Report on disposal properties of carbides as waste form for ^{14}C

Deliverable D-6.2.1 of the
Carbowaste project

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rev. no.	date	description
B	27-4-2012	Final version
A	17 -4- 2012	1st draft sent to RH for review

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Reference:	NRG-22260.12.114127/I&D/EV/IC		
27 pages	27 April 2012		

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Summary

This report is deliverable D - 6.2.1 for the work package 6 “Disposal Behaviour of Graphite & Carbonaceous Wastes” task 6.2 - Disposal Behaviour of Carbonaceous Wastes within the Carbowaste project.
Silicon carbide formed from irradiated graphite (in WP5) was studied under repository conditions. Three leachants were used (granite water, clay pore water and Q-brine), the leaching was done at the room temperature and at 90ºC. The material was leached during a period of 160 days, with sampling every 40 days. Irradiated graphite was studied at the same conditions.

For the silicon carbide experiments, the measured activity of C-14 found in the leachant was in units or tens of Bq/g of silicon carbide. The leachant in Q-Brine was about two –three times higher at the temperature of 90ºC than at the room temperature. It seems that there is no significant influence of temperature on the leaching behaviour of the SiC powder in clay water, in the granite water higher activities are measured at room temperature.

The measured activities of C-14 leached from irradiated graphite are much higher comparing to the ones leached from the SiC made from this graphite. The measured activity of C-14 in the leachant was in hundreds to thousands of Bq/g of irradiated graphite. Also for graphite, the highest activity of C-14 was found in the Q-Brine leachant.

Based on that, it seems that the transformation of irradiated graphite into silicon carbide could be a way of decreasing of the C-14 release from the material. Because of limited amount of available irradiated graphite, the above mentioned tests are done with very small amount of irradiated graphite (0.02 g in 20ml leachant) comparing to the silicon carbide (0.4g in 20 ml leachant), this could have influence on the leaching rates. To confirm that silicon carbide could be a suitable product formed from irradiated graphite concerning the lower C-14 release, more tests must be performed. Long-term tests should be done, better comparable amount of materials to be leached should be studied and material in the form of pellets should be leached as well (if SiC is used as e.g. container material).

Introduction

This report is deliverable D - 6.2.1 for the work package 6 “Disposal Behaviour of Graphite & Carbonaceous Wastes” task 6.2 - Disposal Behaviour of Carbonaceous Wastes within the Carbowaste project.

In the work package 6 of the Carbowaste project disposal behaviour of graphite and carbonaceous wastes is studied. Long-lived ^{14}C and ^{36}Cl complicate the disposal of carbonaceous wastes and graphite. The waste is only suitable for disposal after transforming it by specific conditioning techniques in adequate waste packages, e.g. by confining the waste in stable matrices emplaced inside containers resistant to radiation, corrosion and mechanical damage. Recycled carbon based products may contribute to the packaging and confinement function. The work package comprises four tasks dealing with the characterisation of the disposal properties of i-graphite and of other i-carbonaceous wastes, of associated waste packages and of confinement matrices to improve the disposal behaviour of these waste products. In a final task, the performances of the waste disposal is evaluated.

NRG participates to task 6.2, where properties of silicon carbides made from irradiated graphite are studied. Task 6.2 follows task 5.2 – sub-task 5.2.3. *Carbonaceous ceramics for waste management* . This sub-task addresses graphite canisters for waste storage as well as non-graphite uses of other chemical forms of carbon. The latter category includes materials such as silicon-carbide (SiC) and calcium carbonate. The definition for the purposes of this project of “recycled products” specifically includes products specially manufactured to stabilise carbon in a radioactive waste disposal site, or to act as confinement or packing material for other wastes and thermal management, in the repository site. The task will include the production of materials which are suitable for use in disposal sites as backfill, encapsulants, etc., without oxidation of the carbon and providing safety during processing. In this part, research on silicon carbide formation from graphite and irradiated graphite was done. In the following chapters details about the SiC formation and its characterization are presented.

Within work package 6, the formed silicon carbide is studied under repository conditions by leaching experiments.

1 SiC formation

Literature research on SiC formation from graphite was done, several suitable methods were found and finally a technique published by A. Morancais et al. in the J. of Eur. Ceram. Soc. 23 (2003) 1949–1956 [2], was chosen as method to be tested. In the paper, the method is called “a process involving an SHS stage.”

The preparation of porous SiC ceramics from stoichiometric mixtures of silicon and graphite has been studied. Products with very high pore contents (≈80%) were obtained using a process, shown in the following figure, which consisted of heating the reactive pellets in purified argon, at 15 °C min^{-1}, up to 1430 °C and applying a weak d.c. voltage across the sample for 20 s. The resulting electrical current was necessary for the ignition of a SHS reaction simultaneously in the whole sample. The analysis of the sample microstructure evolution all along the process has enabled the identification of the different mechanisms involved in the SiC formation. Before the SHS stage, the formation of silicon carbide, during heating from about 1325 up to 1430 °C, is associated with a large sample expansion, which mainly determined the final pore volume fraction. The pore transfer mechanisms, which occur during the SHS stage at 1430 °C, have a specific influence on the pore development. Since the final pore size distribution is strongly related to silicon grain size distribution, the porosity of the porous SiC ceramic, obtained by this process, can be easily modulated.

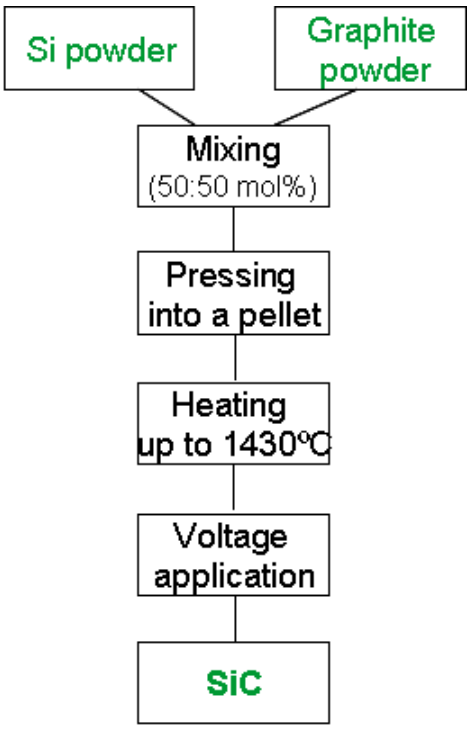

Figure 1-1 Flowchart of the SiC formation method

This method has been applied for the fabrication of SiC directly from silicon and graphite. Many tests were performed to establish the right conditions, and it was found that the voltage applications was not necessary for the SiC formation. First, the method was tested with virgin graphite. When the procedure was established, the formation of SiC from irradiated graphite could start. In this report, only the part of the SiC formation from irradiated graphite is presented.

1.1 Raw materials

1 Silicon powder (Alpha Aesar) – crystalline, 325 mesh, 99,5 % metal basis.

2 Irradiated graphite – irradiated graphite from Carbowaste WP3 – RRT test was used, this graphite originates from UNGG, EdF

3 Ethanol/methanol

1.2 Experimental procedure

Reactive samples were prepared from a stoichiometric ratio of graphite and silicon (30wt% of C – 70wt% of Si) mixed in an ethanol/methanol solution for 30 min. in a ball mill IKA mixer.
When the mixing was finished, the ethanol/methanol was evaporated and the powder mixture was pressed at low pressure into a pellet suitable for the reaction setup. The sample was placed into the oven where a temperature program was applied. The following temperature program was used as the starting basis but was modified as experiments proceeded:
100°C/h to 200°C
200°C for 10 h
200°C/h to 1430°C
(voltage application)
1430°C for 40h
200°C/h to RT.

When finished, the sample was taken from the setup and analyzed by XRD and SEM.

1.3 SiC formation for leaching experiments

When the right conditions of the method were set up, the formation of SiC for the leaching experiments could start. To allow the leaching experiments, an amount of about 8 g of SiC had to be produced. The same procedure was followed to form this silicon carbide, only bigger amounts of the reaction mixtures were used (about 1 g). To allow the reaction to occur properly, the period of thermal treatment was prolonged to 40 hours. Several batches were made and reacted.

1.3.1 XRD analyses

The phase composition of the mixtures was analyzed by powder X-ray diffraction (Bruker D8 Advance). It was measured in the range of 20-80 2θ at room temperature, to avoid the spreading of the active materials, a special sample holder with cover was used. The XRD analyses showed that beta-SiC is formed with small amount (less than 5%) free carbon. Several trials were done to remove the free carbon, but is did not succeed.

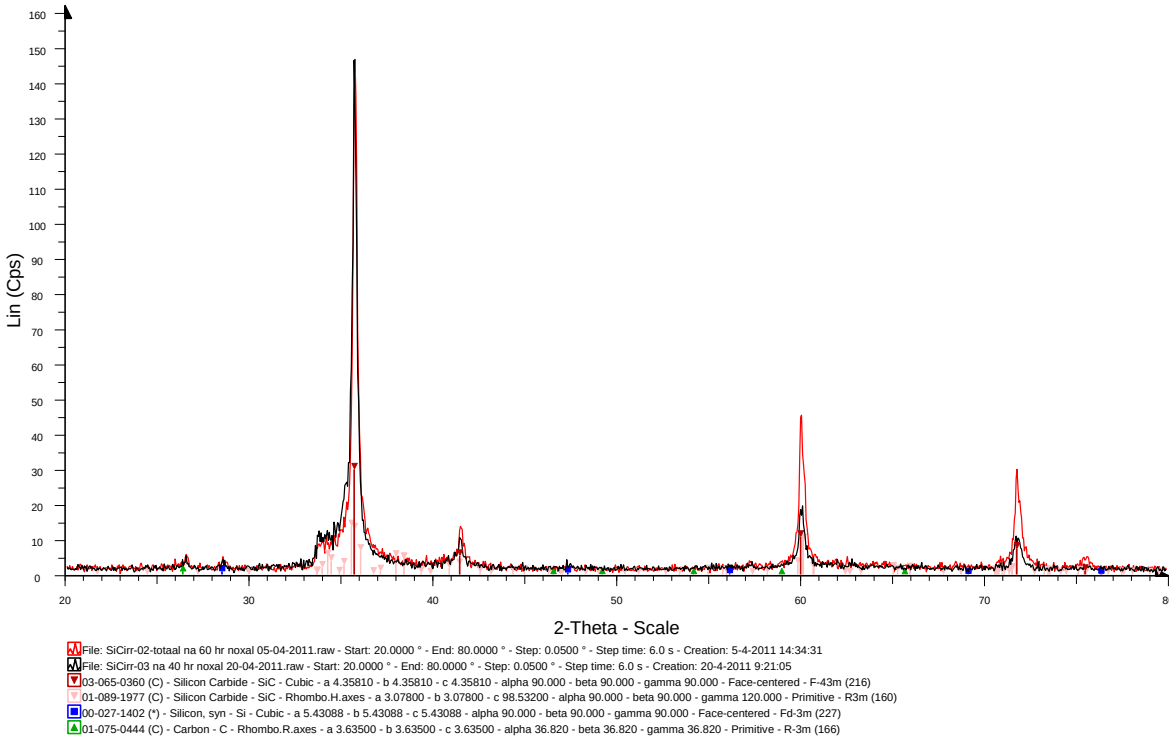

Figure 1-2 XRD of SiC for the leaching experiments – batch 2 and 3

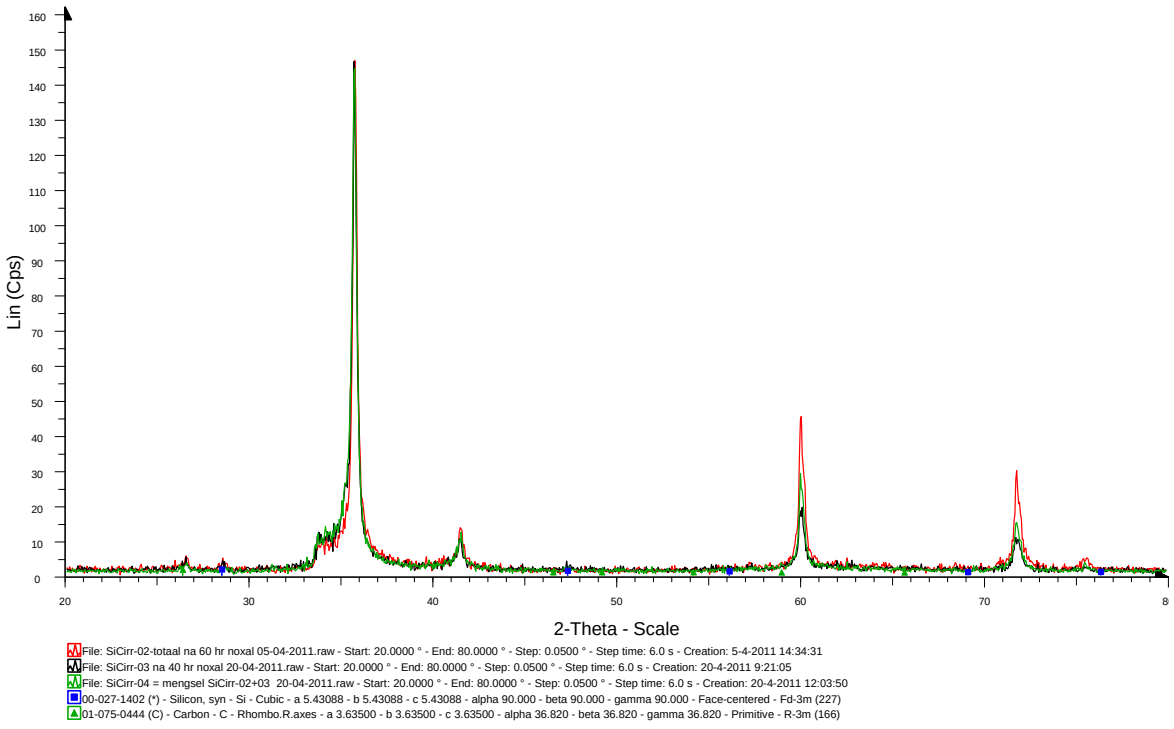

Figure 1-3 XRD of SiC for the leaching experiments – batch 2 and 3 and their mixture – called batch 4

Sufficient amount (8 g) of SiC for the leaching experiments was prepared and this material will be used in the following work.

1.3.2 SEM analysis on silicon carbide formed from irradiated graphite

The irradiated graphite and the formed silicon carbide powders were analyzed by SEM (JEOL 6490 LV SEM).

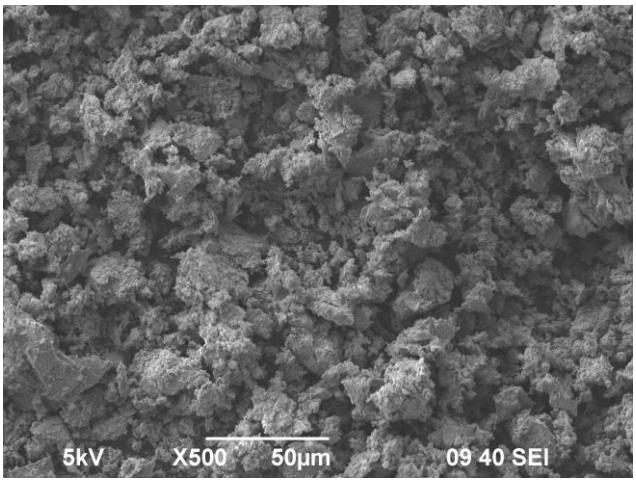

Figure 1-4 SEM picture of SiC formed from irradiated graphite

2 Leaching experiments

The formed SiC powder will be studied under repository conditions such as salt domes, granite-based repositories and clay formations.

2.1 Experiment preparation

Simulants for clay pore water and Q-brine were prepared by dissolving accurately weighted amounts of salts in demineralised water (>18 MΩ). The simulants were stored in PE vessels. Any contact with glass or Si/Zr-containing materials was avoided.

For **clay porewater** the following salts were used (mg/l given within the brackets): $MgSO_4$ (12.0), KCl (20.0), Na_2SO_4 (1.50), NaF (8.0), $NaHCO_3$ (1250), NaCl (44.0) saturated in $CaCO_3$ and filtered over a 0.45 µm cellulosenitrate filter (Schleicher&Sluell). Density: 0.9932 g/cm^3.

For **Q-brine** the following salts were used (g/l in brackets): NaCl (350), $CaCl_2.H_2O$ (3.12), Na_2SO_4 (3.04), K_2SO_4 (3.2) and $MgSO_4.7H_2O$ (2.52). Density: 1.1935 g/cm3.
For Q-brine experiments at 90 °C, additional NaCl (36.0 g) and $CaSO_4.2H_2O$ (7.2 g) was added in order to keep the solution saturated in NaCl and $CaSO_4$.
For **granite water**, the demineralised water was used. Density: 1.0064 g/cm^3.

2.2 Sample preparation

Static corrosion experiments on accurately weighted amounts of SiC powder were performed in PTFE containers (Nalgene). The containers were pretreated as described in the ASTM-C 1220-92 standard test. Each container was weighed before, during and after the leaching period so as to ensure that evaporation of the leachants did not occur.
An amount of approximately 0,4 g of SiC was weighted and put into the prepared vessel, 20 g of leachant was added. The amount of leachant used was weighed, based on the required volume and its density. The samples and the leachants were weighted at the laboratory atmosphere.

The leaching was done for all three leachants and at two temperatures (room temperature and 90ºC). Every experiment was performed in triple and for each condition, a blank was prepared.

Table 2-1 Sample list

Container code	Sample code	Leachant	Temp (°C)	Weighed sample (g)
1	SiCirr-04	water	25	0.40317
2	SiCirr-04	Clay pore	25	0.40491
4	SiCirr-04	Q-brine	25	0.40514
5	SiCirr-04	water	25	0.39468
6	SiCirr-04	Clay pore	25	0.40013
7	SiCirr-04	Q-brine	25	0.39266
8	SiCirr-04	water	25	0.39655
9	SiCirr-04	Clay pore	25	0.39182
10	SiCirr-04	Q-brine	25	0.39723
11	blank	water	25	
12	blank	Clay pore	25	
13	blank	Q-brine	25	
16	SiCirr-04	water	90	0.39811
17	SiCirr-04	Clay pore	90	0.40331
18	SiCirr-04	Q-brine	90	0.40118
19	SiCirr-04	water	90	0.40238
20	SiCirr-04	Clay pore	90	0.40312
22	SiCirr-04	Q-brine	90	0.39548
23	SiCirr-04	water	90	0.39767
24	SiCirr-04	Clay pore	90	0.39649
27	SiCirr-04	Q-brine	90	0.39197
28	blank	water	90	
29	blank	Clay pore	90	
30	blank	Q-brine	90	
31	Cirr (L2-G2)	water	25	0.01367
34	Cirr (L2-G2)	Clay pore	25	0.01979
35	Cirr (L2-G2)	Q-brine	25	0.01473
36	Cirr (L2-G2)	water	90	0.01574
37	Cirr (L2-G2)	Clay pore	90	0.01840
38	Cirr (L2-G2)	Q-brine	90	0.01615

Water = granite water.

The samples studied at 90ºC were placed in the oven (Heraus), the temperature was checked using a certified probe.

Containers 31 to 38 were served to determine the leaching of irradiated graphite used for the SiC formation. This study was performed to check the possible influence of the graphite present (less than 5%) in the formed SiC.

All leaching experiments are performed in a laboratory atmosphere.

Figure 2-1 Picture of the leaching experiments – left at temperature of 90ºC (controlled by certified probe) and right – at room temperature

2.3 Sampling of the leachants

A few days before taking a sample, the container was swirled to ensure that the solution became homogenous. Samples of the solution were taken in the fume hood. The containers that were stored in the oven were handled after 1 hour of cooling to the room temperature.

Using a 1.000 ml Eppendorf pipette, 1 ml of solution was pipetted from the container (making sure that no material was removed from the container) into a glass scintillation vial. The amount of leachant that is sampled is weighed. This weight is used to correct the result, along with the density of the leachant. The containers are weighed before and after sampling.

Samples were taken from the liquid phase above the material at 40, 80, 120 and 160 days into the experiment. An overview of the samples is given in the table 2-2.

Table 2-2 Sampling overview

				1ste monstername					2de monstername					3de monstername					4de monstername			
LSC code	materiaal	leachant	vessel no	vessel voor (g)	lege vial (g)	vial + 1 ml sample (g)	vessel na (g)	LSC code	vessel voor (g)	lege vial (g)	vial + 1 ml sample (g)	vessel na (g)	LSC code	vessel voor (g)	lege vial (g)	vial + 1 ml sample (g)	vessel na (g)	LSC code	vessel voor (g)	lege vial (g)	vial + 1 ml sample (g)	vessel na (g)
lucht - 25°C																						
A1	SiCirr	Clay pore	2	39.6420	15.0522	16.0535	38.6413	A16	38.6323	15.6426	16.6532	37.6194	A31	37.6160	15.5237	16.5235	36.6159	A46	36.6116	15.4401	16.4414	35.6121
A2	SiCirr	Clay pore	6	39.6214	15.0335	16.0381	38.6169	A17	38.6078	15.7646	16.7727	37.6003	A32	37.5952	15.4931	16.4931	36.5971	A47	36.5911	15.5072	16.5088	35.5900
A3	SiCirr	Clay pore	9	40.4246	14.8577	15.8620	39.4206	A18	39.4137	15.5184	16.5259	38.4054	A33	38.4004	15.4311	16.4306	37.4017	A48	37.3962	15.5121	16.5136	36.3949
A4	blanco	Clay pore	12	39.4008	15.0371	16.0432	38.3958	A19	38.3879	15.7284	16.7311	37.3834	A34	37.3780	15.4277	16.4268	36.3798	A49	36.3705	15.6322	16.6332	35.3703
A5	SiCirr	Q-brine	4	43.3842	15.0212	16.2287	42.1770	A20	42.1704	15.6744	16.8690	40.9655	A35	40.9619	15.4996	16.7005	39.76478	A50	39.7591	15.3750	16.5769	38.5594
A6	SiCirr	Q-brine	7	43.4878	14.9010	16.1053	42.2822	A21	42.2764	15.7773	16.9860	41.0680	A36	41.0636	15.4607	16.6615	39.86751	A51	39.8614	15.5200	16.7228	38.6604
A7	SiCirr	Q-brine	10	43.8426	14.9949	16.1984	42.6404	A22	42.6336	15.6919	16.8623	41.4658	A37	41.4613	15.2910	16.4916	40.26278	A52	40.2594	15.5335	16.7366	39.0578
A8	blanco	Q-brine	13	43.5444	15.0057	16.2165	42.3371	A23	42.3299	15.6742	16.8802	41.1271	A38	41.1221	15.4407	16.6029	39.96385	A53	39.9586	15.4570	16.6593	38.7580
A9	SiCirr	water	1	39.3258	15.1663	16.1726	38.3211	A24	38.3116	15.6951	16.7016	37.3064	A39	37.3025	15.4290	16.4261	36.30529	A54	36.2978	15.5113	16.5109	35.2991
A10	SiCirr	water	5	39.3528	14.9931	15.9956	38.3479	A25	38.3396	15.7521	16.7547	37.3378	A40	37.3316	15.3022	16.3003	36.33458	A55	36.3177	15.6411	16.6408	35.3179
A11	SiCirr	water	8	39.4631	14.9873	15.9867	38.4604	A26	38.4522	15.5928	16.6020	37.4442	A41	37.4383	15.5688	16.5659	36.44351	A56	36.4363	15.5452	16.5446	35.4379
A12	blanco	water	11	39.1425	15.0562	16.0581	38.1404	A27	38.1315	15.6435	16.6472	37.1305	A42	37.1234	15.4563	16.4540	36.12778	A57	36.1214	15.4738	16.4740	35.1238
A13	Cirr (L2-G2)	Clay pore	34	38.5129	14.9334	15.9343	37.5123	A28	37.5049	15.5815	16.5830	36.4998	A43	36.4974	15.5906	16.5884	35.49797	A58	35.4934	15.5807	16.5860	34.4871
A14	Cirr (L2-G2)	Q-brine	35	42.6172	14.8848	16.0908	41.4119	A29	41.3695	15.5678	16.7802	40.1552	A44	40.1273	15.5442	16.6758	38.99521	A59	38.9601	15.5979	16.8022	37.7565
A15	Cirr (L2-G2)	water	31	39.1909	14.9725	15.9772	38.1865	A30	38.1789	15.7691	16.7735	37.1758	A45	37.1703	15.5252	16.5223	36.17348	A60	36.1674	15.4691	16.4695	35.1667
lucht - 90°C																						
O1	SiCirr	Clay pore	17	38.4502	15.5480	16.5538	37.4437	O16	36.2377	15.5461	16.5561	35.2280	O31	34.0643	15.4575	16.4541	33.0774	O46	31.8591	15.3640	16.3634	30.8617
O2	SiCirr	Clay pore	20	38.1599	15.6231	16.6253	37.1592	O17	35.9127	15.6723	16.6789	34.9115	O32	33.7257	15.4833	16.4797	32.7322	O47	31.5114	15.5208	16.5206	30.5173
O3	SiCirr	Clay pore	24	37.8640	15.6669	16.6705	36.8581	O18	35.6096	15.8000	16.8059	34.6078	O33	33.4072	15.5527	16.5502	32.4141	O48	31.1789	15.3931	16.3918	30.1858
O4	blanco	Clay pore	29	39.1186	15.7517	16.7501	38.1197	O19	36.9038	15.7410	16.7449	35.9068	O34	34.7277	15.5920	16.5896	33.7318	O49	32.5154	15.5896	16.5880	31.5252
O5	SiCirr	Q-brine	18	43.1774	15.6515	16.8604	41.9682	O20	41.0731	15.0678	16.2824	39.8619	O35	39.0054	15.4989	16.7042	37.8062	O50	36.9216	15.6432	16.8498	35.7212
O6	SiCirr	Q-brine	22	42.9339	15.6194	16.8296	41.7239	O21	40.8510	15.6112	16.8255	39.6420	O36	38.8021	15.3942	16.5962	37.6041	O51	36.7289	15.4707	16.6756	35.5281
O7	SiCirr	Q-brine	27	43.1260	14.8624	16.0742	41.9176	O22	41.0419	15.6578	16.8681	39.8342	O37	38.9881	15.5525	16.7554	37.7905	O52	36.9242	15.6491	16.8531	35.7254
O8	blanco	Q-brine	30	42.3721	14.8606	16.0696	41.1632	O23	40.2683	15.7571	16.9676	39.0631	O38	38.1630	15.4970	16.6981	36.9725	O53	36.0650	15.6499	16.8507	34.8738
O9	SiCirr	water	16	38.3515	14.9585	15.9552	37.3542	O24	36.1043	15.6174	16.6244	35.1038	O39	33.8907	15.4303	16.4254	32.9014	O54	31.6639	15.5164	16.5132	30.6720
O10	SiCirr	water	19	37.3655	14.9922	15.9914	36.3628	O25	35.1107	15.7028	16.6955	34.1247	O40	32.9223	15.4720	16.4665	31.9333	O55	30.7197	15.5183	16.5156	29.7266
O11	SiCirr	water	23	38.8597	14.9761	15.9739	37.8573	O26	36.6258	15.7057	16.7104	35.6252	O41	34.4452	15.4519	16.4463	33.4542	O56	32.2627	15.5132	16.5101	31.2700
O12	blanco	water	28	37.6916	14.8870	15.8834	36.6906	O27	35.4861	15.5877	16.5880	34.4922	O42	33.2891	15.3897	16.3854	32.3014	O57	31.0232	15.6841	16.6819	30.0415
O13	Cirr (L2-G2)	Clay pore	37	38.6826	14.9496	15.9502	37.6790	O28	36.4451	15.7057	16.6949	35.4578	O43	34.2690	15.4966	16.4939	33.2752	O58	32.0523	15.4410	16.4409	31.0562
O14	Cirr (L2-G2)	Q-brine	38	43.1468	14.8100	16.0198	41.9372	O29	41.0535	15.6397	16.8484	39.8479	O44	39.0002	15.2798	16.4847	37.8005	O59	36.9250	15.6174	16.8240	35.7229
O15	Cirr (L2-G2)	water	36	38.3658	15.0889	16.0891	37.3644	O30	36.0744	15.6997	16.7021	35.0807	O45	33.8805	15.5224	16.5186	32.8894	O60	31.6485	15.5479	16.5475	30.6558

3 C-14 measurements

As mentioned above, this study deals with C-14 amount leached from the SiC made from irradiated graphite to the leachants. C-14 as β emitter can be determined by liquid scintillation counting method (LSC). A LSC apparatus Wallac 1414 WinSpectral α/β Liquid Scintillation Counter (LSC) was used for the C-14 analysis. The sample of the leachant (1 ml) is taken, filtered and scintillation cocktail (Ultima Gold XR) is added in the ratio of 1:10. There was a study performed by Perkin Elmer to determine the most suitable scintillation cocktail to be used for the LCS measurements of these leachants. The counting took place according to protocol 4, which was also tested for the Ultima Gold XR cocktail.
The tests show that Ultima Gold XR gives a broad peak on the left of the C14-spectrum, see Figure 3-1.

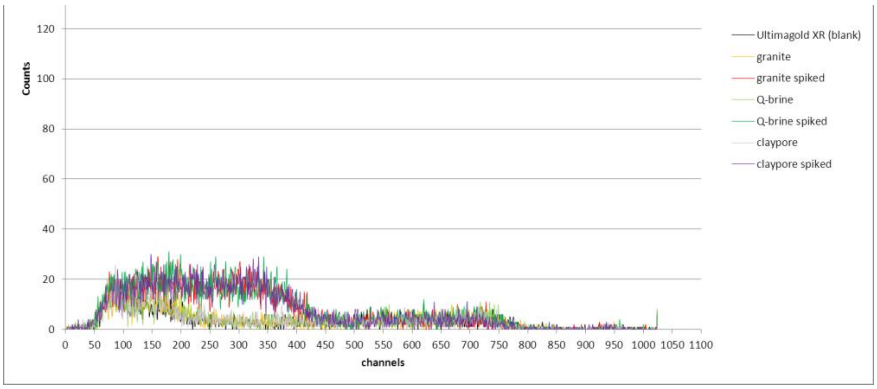

Figure 3-1 LSC spectra on spiked and non-spiked leachants

The settings of the used protocol give a recovery of approx. 70%. The broad peak between 50-250 channels (0.84-8.95keV) are also visible in the blank leachants . Thus caused by the salt matrix of the leachants or caused by the LSC cocktail. The C-14 peak of the spiked leachants appears between 50-450 channels (0.84-46.32keV). The shift of the C-14 peak may be caused by the salt matrix of the leachants. Each spectrum was checked for any contaminations of other isotopes. The SiC is made from irradiated graphite where other β emitting isotopes (e.g. H-3, Cl-36, Co-60, etc.) are present.
The glass scintillation vials were placed in a LSC rack and measured for 7200 seconds for 2 cycles (protocol 04).
The data from the second cycle was used for further calculations (elimination of luminescence).

4 Results and discussions

As described in the previous chapters, all leachants were sampled according to the sampling schedule and C-14 was measured by LSC.

The obtained results are presented in figures as *activity* in Bq/g of leached sample (i.e SiC or graphite) per *leaching period* in days. In all figures followings marks are used:

Clay pore ◆

Granite water ▲

Q-Brine ■

4.1 Leaching of SiC

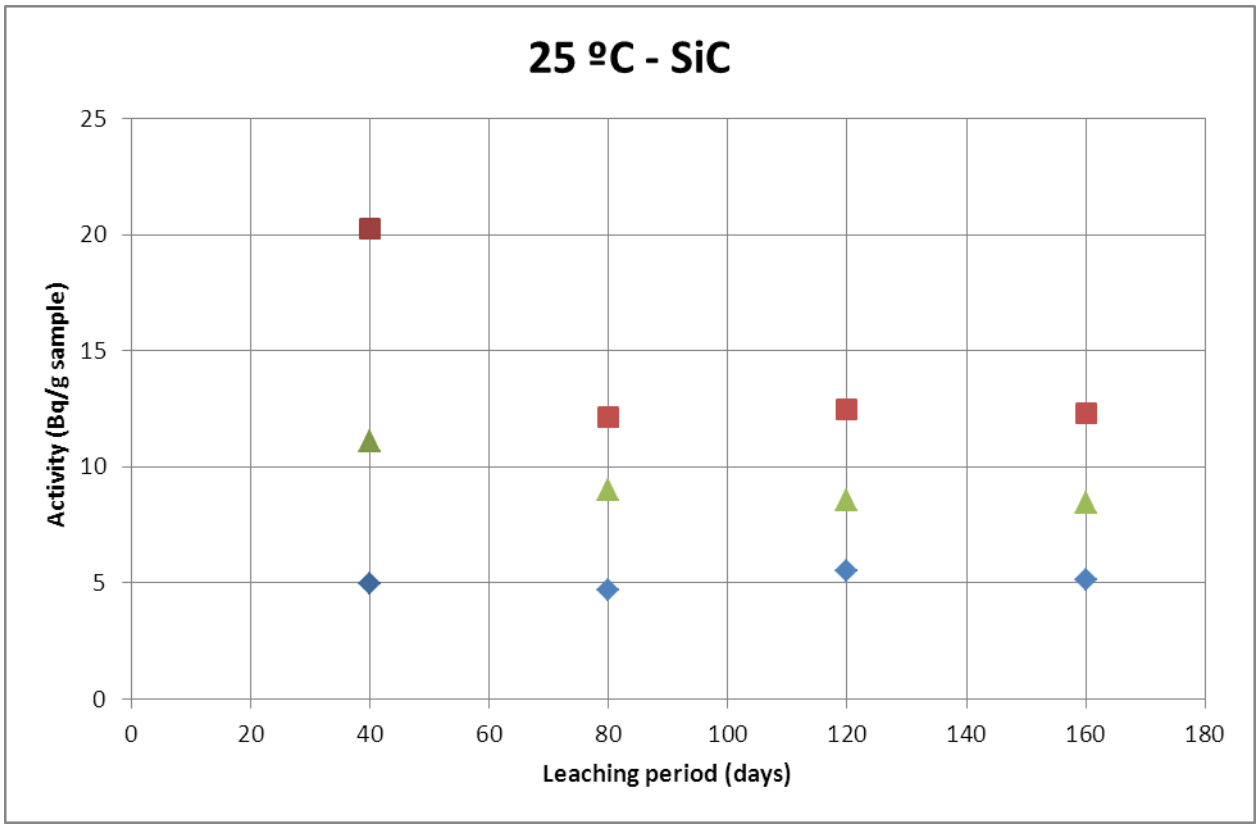

Figure 4-1 Activity measured in the leachant after preset leaching period – SiC at room temperature

The SiC powder was leached for a total period of 160 days, with sampling each 40 days. At the room temperature after 40 days, the highest activity of C-14 was measured in Q-Brine, 20 Bq/g sample against 12 Bq/g sample for granite water and 5 Bq/g sample for clay water. During the other sampling periods, the activity measured in Q-Brine decreased to approx. 12 Bq/g sample and remained constant. The measured activity in granite water decreased slightly and remained constant during the leaching period. In clay water, the measured activity remained about constant during the whole leaching period.

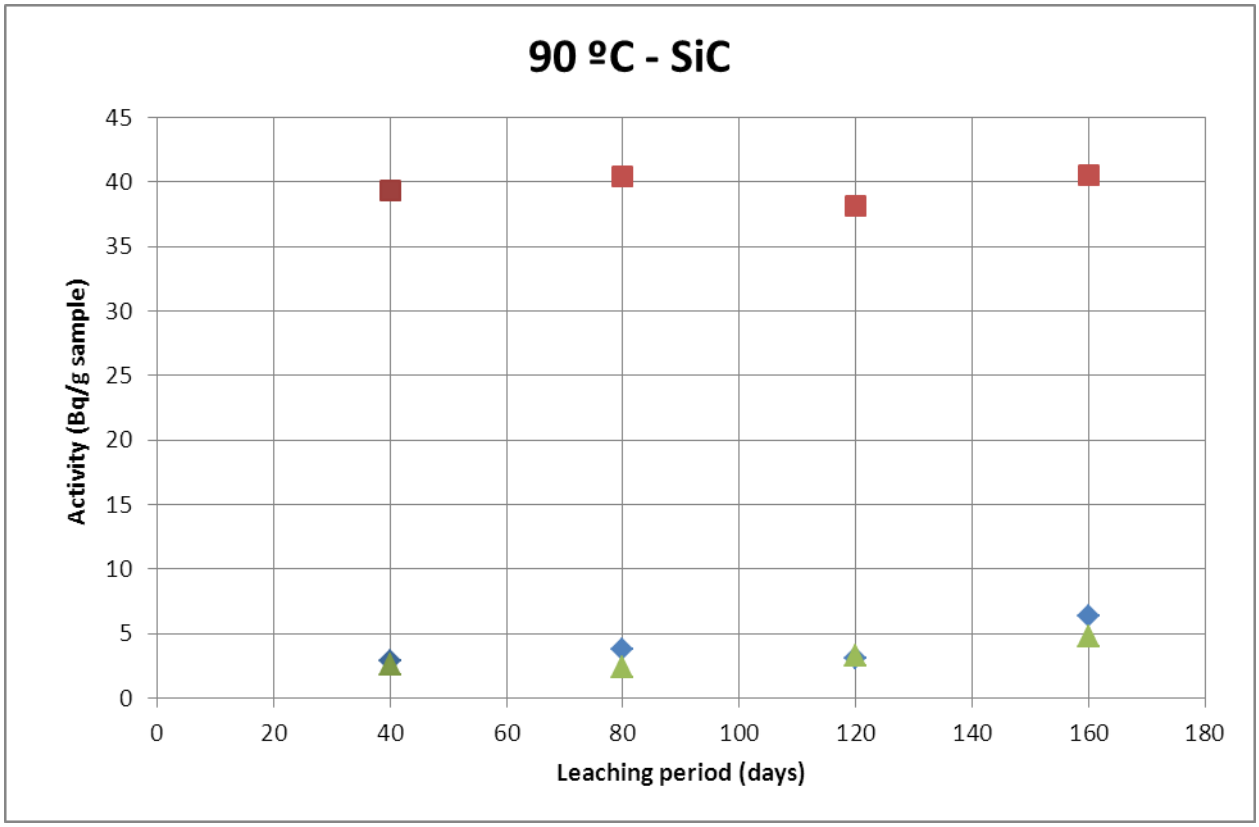

Figure 4-2 Activity measured in the leachant after preset leaching period – SiC at temperature of 90ºC

The SiC powder leached at the temperature of 90ºC showed measured activity in all thre leachants remaining about constant during whole the leaching period. The measured activity in Q-Brine is 10 times higher than in the other two leachants (40 resp. 4 Bq/g sample).

The measured activity of C-14 in Q-Brine is about two –three times higher at a temperature of 90ºC than at room temperature. It seems that there is no significant influence of temperature on the leaching behaviour of the SiC powder in clay water, in the granite water the higher activities are measured at the room temperature.

4.2 Leaching of graphite

A very small amount (0.02 g) of the irradiated graphite from WP3 –RRT which had been used for the SiC formation was leached (20 ml of leachant) as well.

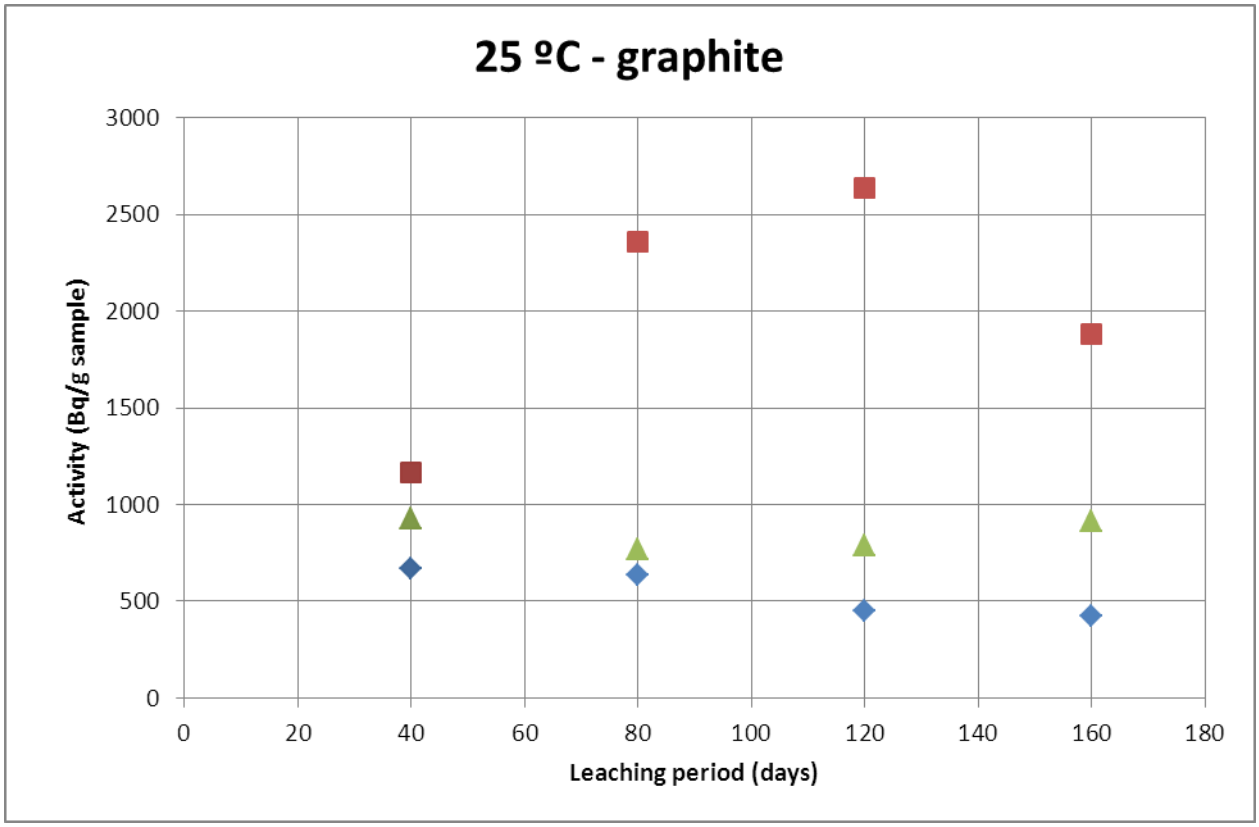

Figure 4-3 Activity measured in the leachant after preset leaching period – graphite at room temperature

The highest activity of C-14 is found in the Q-brine water. After 40 days of leaching the measured activity was about 1200 Bq/g sample, in 80 days it became about two times higher, stayed constant and decreased to about 1800 Bq/g sample after 160 days leaching.

The measured C-14 activity in the granite water was during the whole leaching period 750-900 Bq/g, at the first sampling it was higher, then it decreased slightly and after 160 days it incread to the inicial value.

For the clay water, the activity was about 650 Bq/g during the first two sampling, than it decreased to about 500 Bq/g.

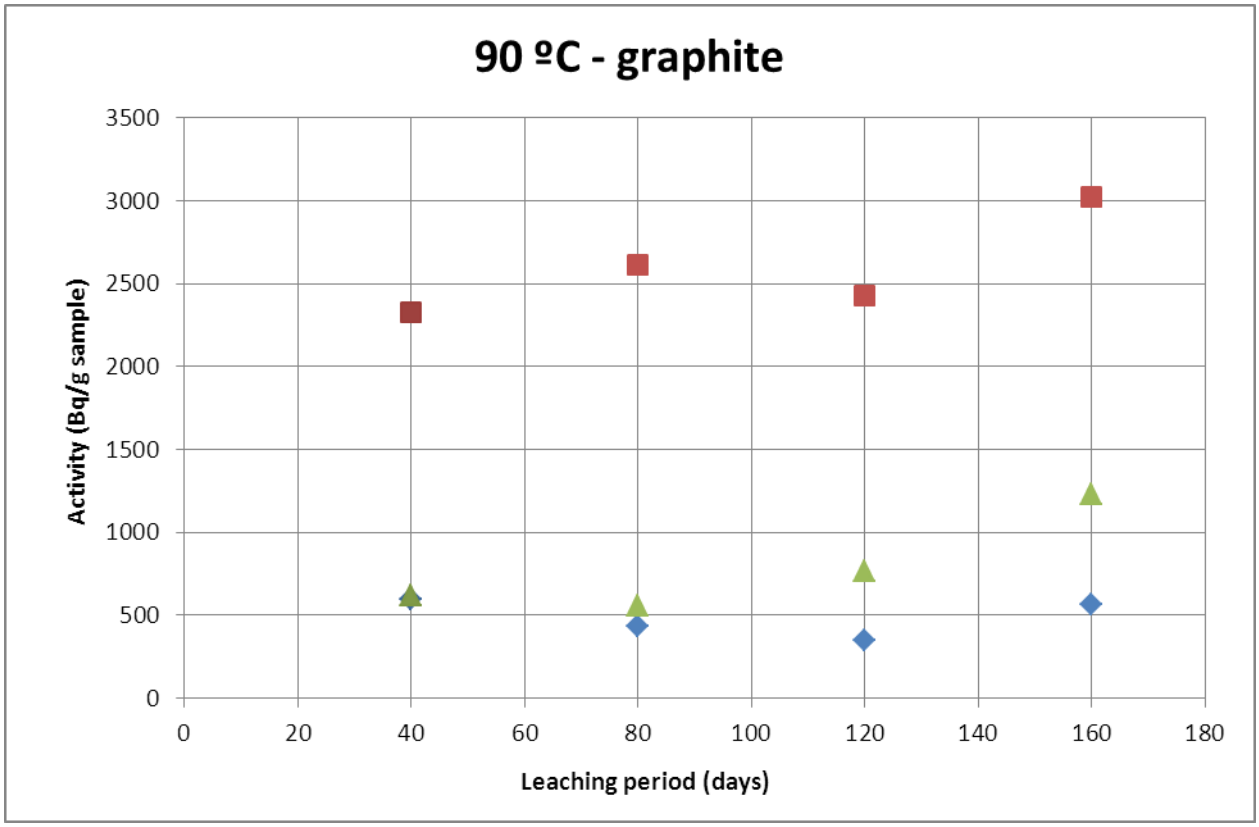

Figure 4-4 Activity measured in the leachant after preset leaching period – graphite at 90ºC

The experiments performed at 90ºC showed that the highest activity of C-14 was measured in the Q-brine leachant, during the first three sampling is was about 2500 Bq/g and it increased to 3000 Bq/g at the 160 days sampling.

In the granite water, the activity of C-14 was about 600 Bq/g, during the 160 days of the leaching period it increased to the activity of about 1200 Bq/g, i.e. the activity became two time higher.

The activity of C-14 in clay pore was about 450- 500 Bq/g and remained constant during the 160 days.

5 Conclusions

The method for formation of SiC directly from graphite and silicon was established within Carbowaste – WP5. This method was applied first to virgin graphite; when the method was modified and established, irradiated graphite was used. The same procedure was applied to the irradiated graphite; unfortunately these two graphite types seem not to react in the same way. Reaction conditions were varied to optimize the procedure to get pure SiC using the irradiated graphite. However, besides the SiC a small amount (less than 5%) of free carbon was always still present after the reaction process.
The synthesis and characterization of SiC was done. This material was used for the leaching experiments within the WP6 – task 6.2.
The leaching experiments were performed in three types of leachants: Q-brine, clay and pore water, at the room temperature and at 90ºC. The formed SiC and irradiated graphite (from the RRT test in WP3) were leached during a period of 160 days with sampling each 40 days. After sampling, the C-14 activity was determined by LSC.

For SiC at the room temperature after 40 days, the highest activity of C-14 was measured in Q-Brine, 20 Bq/g sample against 12 Bq/g sample for granite water and 5 Bq/g sample for clay water. During the other sampling periods, the activity measured in Q-Brine decreased to approx. 12 Bq/g sample and remained constant. The measured activity in granite water decreased slightly and remained constant during the leaching period. In clay water, the measured activity remained about constant during the whole leaching period.
The SiC powder leached at the temperature of 90ºC showed measured activity in all thre leachants remaining about constant during whole the leaching period. The measured activity in Q-Brine is 10 times higher than in the other two leachnats (40 resp. 4 Bq/g sample).
The measured activity of C-14 in Q-Brine is about two –three times higher at the temperature of 90ºC than at the room temperature. It seems that there is no significant influence of temperature on the leaching behaviour of the SiC powder in clay water, in the granite water the higher activities are measured at the room temperature.

For the irradiated graphite, the highest activity of C-14 is found in the Q-brine water, after 40 days of leaching the measured activity was about 1200 Bq/g sample, in 80 days it became about two times higher, stayed constant and decreased to about 1800 Bq/g sample after 160 days leaching.

The measured C-14 activity in the granite water was during the whole leaching period 750-900 Bq/g. At the first sampling it was higher, then it decreased slightly and after 160 days it increased to the initial value. For the clay water, the activity was about 650 Bq/g during the first two sampling, than it decreased to about 500 Bq/g.

The experiments performed at 90ºC showed that the highest activity of C-14 was measured in the Q-brine leachant. During the first three sampling it was about 2500 Bq/g and it increased to 3000 Bq/g at the 160 days sampling.
In the granite water, the activity of C-14 was about 600 Bq/g, during the 160 days of the leaching period it increased to the activity of about 1200 Bq/g, i.e. the activity became two time higher.
The activity of C-14 in clay pore was about 450- 500 Bq/g and remained constant during the 160 days.

The measured activities of C-14 leached from irradiated graphite are much higher comparing to the ones leached from the SiC made from this graphite. Based on that, it seems that the transformation of irradiated graphite into silicon carbide could be a way of decreasing of the C-14 release from the material. Because of limited amount of available irradiated graphite, the above mentioned tests are done with very small amount of irradiated graphite (0.02 g in 20ml leachant) comparing to the silicon carbide (0.4g in 20 ml leachant), this could have influence on the leaching rates. To confirm that silicon carbide could be a suitable product formed from irradiated graphite concerning the lower C-14 release, more tests must be performed. Long-term tests should be done, better comparable amount of materials to be leached should be studied and material in the form of pellets should be leached as well (if SiC is used as e.g. container material).
In addition, since the trace amount of free carbon in the synthetized SiC could be responsible for the observed C-14 leaching, it is also important to further optimize the synthesis procedure.

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