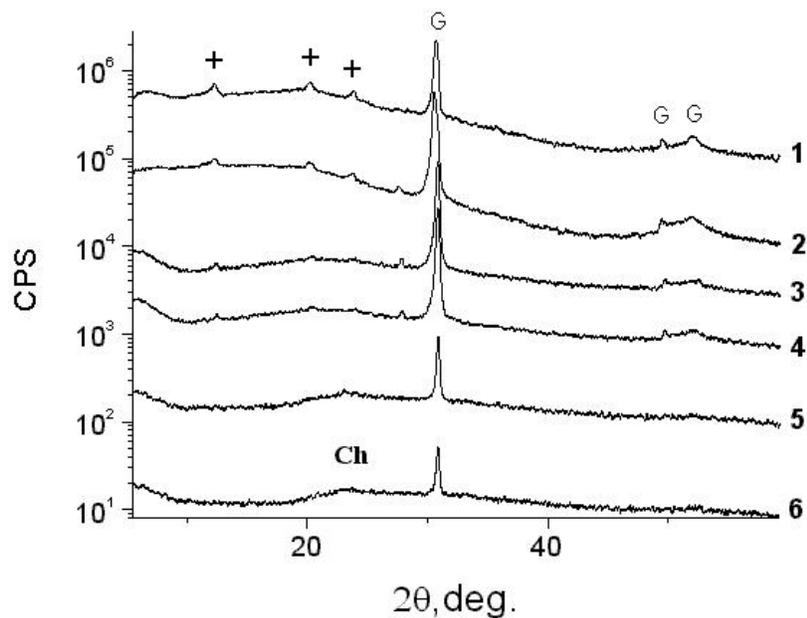
Figure 4. XRD patterns of:

1) initial undoped FCC containing 6.2 wt.% fullerenes (mainly C_{60});
2) undoped FCC after gamma-irradiation for 3.63×10^8 Rad;
3) iodine doped (145 mg/g) FCC after gamma-irradiation for 2.1×10^7 Rad;
4) iodine doped (145 mg/g) FCC after gamma-irradiation for 3.3×10^7 Rad;
5) iodine doped (683 mg/g) FCC;
6) iodine doped (683 mg/g) FCC after gamma-irradiation for 3.63×10^8 Rad.

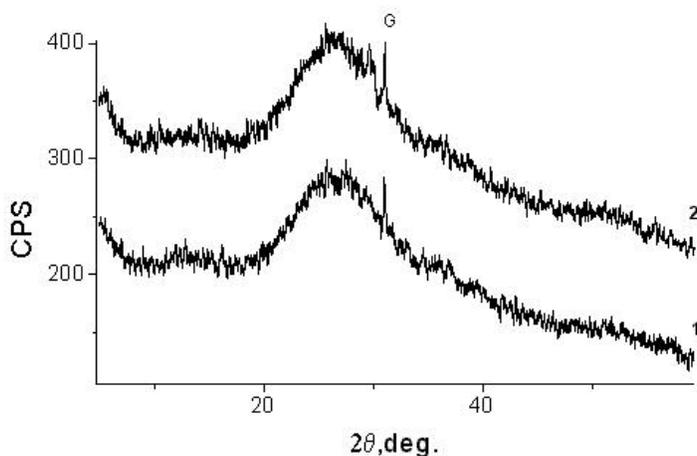Reflections of identified phases are marked as: graphite (**G**); C60 (**+**) and chaoite (**Ch**).

Figure 5. XRD patterns of iodine doped (432 mg/g) activated carbon after gamma-irradiation in nitrogen atmosphere at: 1) 3.3×10^7 Rad and 2) 2.1×10^7 Rad. Reflection of graphite phase is marked as (**G**).

7. XRD analyses of FCC interacted with Si-organics

The initial undoped FCC sample (Fig.6, spectrum #1) consists of three phases: amorphous carbon (see typical broad band in low angle area up to 30 degrees); graphite and fullerenes (mainly C_{60}). Low temperature interaction between FCC and Si-organics (Fig.6, spectrum #2) caused change of XRD spectrum in the area of amorphous carbon what means as assumed the formation of new unknown amorphous phase. In the same time decrease of C_{60} content was observed. Further sintering of this sample in vacuum (Fig.6, spectrum #3) did not cause formation of crystalline Si_xC_y phase; however, it recovered the shape of XRD spectrum in low angle area. Graphite content increased in comparison with initial FCC up to 50-60 %. Our interpretation is that under vacuum conditions at 800 °C amorphous Si-phase evaporated but it should be confirmed by chemical analysis.
A very interesting result was obtained after affecting altered FCC sample by laser beam in air (Fig.6, spectrum #4). Intensity of C_{60} peaks increased, however, the shape of XRD spectrum in low angle area remained the same as before laser affect. This means that laser helps formation of new fullerenes as well as it does not destroy new-formed amorphous unknown phase (probably, Si-C-phase). This assumption correlates with essential decrease of graphite content – up to 40 % in comparison with initial FCC.

Current experiments on iodine doping completely confirmed our previous results that iodine actively interact with FCC. This interaction is accompanied with partial destruction of graphite and fullerenes and formation of carbyne chains (Fig.2, spectrum #5, low angle area). Interaction of iodine doped FCC with Si-organics in air at low temperature (Fig.7, spectrum #6) and under vacuum conditions at 400 °C (Fig.7, spectrum #7) cased increase of graphite content. After sintering in vacuum increase of graphite was about 50 %, which is the same as for undoped FCC (Fig.7, spectrum #3).

The behavior of iodined doped FCC altered by Si-organics under laser beam (Fig.7, spectrum #8) is similar to undoped FCC: there is no change of XRD spectrum in low angle area (therefore, no destruction of new formed unknown amorphous phase, possibly, Si-C) and decrease of graphite content up to 40 % in comparison with initial iodine doped FCC (although, formation of new fullerenes was not clear confirmed).

8. XRD analyses of activated carbon interacted with Si-organics

It is important to note that admixtures of different crystalline phases (calcite and unknown organic phase) and elemental amorphous sulfur (Fig.8, spectrum #1) in undoped activated carbon SKT-3S made interpretation of XRD data essentially difficult. Interaction with Si-organics at low temperature in air slightly changed the shape of XRD spectrum in low angle area (Fig.8, spectrum #2), however, the interpretation is unclear. Sintering in vacuum initiated chemical interaction between admixtures of sulfur and calcite and caused formation of CaS (Fig.8, spectrum #3). Also, the destruction of unknown crystalline organic phase has been observed as well as quartz crystallization. (Fig.8, spectrum #3). Process of iodine doping initiated interaction between elemental sulfur and calcite that caused formation of anhydrite, $CaSO_4$ (Fig.9, spectrum #4). The chemical reason of this process so far is unclear. Interaction of iodine doped activated carbon with Si-organics at low temperature in air did not change essentially the XRD spectrum, excepts decrease of anhydrite reflections (Fig.9, spectrum #5).
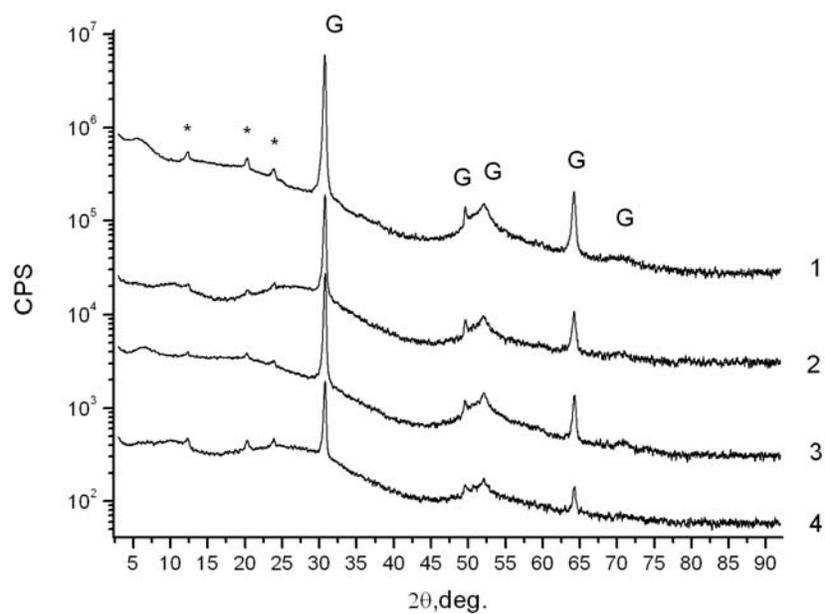
Figure 6. XRD patterns of undoped FCC: (1)- initial and (2-4) after interaction with Si-organics under different conditions. Peaks of graphite are marked as "**G**" and C_{60} as *****.
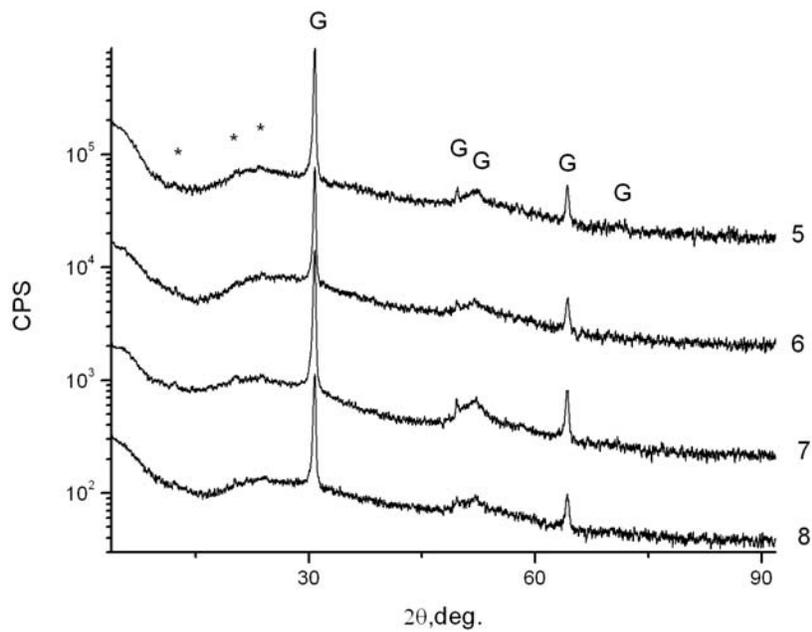

Figure 7. XRD patterns of iodine doped FCC: (5)- initial and (6-8) after interaction with Si-organics under different conditions. Peaks of graphite are marked as "**G**" and C_{60} as *****.
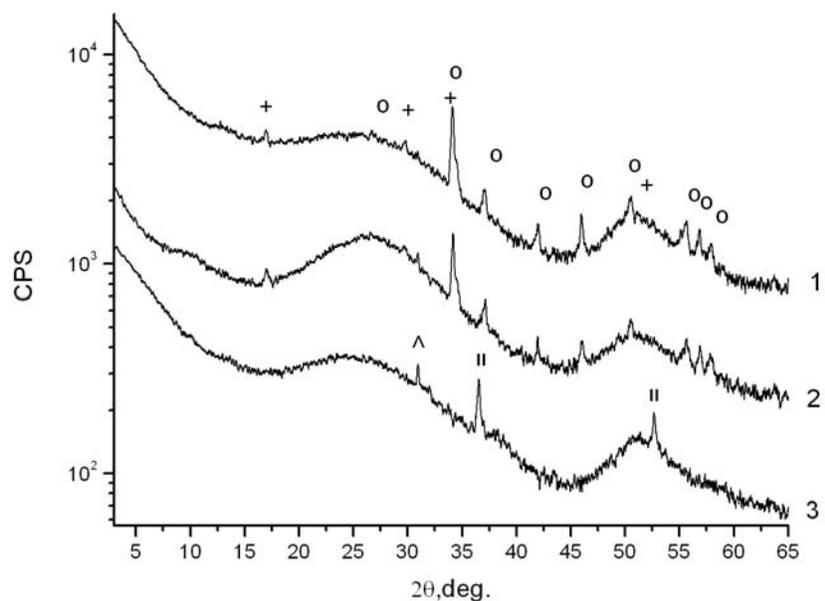
Figure 8. XRD patterns of undoped activated carbon SKT-3S: (1)- initial and (2-3) after interaction with Si-organics under different conditions. Peaks of calcite, $CaCO_3$, are marked as "**o**"; unknown organic phase as "**+**"; calcium sulfide, CaS, - "**II**" and quartz -"**^**".
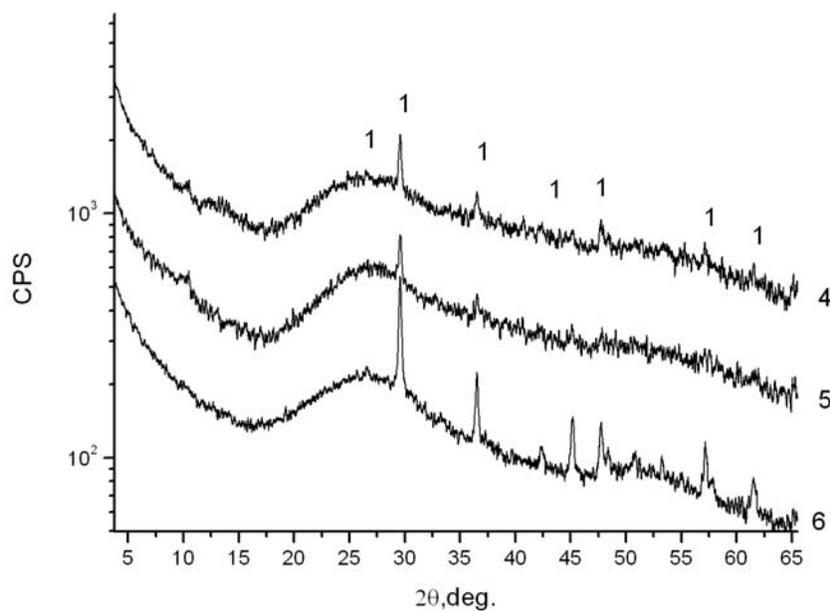

Figure 9. XRD patterns of iodine doped activated carbon SKT-3S: (4)- initial and (5-6) after interaction with Si-organics under different conditions. Peaks of anhydride, $CaSO_4$, are marked as "**1**".

Further sintering of this sample in vacuum caused better crystallization of anhydrite (Fig.9, spectrum #6) and it was accompanied with complete loss of iodine. It is necessary to note that we used for this sample the low iodine doping level (57 mg/g) in order to provide the most reliable iodine sorption and fixation. The absence of quartz or Si-carbide phases in this sample means as assumed a significant evaporation of Si-organics before its chemical destruction or interaction with carbon. We might conclude that activated carbon SKT-3S easily loses iodine at temperature of possible chemical interaction between Si-organics and carbon. There are still some uncertainties concerning the influence of chemical admixtures in SKT-3S to iodine loss.

9. Static leach test of FCC altered with Si-organic

For each temperature of FCC calcination the loss of iodine during leach test has been studied (Table 1). Activated carbon completely lost iodine during calcination under the same conditions.

Table 1. Correlation between FCC calcination temperature and iodine release after static leach test at 90°C for 7 days in distilled water.

Calcination temperature, °C	Iodine loss	
	in mg/g	in wt.% of initial content
300	less 0.04	less 0.02
400	0.20	0.06
420	0.37	0.11

It was demonstrated that higher temperature of calcination provides increase of mechanical durability of the final ceramic-like material, however, it causes increase of iodine release during leach test. This means that tetraethoxysilane is not optimal chemical compound for low temperature interaction with FCC as well as with activated carbon. The results of XRD analysis did confirm formation of crystalline Si-carbide phase. We assumed that future TEM study of ceramic-like samples would be useful to check the presence and making identification possible impurities of crystalline S-C phases. Optimal conditions for more effective conversion of iodine doped FCC into Si_xC_y material avoiding iodine loss are still the subject for further research.

10. Conclusions

The results obtained allow us to make the following conclusions:
1) Iodine actively interacts with FCC. Iodine doping is accompanied with change of FCC structure and phase composition. As a result the **chaoite** crystalline phase substitutes fullerene C_{60} phase and graphite content decreases. General structure of initial FCC based on **benzene-like** carbon rings changes under iodine doping to **carbyne** chains.
2) Iodine doping of activated carbon, which does not contain crystalline phases, might cause similar process of carbon rings destruction and formation of carbyne chains. However, it should be confirmed by further investigation.
3) Gamma-irradiation of initial **undoped FCC** in nitrogen atmosphere causes partial conversion of C_{60} into amorphous carbon and essential **increase of graphite content**.

4) Gamma-irradiation of **iodine doped FCC** in nitrogen atmosphere is characterized by essential **decrease of graphite content**. It is assumed that gamma-irradiation stimulates interaction between iodine and carbon rings and formation of carbyne carbon chains.

5) Formation of crystalline phase Si_xC_y as a result of interaction between pure and iodine doped FCC and activated carbon SKT-3S has not been observed under applied conditions. Some evidences of possible formation of amorphous Si-C-phase were obtained only for FCC samples. It should be confirmed by further study using TEM method.

6) Sintering of pure and iodine doped FCC at 400 and 800°C in vacuum before and after alteration with Si-organics cased essential (up to 50-60 %) increase of graphite content.

7) No graphite formation was observed in pure and iodine doped activated carbon under similar conditions before and after alteration with Si-organics.

8) Laser beam affecting of pure and iodine doped FCC altered by Si-organics caused essential decrease of graphite content. Also, for undoped FCC the **increase of fullerene content** after laser impact has been observed.

9) Activated carbon SKT-3S easily loses iodine at 300°C before start of any possible chemical interaction between Si-organics and carbon.

Dr. Michael Savopulo, Principal Investigator

Dr. Boris E. Burakov , Head of Mineralogical Group