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Aqueous Phase Corrosion of Silicon Carbide

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1. Summary

At present, spent HTR fuel elements are considered for direct disposal in deep geological formations. From a chemical point of view, direct disposal of spent HTR fuel is justified by some favorable characteristics of HTR fuel elements, in particular the presence of chemically resistant coating layers around the radioactive fuel kernels such as SiC which are further embedded in a highly stable graphitic matrix.
In this study the chemical resistance of SiC is determined under repository conditions such as salt domes, granite-based repositories and clay formations. Both long leaching experiments (40 days) as short (hours) experiments have been employed.
Lifetimes between $1E^3$ and $1E^5$ have been measured (taking some assumptions into account) depending on the kind of repository and temperature.

2. Description of progress

2.1 Materials

The following materials have been used for aqueous SiC corrosion experiments sofar (see Table 1):

Table 1 Non-irradiated SiC materials for corrosion experiments

material	Status 40 days leaching	Status short leaching (kinetics)
RS-SiC (alfa-Aeser)	finished	finished in part, variable temperatures ongoing
CVD-SiC	finished	to be started
CVD coated kernels	non received yet, in progress	non received yet, in progress

RS: reaction sintered, CVD: chemical vapour deposited

In an attempt to eliminate the content of surface impurities, such as SiO_2, and free silicium, 25 g of SiC powder was treated in 25 ml of 40 % HF (aq) for 30 minutes, filtered over 5 µm PTFE membrane filter and thoroughly washed with demineralized water. After drying at 90 °C, the HF-treated SiC powder was found to be more pure by XRD as compared to the untreated material. Also XRD line broadening was less in the HF-treated sample which suggests that ultrafine SiC particles have also been removed by the HF-treatment and subsequent filtering steps. The following surface area's before and after HF-treatment were found (BET-analysis):

RS-SiC untreated: 12,908 m^2/g
RS-SiC HF-treated: 4,90 m^2/g
CVD-SiC untreated: 0,6819 m^2/g
CVD-SiC treated: 1,3745 m^2/g

In coordance with expectations, the HF treatment removes fine particles and therefore lowers the specific surface area in case of the reaction-sintered SiC. For the chemical vapour deposited material, the reversed situation is found, although reflected in just a small change of surface area.. This change is not well understood but etching of the surface might cause the increase.

2.2 Leachants

Simulants for clay porewater and Q-brine were prepared by dissolving accurately weighted amounts of salts in demineralized water (>18 MΩ).
For clay porewater (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 0.45 µm. For some clay pore water experiments, the pH was adapted to pH 12.0 with diluted NaOH (aq).
For Q-brine (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). For Q-brine experiments at 90 °C, additional NaCl (36.0 g) and CaSO4.2H2O (7.2 g) was added in order to keep the solution saturated in NaCl and $CaSO_4$.

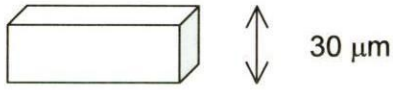
2.3 Method

Corrosion experiments on accurately weighted amounts of SiC powders were performed in PTFE containers (Nalgene for low temperature experiments), or in 23 ml Parr Acid digestion bombs at T = 200 °C. The PTFE containers were pretreated as described in the ASTM-C 1220-92 standard test. Corrosion was followed by recovering the powder after preset time periods. This was accomplished by filtering over 0.45 µm cellulosenitrate filter (Schleicher&Sluell), careful drying and weighing the residual mass left on the filter. Alternatively, the Si content in the aqueous phase was determined by ICP-AES analysis without further sample treatment. Before calculating the corrosion rates, all analytical results were corrected for blancs.

2.4. Calculation of SiC lifetimes

The following assumptions have been made with respect to calculating tife-times of the SiC layer:

- uniform leaching rate without pit corrosion
- stoechiometry (Si=C)
- minimum density SiC = 3.18 g/cc (HTR-F specifications), TD = 3.21 g/cc
- deviation in life-time = 5% (based on detection deviation of ICP-AES)
- SiC layer thickness: 30 µm



The volume of a SiC layer of 30 micron and 1 cm^2 surface area amounts to $3E^{-3}$ cm^3. The SiC content within this volume (based upon the minimal density as formulated in HTR-F) is $9{,}54E^{-3}$ gram. The life-time of the SiC layer has been calculated presuming a uniform leaching rate over the specified surface area which is constant over the period of the experiment (short as well as long term experiments). Leaching rates, normalised to the specific surface area of the material, can then be recalculated to a maximum lifetime. Due to disuniform leaching, lifetimes may be shorter. Inside on the kind of leaching (uniform, disuniform) will be obtained with Scanning Electron Microscopy (SEM).

3. Results

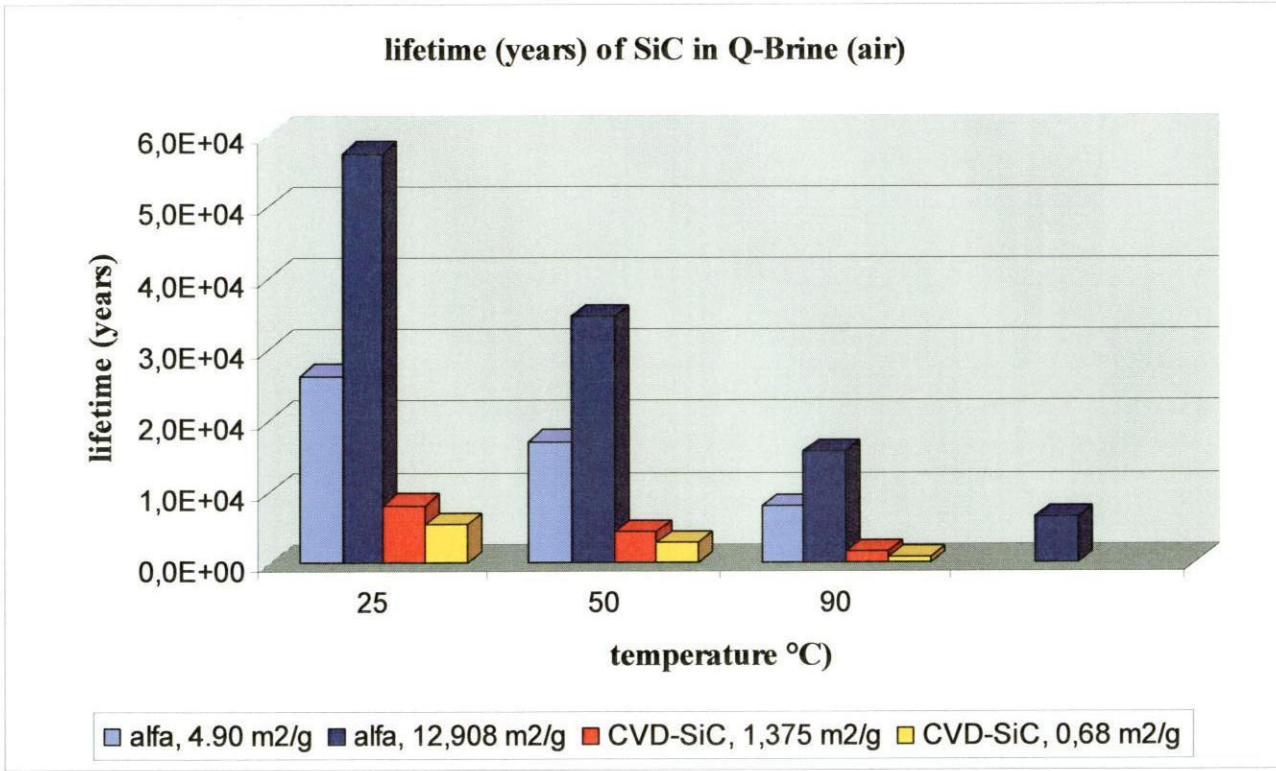
The corrosion rates of the SiC powders have been summarized in Table 2. Rates are normalised to the specific surface area of the samples. It was found that loss of water out of the leachants due to

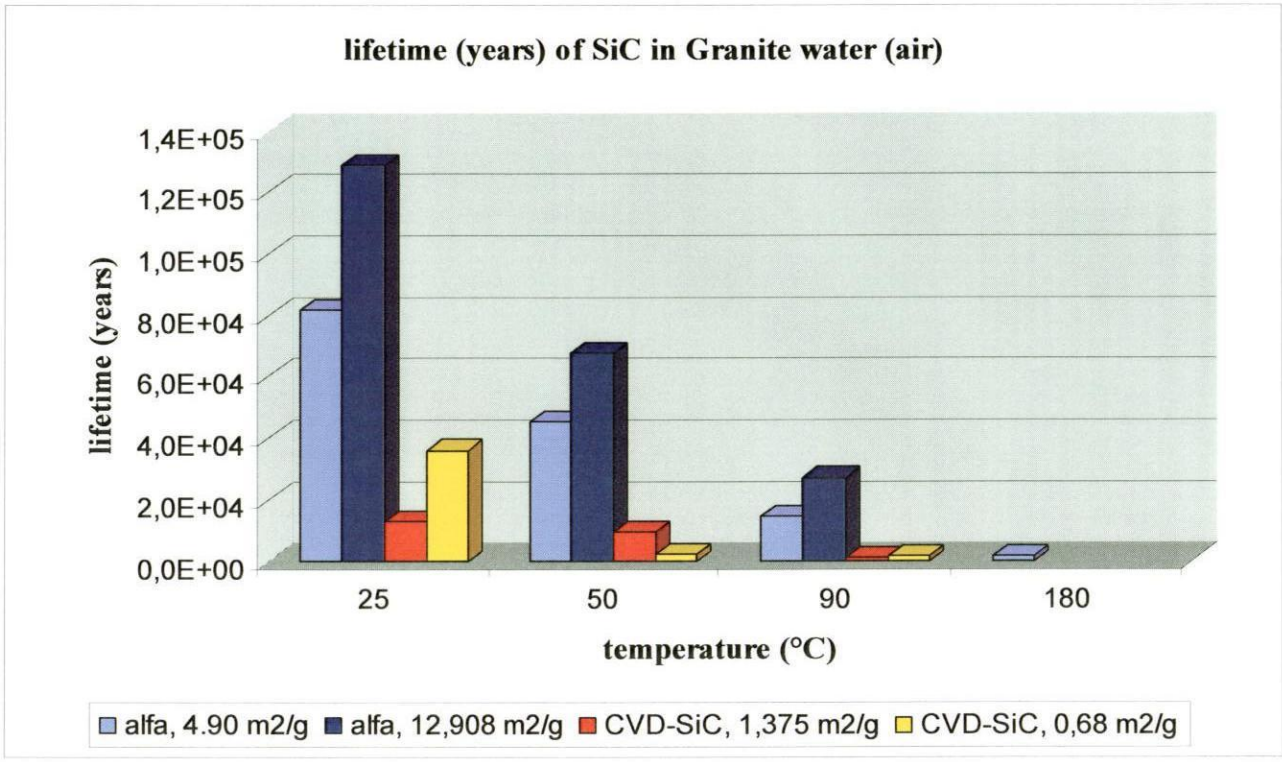
evaporation amounted to < 0,02% (25°C), < 0.3% (50°C) and < 4% (90°C) for a 40 days period and 10 ml of leachant. The error in ICP by far outweights errors caused by these values.

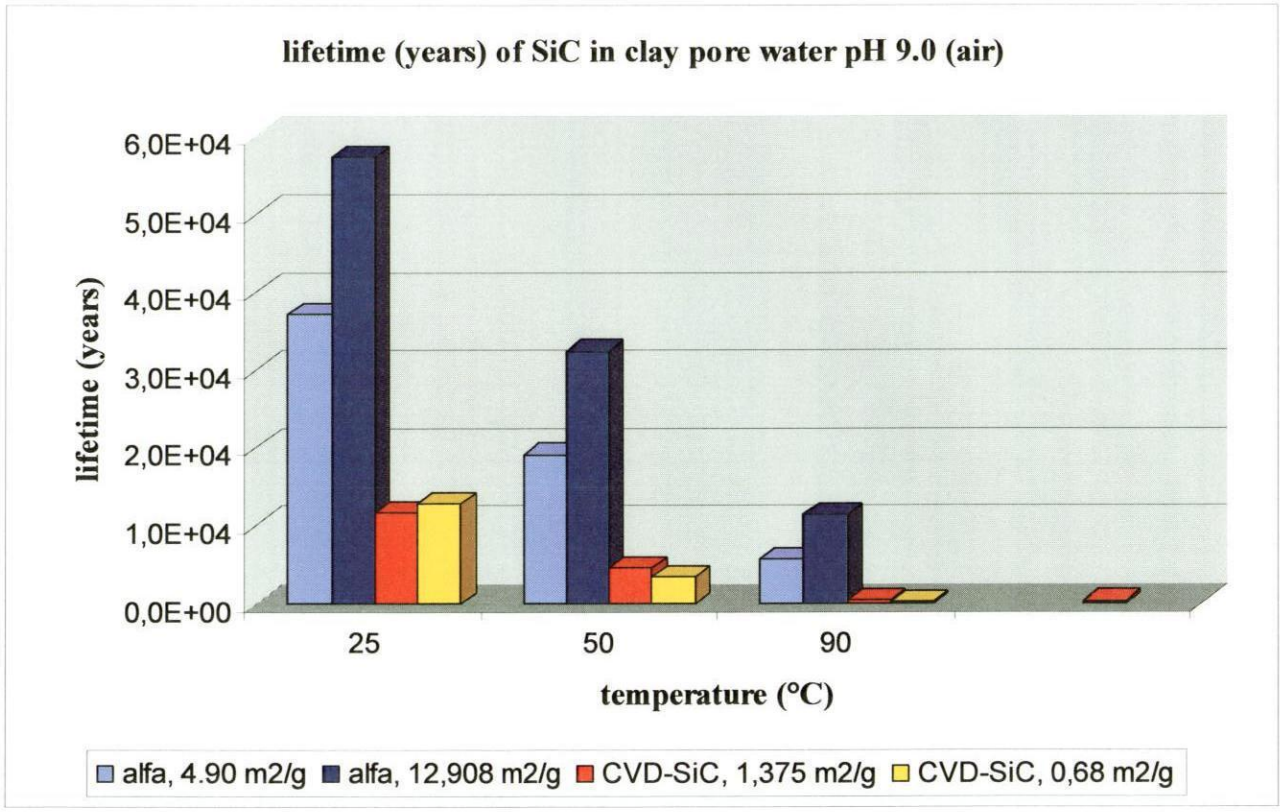
Table 2 Aqueous corrosion rates of SiC powders in clay pore water and Quinary-brine (results in $g/cm^2/d^1$)

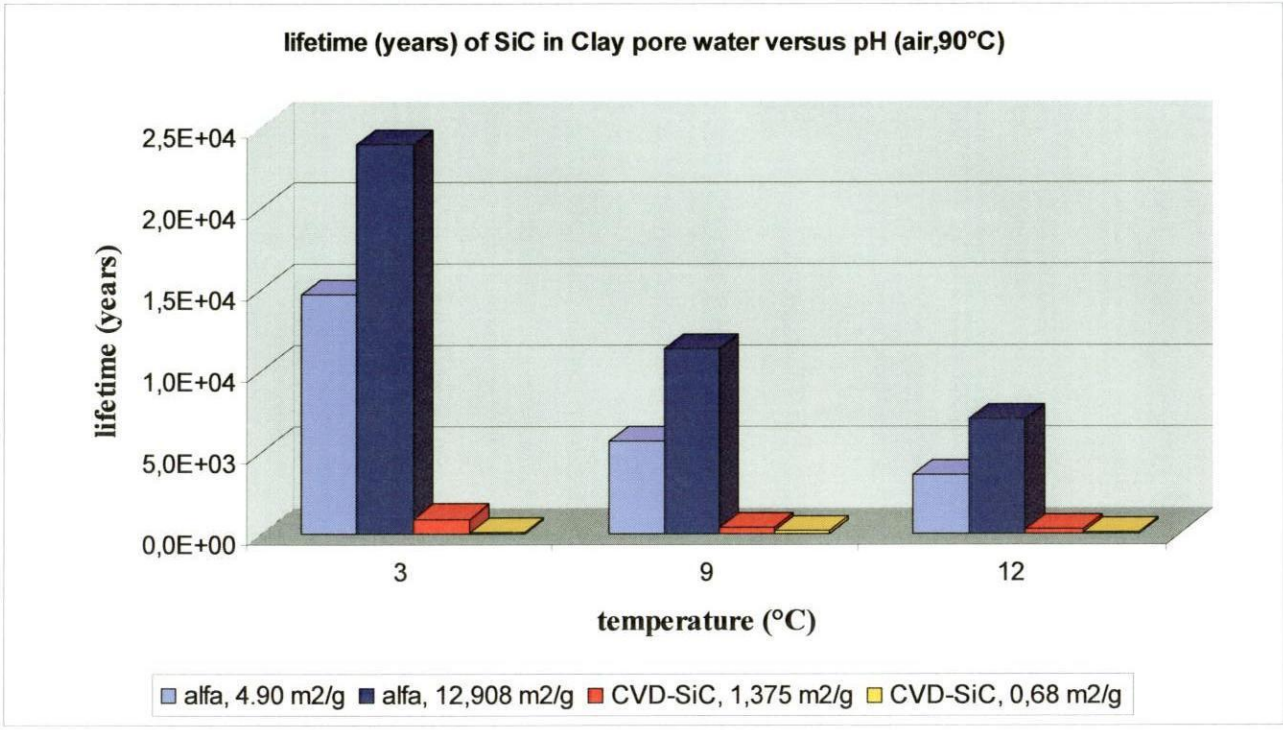
Granite water, RS 4,9					**Granite water, RS 12,9**				
temp °C)	25	50	90	180	temp °C)	25	50	90	180
g/m2.d	3,20E-06	5,78E-06	1,82E-05	1,91E-04	g/m2.d	2,03E-06	3,84E-06	9,64E-06	
Granite water, CVD 1,37					**Granite water, CVD 0,68**				
g/m2.d	2,02E-05	2,80E-05	2,16E-04		g/m2.d	7,23E-06	1,14E-04	1,81E-04	
Q-brine, RS 4,9					**Q-brine, RS 12,9**				
g.m2.d	9,96E-06	1,53E-05	3,27E-05		g/m2.d	4,55E-06	7,54E-06	1,68E-05	4,09E-05
Q-brine CVD 1,37					**Q-brine, CVD 0,68**				
g/m2.d	3,21E-05	5,78E-05	1,56E-04		g/m2.d	4,70E-05	8,92E-05	3,52E-04	
Clay pore pH9 RS 4,9					**Clay pore pH9 RS 12,9**				
g/m2.d	7,04E-06	1,37E-05	4,57E-05		g/m2.d	4,56E-06	8,07E-06	2,30E-05	
Clay pore pH9 CVD 12,9					**Clay pore pH9, CVD 0,68**				
g/m2.d	2,26E-05	5,70E-05	5,91E-04	9,08E-04	g/m2.d	2,05E-05	7,95E-05	1,54E-03	
Clay pore pH12 RS 4,9					**Clay pore pH12 RS 12,9**				
g/m2.d	1,34E-05	2,84E-05	7,27E-05		g/m2.d	8,95E-06	1,61E-05	3,70E-05	
Clay pore pH12 CVD 12,9					**Clay pore pH12, CVD 0,68**				
g/m2.d	4,34E-05	1,36E-04	9,43E-04		g.m2.d	6,00E-05	3,30E-04	2,01E-03	3,57E-03
Clay pore pH3 RS 4,9					**Clay pore pH3 RS 12,9**				
g/m2.d	8,36E-06	6,90E-06	1,78E-05		g/m2.d	3,76E-06	4,45E-06	1,09E-05	
Clay pore pH3 CVD 12,9					**Clay pore pH3, CVD 0,68**				
g/m2.d	5,00E-05	1,02E-04	2,77E-04		g/m2.d	3,78E-05	1,01E-04	4,55E-04	2,14E-03

The following graphs visualise and compare the calculated life-times of SiC (Hf-treated and untreated):




lifetime (years) of SiC in Granite water (air)
1,4E+05
1,2E+05
1,0E+05
8,0E+04
6,0E+04
4,0E+04
2,0E+04
0,0E+00
lifetime (years)
25
50
90
180
temperature (°C)
alfa, 4.90 m2/g
alfa, 12,908 m2/g
CVD-SiC, 1,375 m2/g
CVD-SiC, 0,68 m2/g


lifetime (years) of SiC in clay pore water pH 9.0 (air)
6,0E+04
5,0E+04
4,0E+04
3,0E+04
2,0E+04
1,0E+04
0,0E+00
lifetime (years)
25
50
90
temperature (°C)
alfa, 4.90 m2/g
alfa, 12,908 m2/g
CVD-SiC, 1,375 m2/g
CVD-SiC, 0,68 m2/g



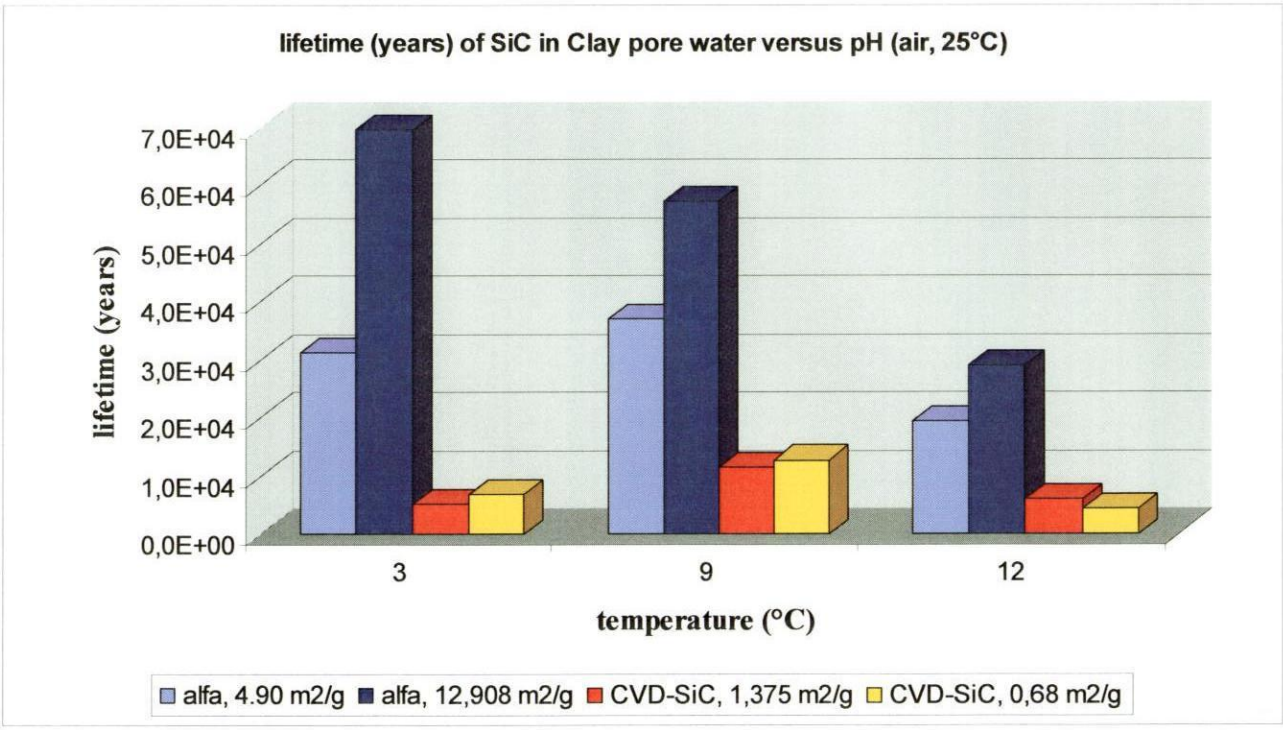


Figure 1: lifetimes of SiC exposed to relevant repository leachants

It is clear from the graphs that the temperature is one of the most promanent parameters determining leaching rates and therefore lifetimes. The higher the temperature in the repository,

the shorter lifetimes will be. Secondly, the CVD SiC is leaching faster then the reaction sintered material. Differences in stoechiometry might cause this phenomenon.

Additionally, the untreated reaction sintered SiC (with the highest surface area) has the highest lifetime. Such a behaviour can only be explained if some equilibrium situation (e.g. encapsulation) occurs which requests some available surface area.and contact to the leachant. If metallic Si is present (as Si or oxidised) then encapsulation might be enhanced. Note: this is speculative.

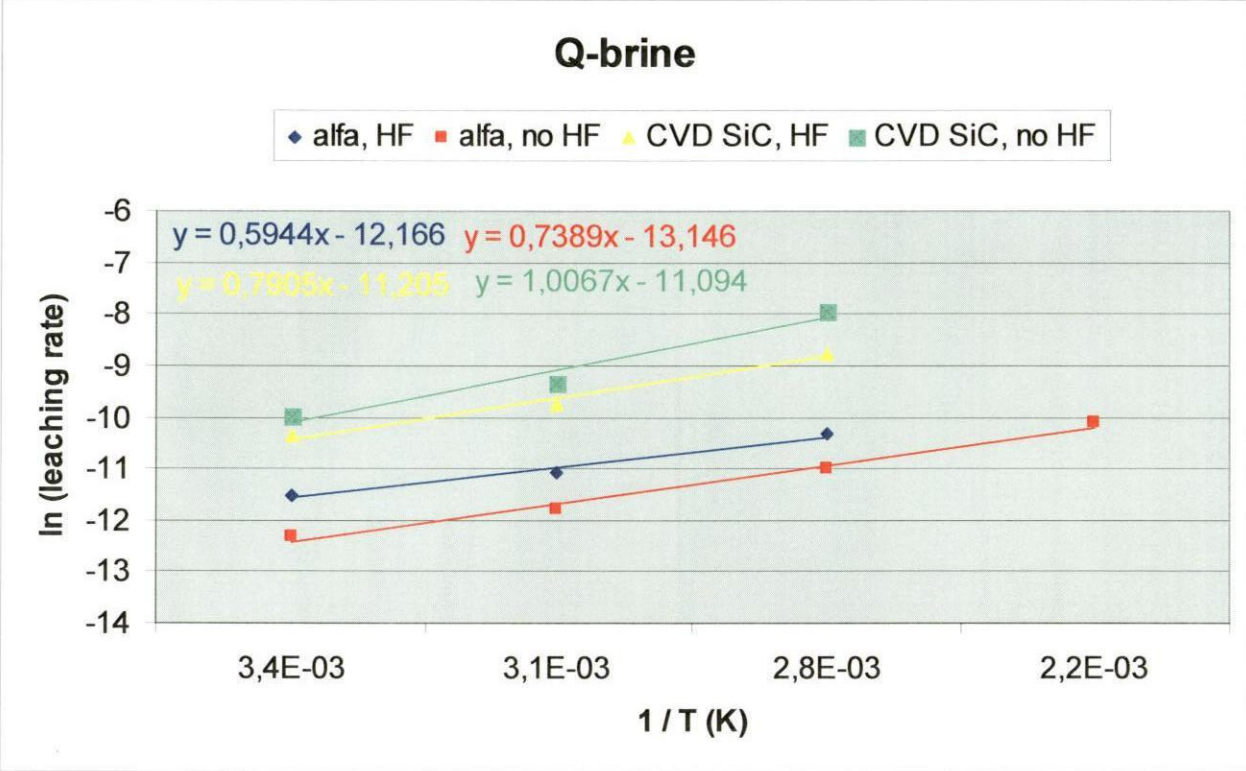


Figure 2: Arrhenius-plot (Q-Brine)

Figure 2 depicts, as an example, the Arrhenius-plot of leaching in Q-Brine. From the slope of the equations, the apparent energie of the leaching process can be determined. Note that the leaching rates are the rates found over a period of 40 days and therefore averaged leaching rates, presuming a constant rate over the time period. Fast leaching at initial contact of the material to the leachant when no thermodynamical equilibrium may exist, is therefore also averaged. In order to find the apparent energies involved in the early stage of the leaching process, short term experiments as a function of temperature have to be performed. These experiments are in process. The calculated energies here are avaraged values over the whole leaching process of 40 days.

In Table 3, all calculated results are listed:

Table 3: Apparent Energies

E (J / mol)					
sample	granite	Q-brine	Clay 9.0	Clay 12.0	Clay 3.0
alfa HF (4,90 m2/g)	-0,16	-0,07	-0,11	-0,10	-0,05
alfa no HF (12,908 m2/g)	-0,09	-0,09	-0,10	-0,09	-0,06
CVD SiC HF (1,3745 m2/g)	-0,14	-0,10	-0,16	-0,19	-0,10
CVD SiC no HF (0,6819 m2/g)	-0,19	-0,12	-0,26	-0,21	-0,16

The involved energies found are low. This can be understood from the high insolvability, a feature of SiC that is very beneficial in final disposal scenario's.

In order to establish if leaching rates are constant in time, time-on-stream experiments have been set-up. Here, leaching experiments have been performed with 7 vessels in which SiC has been exposed to the leachant with a different leaching time. Especially, in the initial stage of the process thermodynamic instability may exist (due to changing of thermostability in air to stability in leachant), changing the leaching rate.

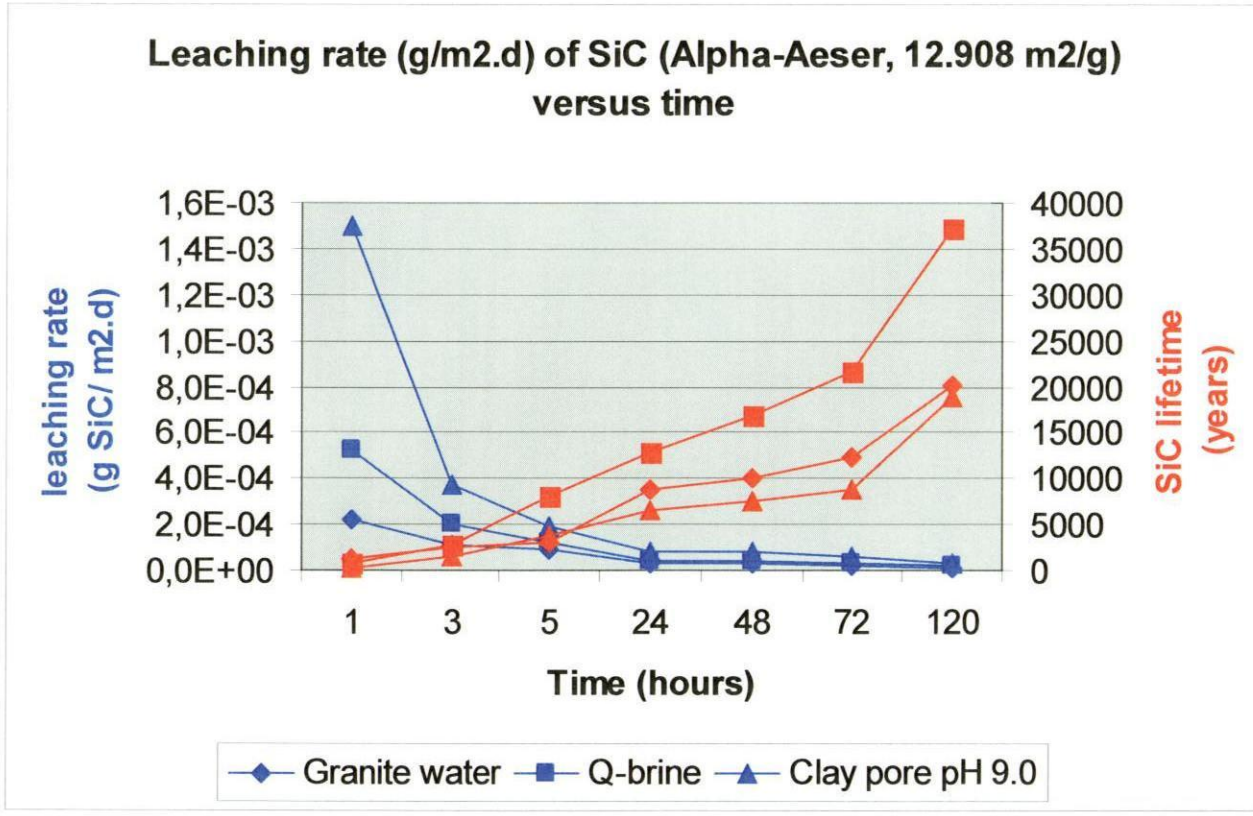


Figure 3: Time-on-stream leaching

In Figure 3 it can be clearly seen that in the first hours, the leaching-rates are higher. After one day, leaching is near to constant due to a new equilibrium. This may be caused by encapsulation of the surface area. It is clear that the apparent energy, calculated in Figure 2 and Table 3, are averaged

values over the total leaching period of 40 days. If short term experiments are performed (e.g. over the first 2 hours versus temperature), higher apparent energies will be found. Performing such experiments is under discussion.

5. Conclusions

First results have been obtained on leaching rates of commercial available reaction-sintered SiC and chemical vapour deposited SiC. It is clear that differences of the materials (e.g. presence of Si, non-stoechiometry etc.) can change rates dramastically. It is therefore essential to investigate kernels provided with a SiC layer as prepared today.
Note that leaching rates are maximum values. If non-uniform corrosion occurs, e.g. pit corrosion, then lifetimes are reduced presuming the definition that the lifetime of the SiC layer is determined by the moment of release of fission products. This may not be the moment when on distinct places the layer has dissolved completely but caused by changes in porosity, this moment might be sooner.