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Document title

Report on the leaching behavior of FP-containing SiC/ZrC

Executive 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 favourable characteristics of HTR fuel elements, in particular the presence of chemically resistant coating layers around the radioactive fuel kernels such as SiC or the envisaged alternative ZrC which are further embedded in a highly stable graphitic matrix.
One of the very important tasks in the understanding of the possible behaviour of SiC and ZrC is studying the interaction between fission products and these carbides. Cs and Ag are among the fission products which may well come in contact with carbide layer. The interaction may result in the formation of new phases which may have a negative effect on the stability of the carbide layer. And thus its leaching behaviour. Knowledge of the carbide-FP system is therefore of utmost importance. Mixture of carbides and suitable Ag/Cs compounds were subjected to a leaching test in order to assess the effect of additional phase formation on the behaviour of the carbides.
In this study the chemical resistance of SiC and ZrC in the interaction with FP is determined under repository conditions such as salt domes, granite-based repositories and clay formations.

Revisions

Rev.	Date	Short description	Author	WP Leader	SP Leader	Coordinator
00	14/10/2008	First draft	E. de Visser Týnová NRG	J. Fachinger FZJ	W. von Lensa FZJ	Name, Organisation *Signature*
01	15/12/2009	Final	E. de Visser Týnová NRG	J. Fachinger FZJ	W. von Lensa FZJ	E. Bogusch FANP

1.1 Objective

An open fuel cycle with direct disposal of conditioned or non-conditioned fuel elements is one of the back end options for spent HTR fuel elements as proposed in the EC. In order to develop a realistic descriptive model for the long term behaviour of spent HTR fuel in aqueous phases of host rock systems in terms of possible release of radionuclides, the behaviour of the fuel kernel and all subsequent coating layers under repository conditions need to be understood. The carbide coating serves as a barrier for immobilising the fission products in HTR fuel. After ingress of naturally occurring fluids in the surrounding graphite through pores or damaged parts, the carbide layer is subjected to corrosion. The corrosion velocity of this layer is one of the most important parameters determining radionuclide release since it serves as a barrier to trap the formed fission products.
In recent years, zirconium carbide has come to fore as an alternative for the existing silicon carbide coating. Silicon carbide can form unwanted phases with fission products like silver, altering the integrity of the layer.
Data with respect to corrosion velocities of zirconium carbide is lacking and consequently, comparison between both carbides from a disposal point of view cannot be made. This report describes results from corrosion studies, addressing both carbide materials.

The envisaged fuel elements for a HTR are shown in Figure 1. Coated fuel containing particles, consisting of several layered materials are distributed in graphite pebbles. The existing coated particles have an internal SiC layer that serves as fission product barrier. In Figure 1, the different coatings are shown.

The external pyrocarbon layer (PyC) present on existing coated particles prevent corrosion studies with respect to the SiC (or ZrC) layer since contact of an intact pyrocarbon coating prevents/limits water ingress and therefore contact of natural existing liquids with the carbide layer. In principle, the outer pyrocarbon coating may be removed by oxidation at elevated temperatures but this may change the state of the coating, e.g. by formation of silicon (or zirconium) oxide or oxicarbides. The formation of such reaction products will influence the corrosion velocity of the carbide layer.
Therefore, the need exists for coated particles where the external pyrocarbon coating has not been applied.

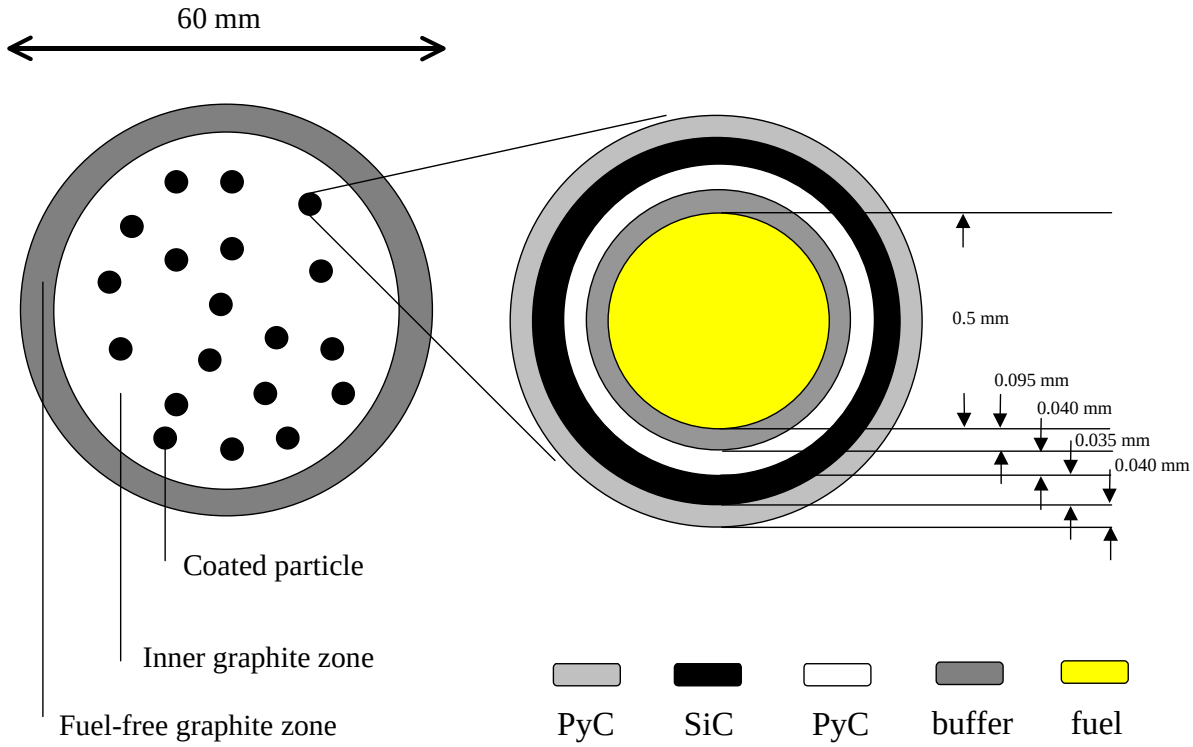


Figure 1: Pebbles (left) and fuel kernels (right) showing the subsequent layer materials

In recent years, novel coated particles have been produced. By interrupting the developed coating process, particles have become available lacking the outer pyrocarbon coating. This allows a thorough investigation of the corrosion resistance of the carbide layer and more realistic corrosion rates can now be measured, refining modelling data and improving the descriptive model for HTR fuel disposal behaviour.

One of the very important tasks in the understanding of the possible behaviour of SiC and ZrC is studying the interaction between fission products and these carbides. Cs and Ag are among the fission products which may well come in contact with carbide layer. The interaction may result in the formation of new phases which may have a negative effect on the stability of the carbide layer. And thus its leaching behaviour. Knowledge of the carbide-FP system is therefore of utmost importance. Mixture of carbides and suitable Ag/Cs compounds will be subjected to a leaching test in order to assess the effect of additional phase formation on the behaviour of the carbides.

Here presented study follows up the leaching experiments of carbides reported in the deliverable D-BF 3.2 (Marcel den Exter, NRG, 2007). Now reported experiments are based and make use of the results in the deliverable D-BF-3.2. The methodology of performing of the leaching experiments and calculations have been led in the same manner.

1.2 Materials

1.2.1 Leachant specifications

Simulants for clay porewater 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.

1.2.2 Powder specifications/characterisation

The used carbide powders have the following specifications:

- **Beta-SiC**: Alfa-Aesar, 99.8% (metals basis),
- $A_{spec.}$ = 12.91 m^2/gram
- **ZrC**: Alfa-Aesar, 99.5% (metals basis excluding Hf), Hf < 200 ppm,
- $A_{spec.}$ = 0.43 m^2/gram

The used nitrates to introduce the studied fission products have the following specifications:

- **$AgNO_3$**: Alfa Aesar, 99.8% (metal basis)
- **$CsNO_3$**: Alfa Aesar, 99.8% (metal basis)

All used materials have been characterized by X-ray diffraction measurements. These measurements were carried out on a Bruker D8-Advance. All performed analyses were realised in the range of 10-100 2Θ, locked coupled, with increment 0.05, in the air.

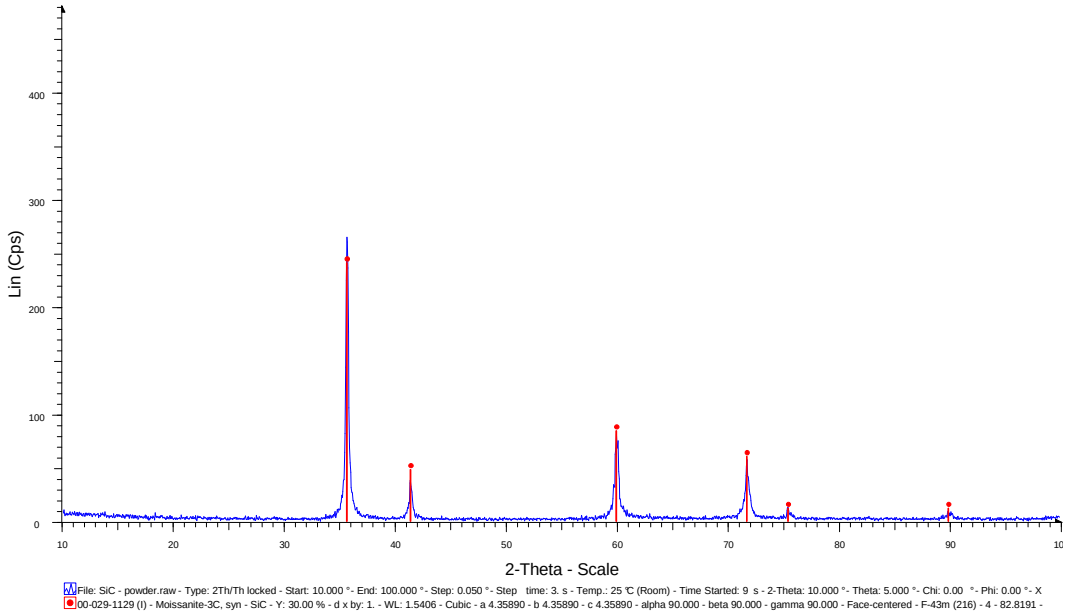


Figure 2 XRD analysis of SiC ; in red pattern of SiC , beta

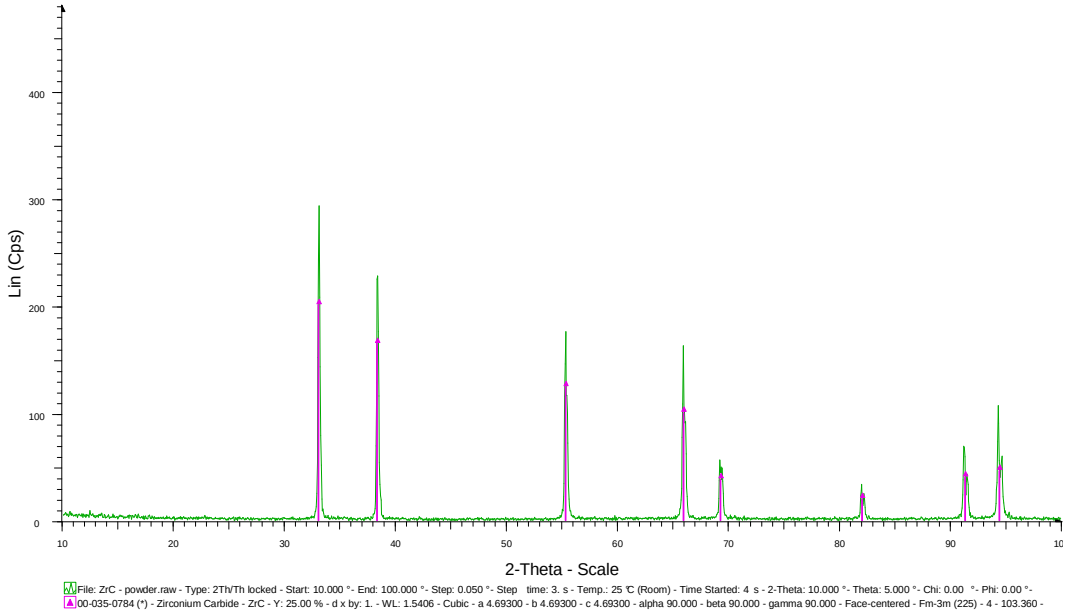


Figure 3 XRD analysis of ZrC ; in rose pattern of ZrC

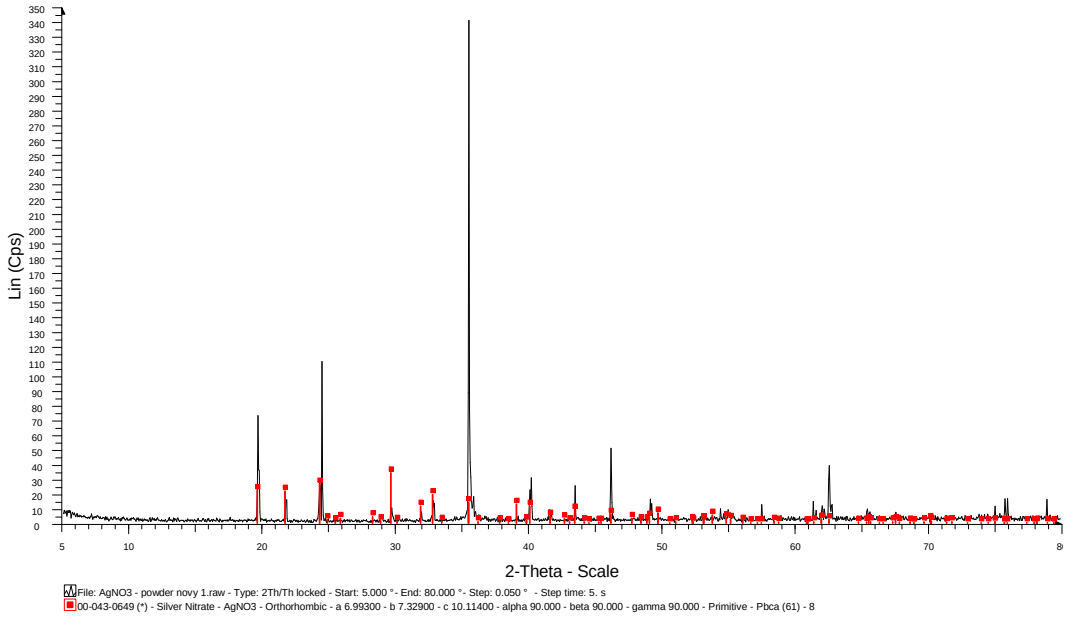


Figure 4 XRD analysis of $AgNO_3$, in red pattern of $AgNO_3$

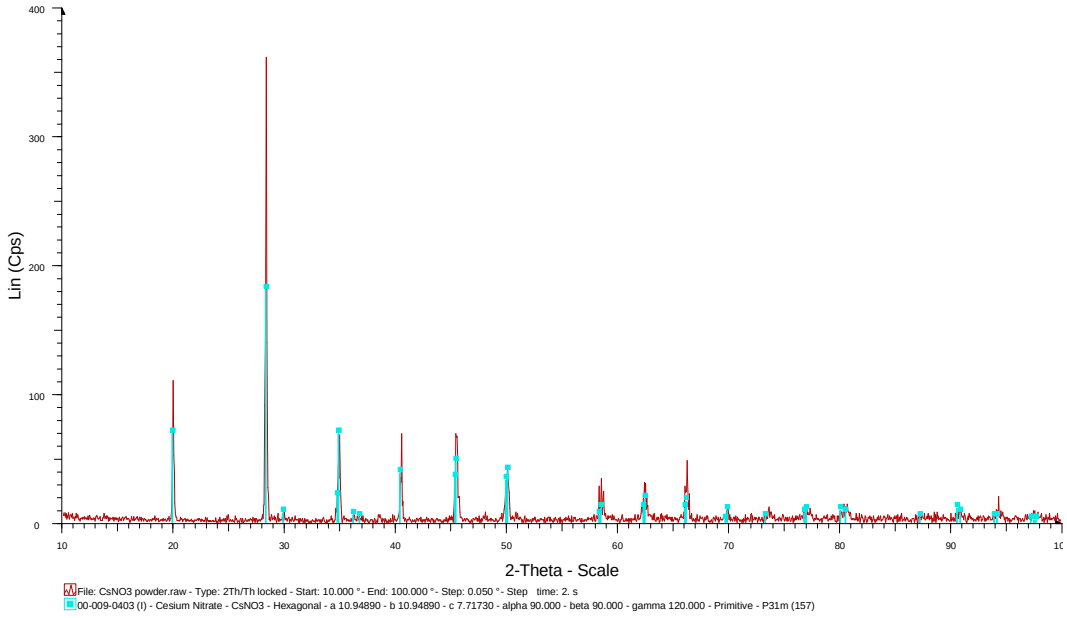
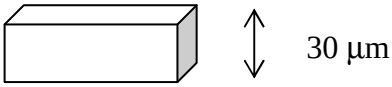


Figure 5 XRD analysis of $CsNO_3$, in light blue pattern of $CsNO_3$

1.3 Calculation procedure of lifetimes

The following assumptions have been made with respect to calculating lifetimes of the SiC and ZrC layer from corrosion data obtained for the powder samples:

- uniform leaching rate without pit corrosion
- stoechiometry (Si=C, Zr=C)
- minimum density SiC = 3.18 g/cc (HTR-F specifications*), TD = 3.21 g/cc
  minimum density ZrC = 6.67 g/cc*, TD = 6.73 g/cc
- deviation in lifetime = 5% (based on detection deviation of ICP-AES)
- SiC/ZrC layer thickness: 30 µm



* the minimum density is defined as 99.07 % of the theoretical density (TD); accordingly, for ZrC the same percentage has been chosen. XRD-analysis confirms an X-ray density of 6.66 g/cc.

The volume of a SiC or ZrC layer of 30 micron thickness and 1 m2 surface area amounts to 3.1 E-5 m3. The SiC and ZrC content within this volume (based upon the minimal density as formulated in HTR-F) is 95.4 gram and 200.01 gram, respectively. The lifetime of the layer has been calculated presuming a uniform leaching rate over the specified surface area which is constant over the period of the experiment. Leaching rates, normalised to the specific surface area of the material, can then be recalculated to a maximum lifetime expressed in years of according to the following equations:

- lifetime SiC (years) = (95.4) / leach rate (g/m2/d) / 365
- lifetime ZrC (years) = (200.01) / leach rate (g/m2/d) / 365

1.4 Leaching procedure and equipment

Static leach experiments are carried out using the following method:

Static corrosion experiments on accurately weighted amounts of SiC powder and ZrC 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 accurately before and after the leaching period so as to ensure that evaporation of the leachants did not occur. After the preset contact time period, the powder was separated from the leachate, accomplished by filtering over a 0.45 µm cellulose nitrate filter (Schleicher&Sluell). The Si or Zr content in the aqueous phase was determined by ICP-AES analysis. The Si and Zr content of the leachants were measured also and serve as a blanc correction on the ICP-AES data.

Then, the Nalgene vessels were treated ultrasonically for 5 minutes with a known amount (the optimal amount has been determined already as described in the deliverable D-BF 3.2) of diluted nitric acid for additional ICP-AES measurements so as to check if the vessel walls contain leached material that has reprecipitated e.g. as colloidal oxidic particles.

The same procedure as described in the deliverable has been used to wash the vessels. They were washed directly after removal of the leachate from the vessel with a weighted amount of 1.0 molar nitric acid and wash the particles similarly with a 0.16 molar nitric acid solution with known weight to check if colloidal particles may be adhered to the powder or coated particles. Both washing solutions were filtered over a 0.45 micron filter prior to the ICP-AES analyses.

The amount of leachant used was weighed, based on the required volume and its density. For the SiC powder (BET specific surface area: 12.908 m^2/gram), 10 ml leachant per 0.05 gram of powder was applied (surface-to-volume ratio S/V = 64540 m^{-1}), similar to the ratio used in the HTR-N/N1 programme. Accordingly, 10 ml leachant per 0.05 gram was applied for all experiments with ZrC powder. Based on its specific surface area (BET: 0.4301 m^2/gram), this results in a S/V = 2151.

Experiments under oxidizing conditions have been carried out by weighing the samples and leachants in air and closure of the vessels in air. For the corrosion experiments under inert/reducing atmosphere, all materials and leachants were posted into the glove box and weighed there. The glove box contains 2 ppm of oxygen as a maximum. In order to maintain reducing conditions, NaS was added to the leachants in an amount of 25.73 ppm, 25.42 ppm and 29.50 ppm for granite water, Q-brine and clay pore water, respectively.

For weighing the powders, an antistatic ring was used, connected to the balance, since both ZrC and SiC powders tend to be static.

A special oven has been designed that can be placed inside an argon filled glove box for carrying out corrosion experiments under inert/reducing atmosphere. The oven has dimensions that allow moving inside and outside the box through the lock for maintenance. The oven controller is compact and smaller than the oven and is placed inside the glove box as well. The oven is isolated sufficiently for keeping the temperature of the argon atmosphere inside the box below 30°C. The oven is suitable for containing 15 Nalgene vessels at the same time. In Figure 6 and 7, the design of the oven and the glove box is shown.

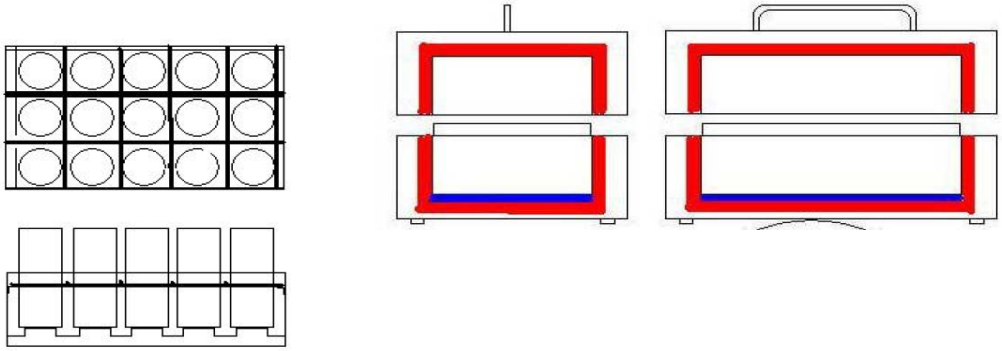


Figure 6: Design of the oven for corrosion studies under inert atmosphere

Figure 7: Argon-filled glove box for corrosion studies under inert atmosphere – running tests at elevated temperature

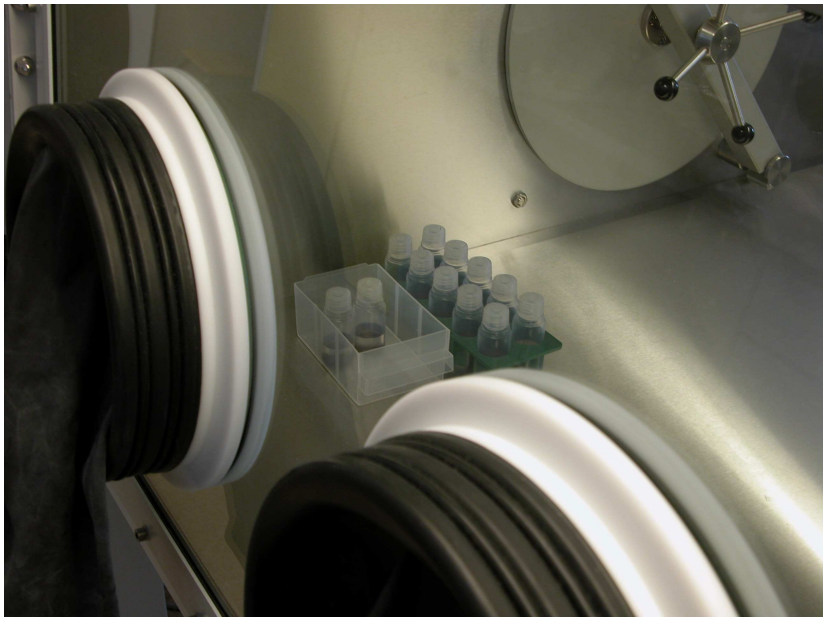


Figure 8: Tests under reducing conditions at room temperature

1.5 Corrosion results

In the following paragraphs results of the leaching experiments are presented. Results are shown in the figures in the form of calculated lifetimes (see part 1.3) dependent on temperatures and kind of leachants. All graphics are presented in the logarithmic scale. Detailed results are then listed in the annexes.
For most of the experiments with ZrC, the leached amount of Zr in the leachant to be analysed was extremely low, even round the detection limits of the ICP/MS technique. This can lead to not negligible uncertainties in the calculated lifetimes of the ZrC layer. The performed leaching experiments should allow only a comparison between the two layers in the mean of expected lifetimes; they should not give any exact numbers.

1.5.1 Comparison corrosion rates of SiC and ZrC powder in interaction with Ag under reducing conditions

On the following figures, results of the performed leaching experiments of SiC and ZrC in interaction with Ag under reducing conditions are depicted.

For SiC the calculated lifetimes decrease as expected with increasing temperature, they are in the range of 1E+04, in granite water – the values reach even 1E+05.
ZrC powders shows lifetimes for granite water and Q- brine in the range of 1E+07, for clay pore water lifetimes of 1E+05 are reached.

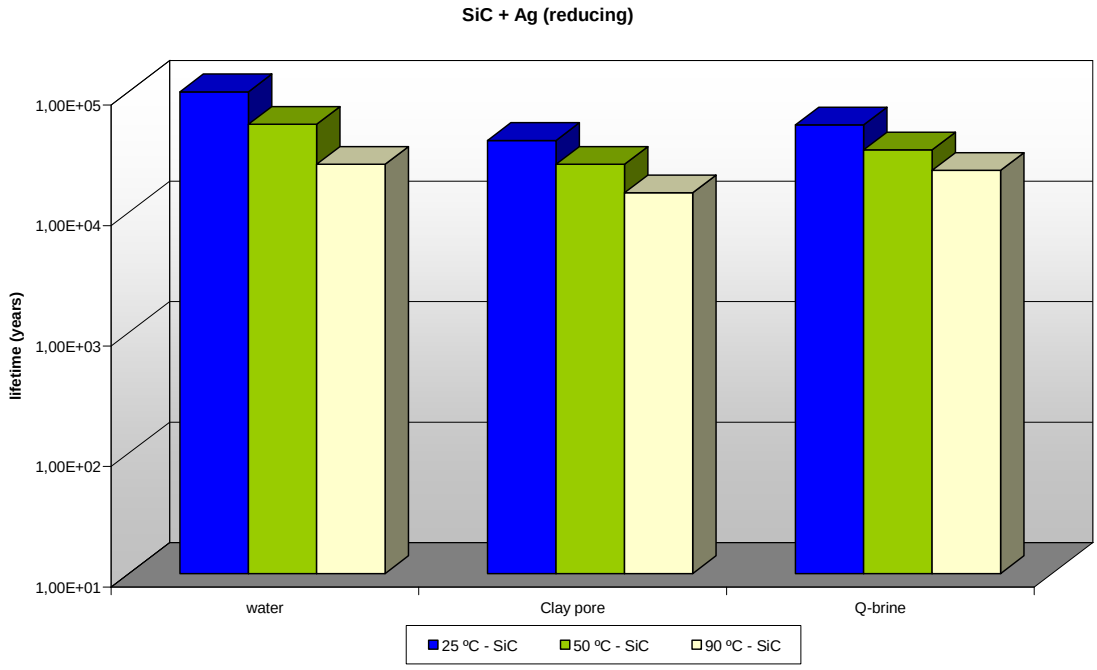


Figure 9: Calculated lifetimes for SiC powder in interaction with Ag under reducing conditions

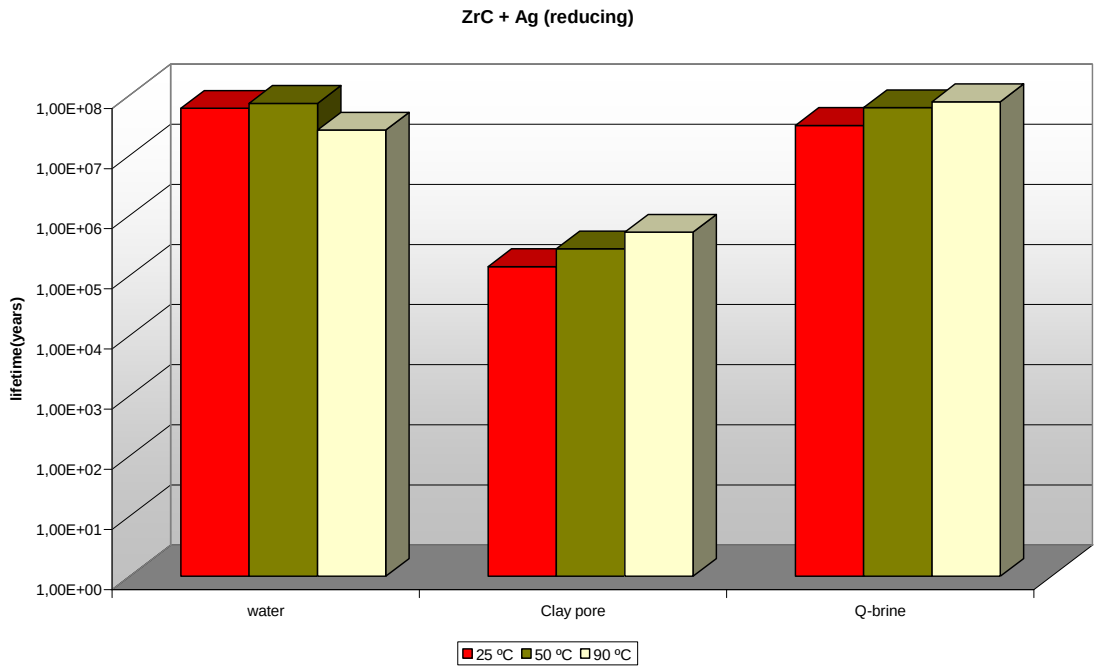


Figure 10: Calculated lifetimes for ZrC powder in interaction with Ag under reducing conditions

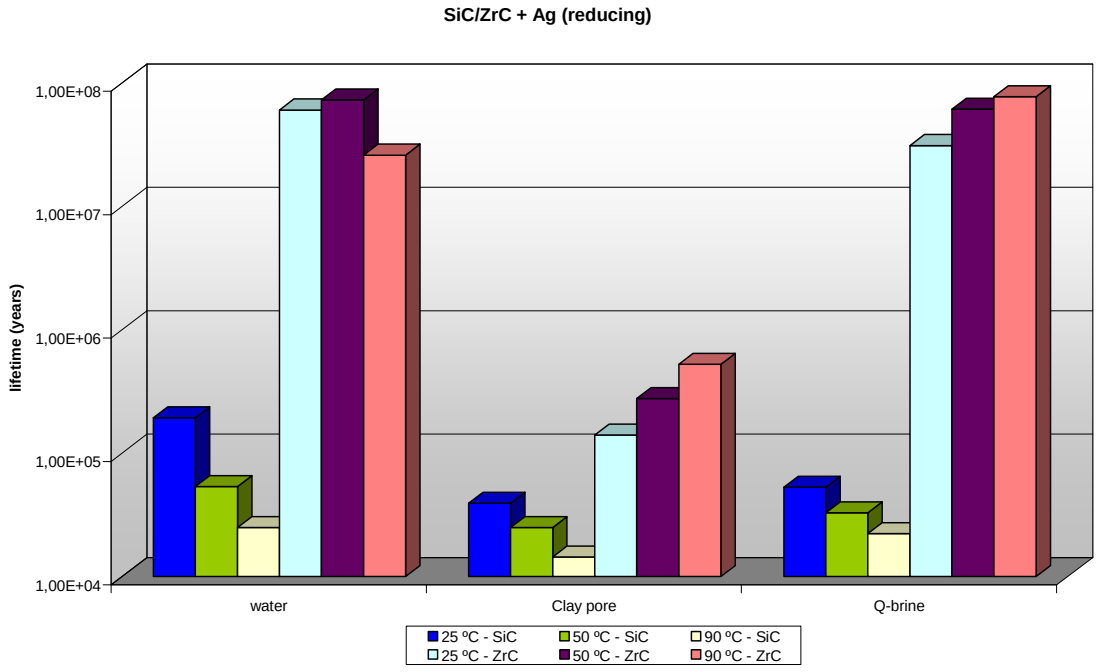


Figure 11: Comparison of calculated lifetimes for SiC and ZrC powder in interaction with Ag under reducing conditions

1.5.2 Comparison corrosion rates of SiC and ZrC powder in interaction with Cs under reducing conditions

On the following figures, results of the performed leaching experiments of SiC and ZrC in interaction with Cs under reducing conditions are depicted.

For SiC the calculated lifetimes decrease as expected with increasing temperature, they are in the range of 1E+04, there is no significant influence of the leachant.

ZrC powders shows lifetimes for granite water and Q- brine in the range of 1E+07, for clay pore water lifetimes of 1E+05 are reached. In Q-brine water, calculated lifetimes are about 10 times higher comparing to the other two leachants.

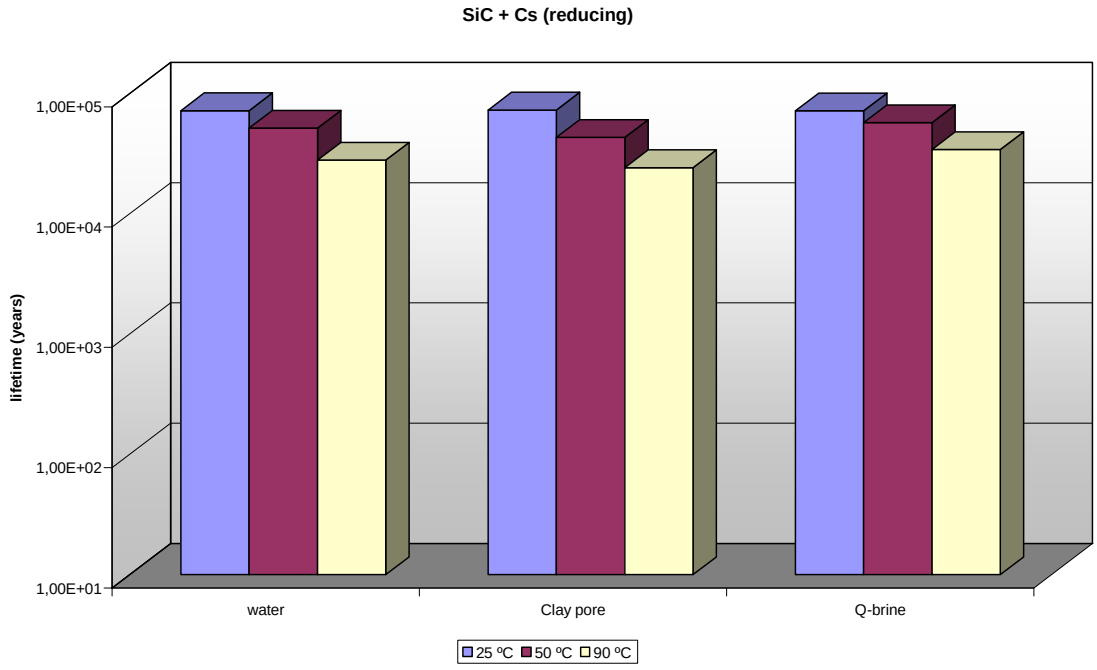


Figure 12: Calculated lifetimes for SiC powder in interaction with Cs under reducing conditions

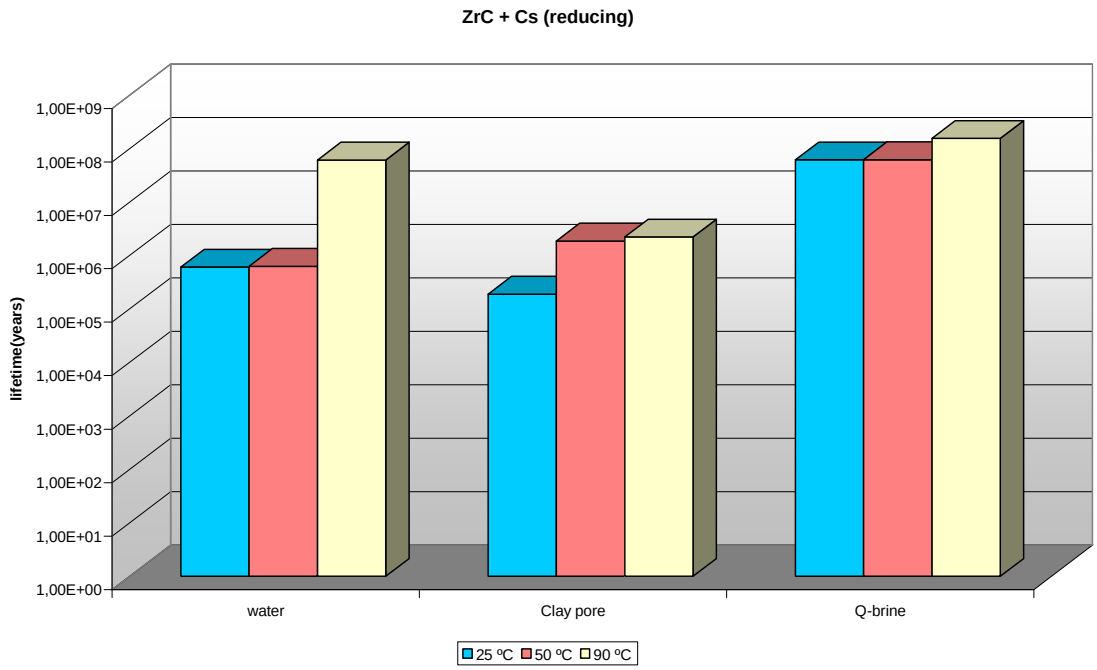


Figure 13: Calculated lifetimes for ZrC powder in interaction with Cs under reducing conditions

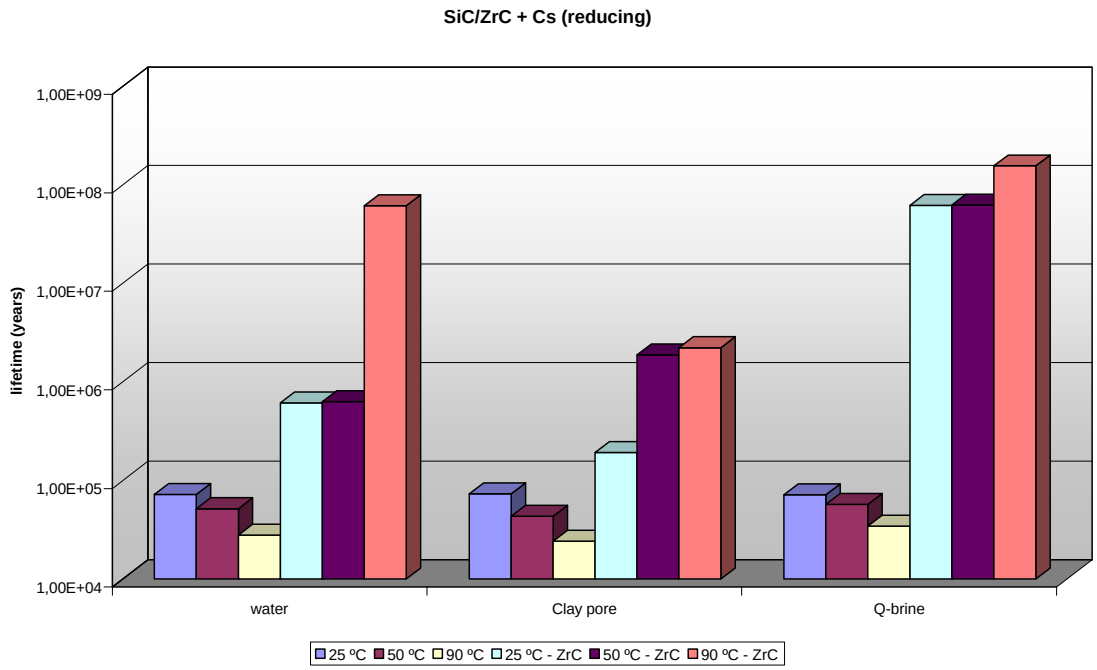


Figure 14: Comparison of calculated lifetimes for SiC and ZrC powder in interaction with Cs under reducing conditions

1.5.3 Comparison corrosion rates of SiC and ZrC powder in interaction with Ag under oxidizing conditions

On the following figures, results of the performed leaching experiments of SiC and ZrC in interaction with Ag under oxidizing conditions are depicted.

For SiC the calculated lifetimes decrease as expected with increasing temperature, they are in the range of 1E+04, in granite water at the temperature of 25 ºC even 1E+05.

ZrC powders shows lifetimes for granite water and Q- brine in the range of 1E+07, for clay pore water lifetimes of 1E+05 are reached.

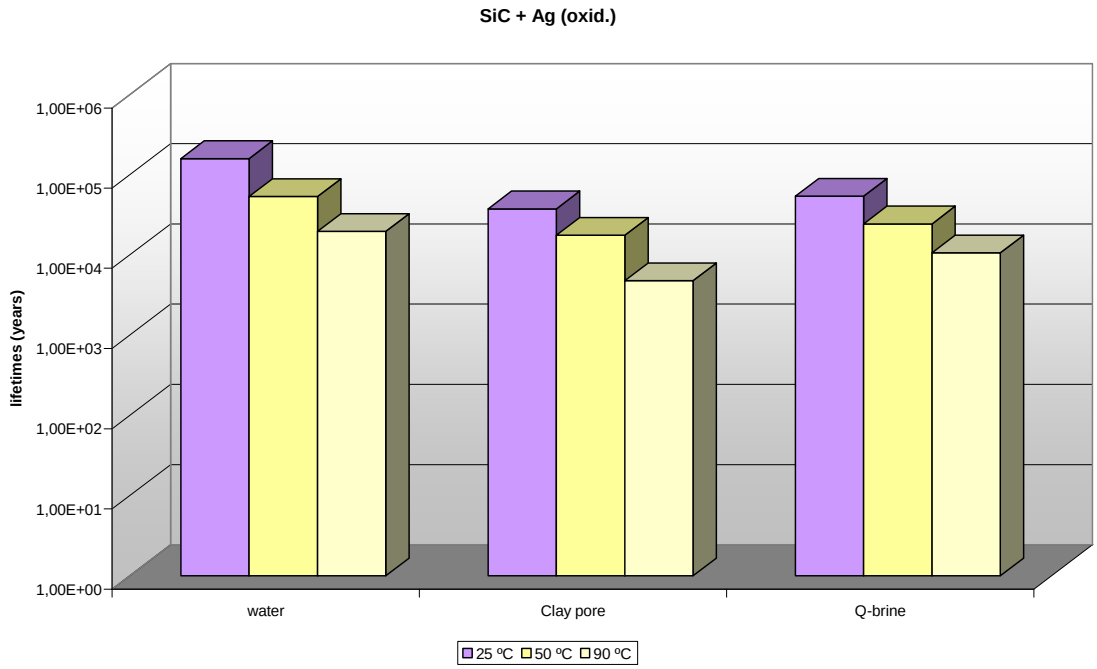


Figure 15: Calculated lifetimes for SiC powder in interaction with Ag under oxidizing conditions

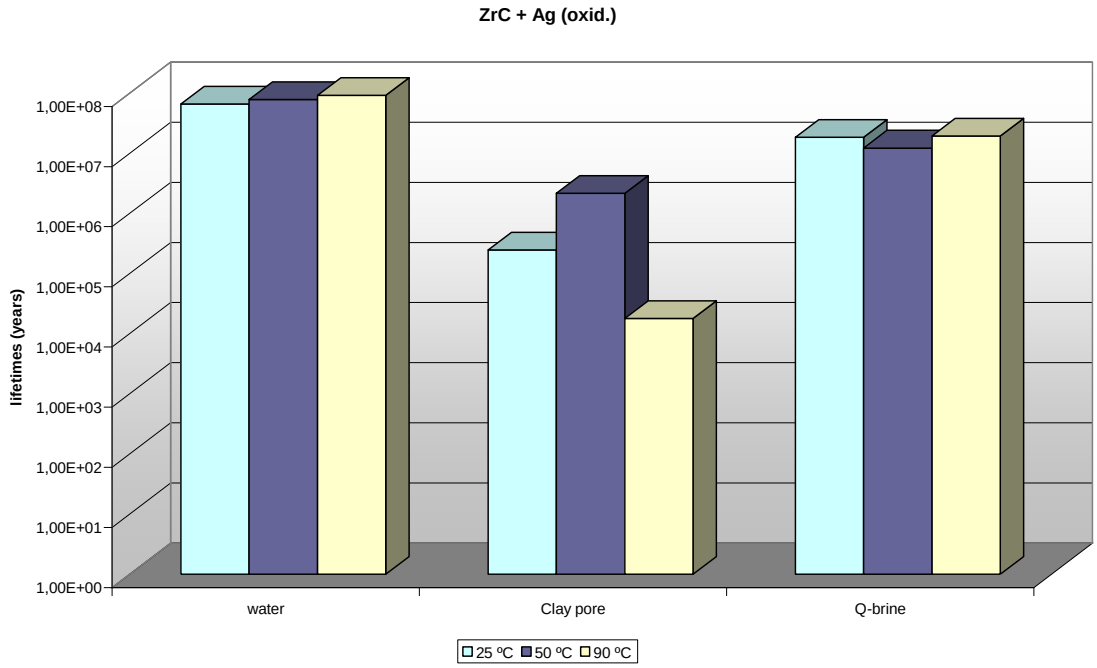


Figure 16: Calculated lifetimes for ZrC powder in interaction with Ag under oxidizing conditions

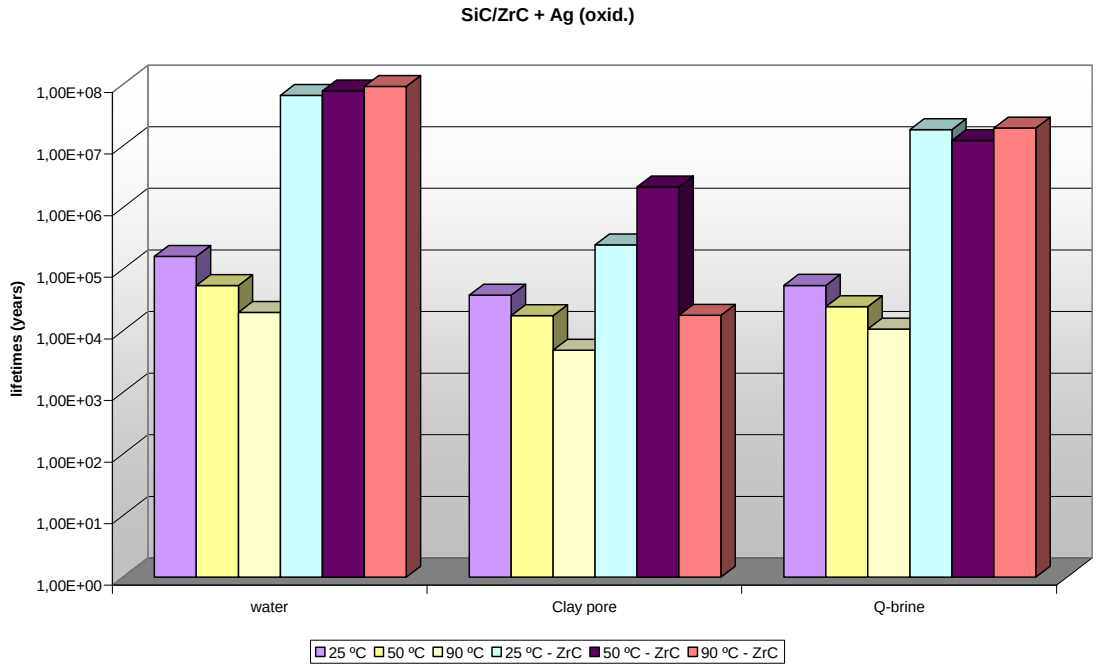


Figure 17: Comparison of calculated lifetimes for SiC and ZrC powder in interaction with Ag under oxidizing conditions

1.5.4 Comparison corrosion rates of SiC and ZrC powder in interaction with Cs under oxidizing conditions

On the following figures, results of the performed leaching experiments of SiC and ZrC in interaction with Cs under oxidizing conditions are depicted.

For SiC the calculated lifetimes decrease as expected with increasing temperature, they are in the range of 1E+04, in granite water at the temperature of 25 ºC even in the range of 1E+05.

ZrC powders shows lifetimes for granite water and Q- brine in the range of 1E+07, for clay pore water lifetimes of 1E+05 are reached.

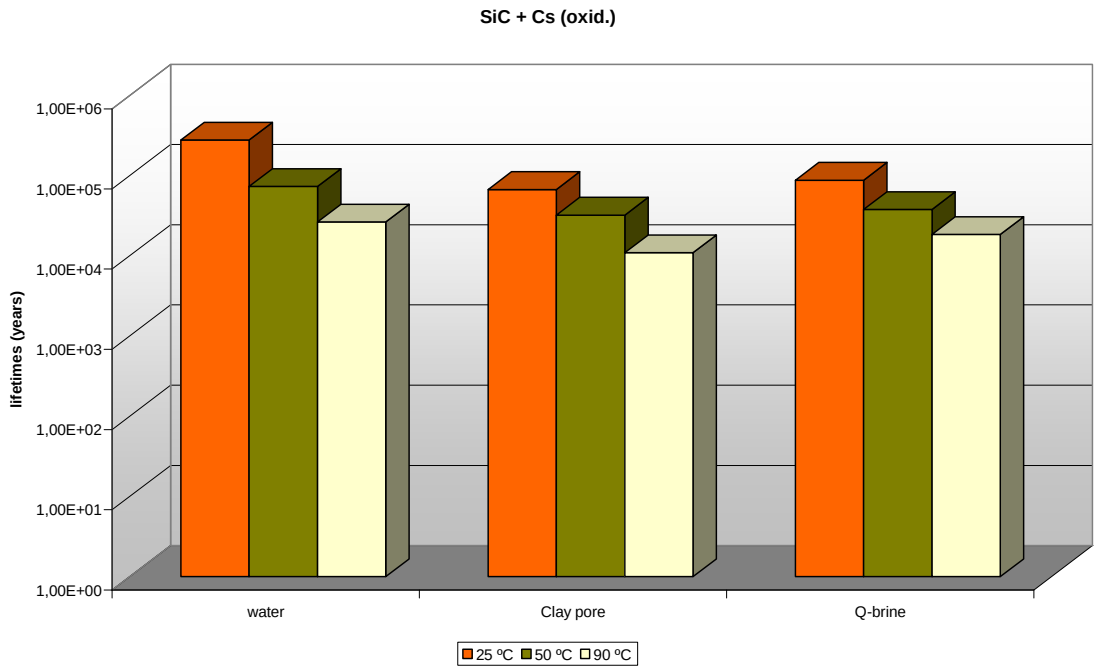


Figure 18: Calculated lifetimes for SiC powder in interaction with Cs under oxidizing conditions

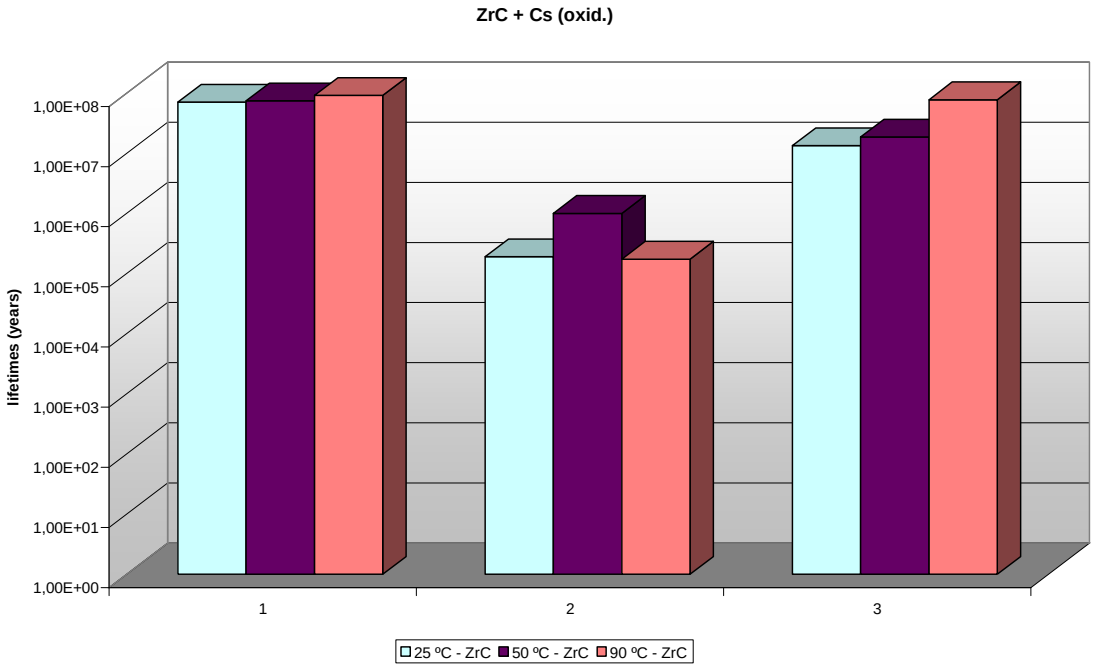


Figure 19: Calculated lifetimes for ZrC powder in interaction with Cs under oxidizing conditions

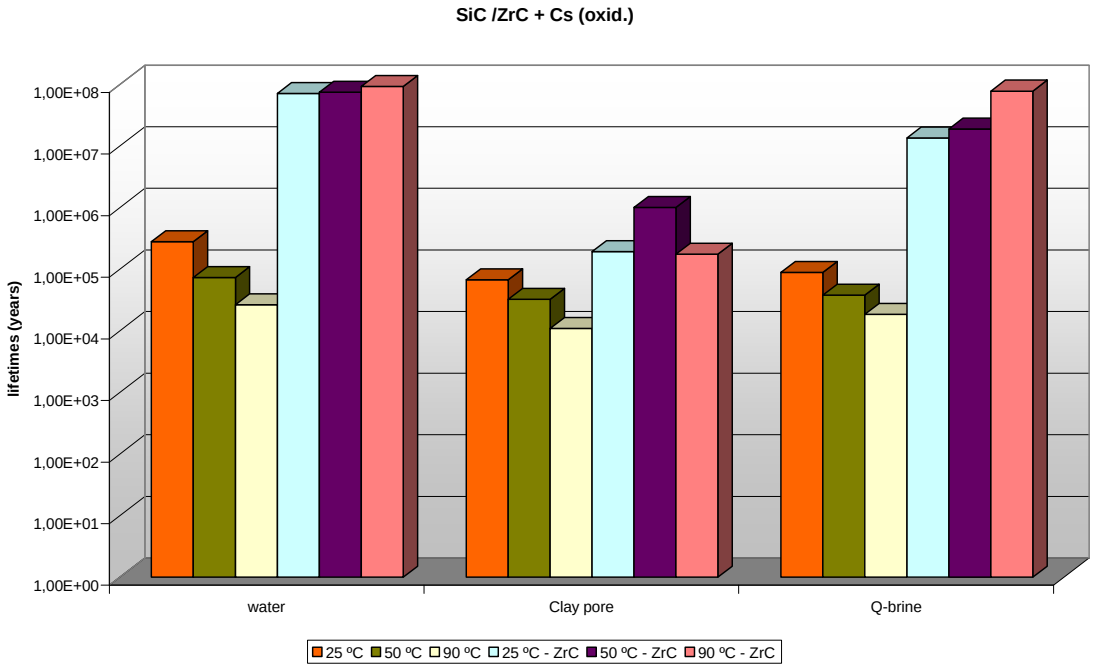


Figure 20: Comparison of calculated lifetimes for SiC and ZrC powder in interaction with Cs under oxidizing conditions

1.6 Conclusions

Possible influence of fission products (Ag, Cs) on the layer of SiC and ZrC has been studied by leaching experiments. In this study the chemical resistance of SiC powder and ZrC powder in the interaction with FP has been determined under repository conditions such as salt domes, granite-based repositories and clay formations. Tests have been performed under reducing and oxidizing conditions.

As mentioned already in the results, for most of the experiments led with ZrC, the leached amount of Zr in the leachant to be analysed was extremely low, very close to the detection limits of the ICP/MS technique. That can lead to not negligible uncertainties in the calculated lifetimes of the ZrC layer. The performed leaching experiments should allow only a comparison between the two layers in the mean of expected lifetimes; they should not give any exact numbers.

Generally, leaching rates of ZrC are lower then by SiC, i.e. calculated lifetimes are longer. SiC leaching rates are in the range of 1E-06 to 1E-05 and lifetimes are between 1E+05 to 1E+04. Calculated lifetimes decrease with increasing temperature of the leaching experiment, higher calculated lifetimes occur in the granite water. For ZrC powder, the leaching rates vary from 1E-05 (clay pore water) to 1E-09, i.e. the calculated lifetimes could be in the range of 1E+05 to 1E+08.

According to the performed experiments, ZrC layer could be considered as more suitable in the meaning of stability under repository conditions.

Annex 1: Leach rates and lifetimes calculated from ICP-AES analysis results (corrected for blancs) – for **Ag**

Temp. (°C)	Leachant	Days of exposure	Atmosphere	Leach rate (g/m2.d)	Lifetime (years)
SiC powder					
25	Granite	40	Air	1.63E-06	1.60E+05
25	Clay-pore	40	Air	6.95E-06	3.76E+04
25	Q-brine	40	Air	4.82E-06	5.42E+04
50	Granite	40	Air	4.85E-06	5.39E+04
50	Clay-pore	40	Air	1.48E-05	1.76E+04
50	Q-brine	40	Air	1.06E-05	2.46E+04
90	Granite	40	Air	1.33E-05	1.97E+04
90	Clay-pore	40	Air	5.46E-05	4.79E+03
90	Q-brine	40	Air	2.46E-05	1.06E+04
ZrC powder					
25	Granite	40	Air	3.98E-09	6.56E+07
25	Clay-pore	40	Air	1.06E-06	2.46E+05
25	Q-brine	40	Air	1.42E-08	1.83E+07
50	Granite	40	Air	3.36E-09	7.78E+07
50	Clay-pore	40	Air	1.22E-07	2.15E+06
50	Q-brine	40	Air	2.15E-08	1.22E+07
90	Granite	40	Air	2.84E-09	9.18E+07
90	Clay-pore	40	Air	1.46E-05	1.79E+04
90	Q-brine	40	Air	1.35E-08	1.93E+07

Temp. (°C)	Leachant	Days of exposure	Atmosphere	Leach rate (g/m2.d)	Lifetime (years)
SiC powder					
25	Granite	40	Ar/NaS	1.35E-06	1.94E+05
25	Clay-pore	40	Ar/NaS	6.63E-06	3.94E+04
25	Q-brine	40	Ar/NaS	4.91E-06	5.31E+04
50	Granite	40	Ar/NaS	4.86E-06	5.38E+04
50	Clay-pore	40	Ar/NaS	1.05E-05	2.50E+04
50	Q-brine	40	Ar/NaS	7.94E-06	3.29E+04
90	Granite	40	Ar/NaS	1.05E-05	2.50E+04
90	Clay-pore	40	Ar/NaS	1.80E-05	1.45E+04
90	Q-brine	40	Ar/NaS	1.17E-05	2.23E+04
ZrC powder					
25	Granite	40	Ar/NaS	4.31E-09	6.06E+07
25	Clay-pore	40	Ar/NaS	1.86E-06	1.40E+05
25	Q-brine	40	Ar/NaS	8.36E-09	3.12E+07
50	Granite	40	Ar/NaS	3.57E-09	7.31E+07
50	Clay-pore	40	Ar/NaS	9.44E-07	2.77E+05
50	Q-brine	40	Ar/NaS	4.24E-09	6.17E+07
90	Granite	40	Ar/NaS	1.00E-08	2.61E+07
90	Clay-pore	40	Ar/NaS	4.98E-07	5.25E+05
90	Q-brine	40	Ar/NaS	3.38E-09	7.73E+07

Annex 2: Leach rates and lifetimes calculated from ICP-AES analysis results (corrected for blancs) – for **Cs**

Temp. (°C)	Leachant	Days of exposure	Atmosphere	Leach rate (g/m2.d)	Lifetime (years)
SiC powder					
25	Granite	40	Air	9.42E-07	2.78E+05
25	Clay-pore	40	Air	3.89E-06	6.71E+04
25	Q-brine	40	Air	2.98E-06	8.78E+04
50	Granite	40	Air	3.58E-06	7.31E+04
50	Clay-pore	40	Air	8.10E-06	3.23E+04
50	Q-brine	40	Air	6.89E-06	3.79E+04
90	Granite	40	Air	9.92E-06	2.64E+04
90	Clay-pore	40	Air	2.40E-05	1.09E+04
90	Q-brine	40	Air	1.41E-05	1.85E+04
ZrC powder					
25	Granite	40	Air	3.70E-09	7.07E+07
25	Clay-pore	40	Air	1.37E-06	1.91E+05
25	Q-brine	40	Air	1.96E-08	1.34E+07
50	Granite	40	Air	3.53E-09	7.40E+07
50	Clay-pore	40	Air	2.62E-07	9.98E+05
50	Q-brine	40	Air	1.40E-08	1.87E+07
90	Granite	40	Air	2.85E-09	9.16E+07
90	Clay-pore	40	Air	1.51E-06	1.74E+05
90	Q-brine	40	Air	3.38E-09	7.74E+07

Temp. (°C)	Leachant	Days of exposure	Atmosphere	Leach rate (g/m2.d)	Lifetime (years)
SiC powder					
25	Granite	40	Ar/NaS	3.64E-06	7.18E+04
25	Clay-pore	40	Ar/NaS	3.59E-06	7.28E+04
25	Q-brine	40	Ar/NaS	3.65E-06	7.17E+04
50	Granite	40	Ar/NaS	5.08E-06	5.15E+04
50	Clay-pore	40	Ar/NaS	6.06E-06	4.31E+04
50	Q-brine	40	Ar/NaS	4.57E-06	5.72E+04
90	Granite	40	Ar/NaS	9.35E-06	2.79E+04
90	Clay-pore	40	Ar/NaS	1.08E-05	2.41E+04
90	Q-brine	40	Ar/NaS	7.64E-06	3.42E+04
ZrC powder					
25	Granite	40	Ar/NaS	4.30E-07	6.08E+05
25	Clay-pore	40	Ar/NaS	1.37E-06	1.91E+05
25	Q-brine	40	Ar/NaS	4.25E-09	6.15E+07
50	Granite	40	Ar/NaS	4.17E-07	6.27E+05
50	Clay-pore	40	Ar/NaS	1.40E-07	1.87E+06
50	Q-brine	40	Ar/NaS	4.23E-09	6.18E+07
90	Granite	40	Ar/NaS	4.28E-09	6.11E+07
90	Clay-pore	40	Ar/NaS	1.18E-07	2.21E+06
90	Q-brine	40	Ar/NaS	1.69E-09	1.55E+08