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Document title

Report on thermodynamic calculations and identification of phases of FP and SiC/ZrC

Executive summary

The interaction of SiC with water has been assessed by geochemical modeling and associated thermodynamic databases. The temperature range studied was between 25 and 200°C. The calculations have shown that SiO_2 is the principal solid reaction product. Under reducing aqueous redox conditions, organic reaction products are expected to be formed as well, while under oxidizing conditions CO_2 is calculated to be the principal carbon containing reaction product. The formation of SiO2 as principal solid reaction product is confirmed by literature data. The SiO2 seems to form a tight dense layer at the surface of SiC, which may play the role of a protective layer. If confirmed, this may imply a diffusion-controlled dissolution of SiC.

Revisions

Rev.	Date	Short description	Author	WP Leader	SP Leader	Coordinator
00	21/11/2006	First issue	Grambow Armines		Von Lensa, FZJ	Bogusch, ANP
01	18/12/2006	Final				

Table of Contents

1 Introduction

High temperature gas cooled reactors (HTR) use sub-mm sized coated fuel particles embedded in the graphite matrix of fuel pebbles or block type fuel. The small fuel particles (kernels) surrounded by buffer carbon (BC), inner pyrolytic carbon (IPyC), silicon carbide (SiC) and outer pyrolytic carbon (OPyC) [1,2] are called "TRISO fuel particles". All coatings are designed to better confine gaseous and metallic fission products formed during the operation of the reactor.

Merz et al. [3] demonstrated that the fuel particles embedded in the graphite matrix of the fuel pebbles could be directly stored in a salt mine in Germany. Fachinger et al. [4] have shown that the HTR fuel may be considered as a small system of multiples barriers against radionuclide release not only in a nuclear reactor but as well during geological disposal. This is true not only in salt but as well in clay waters. The outermost barrier is the graphite matrix. Groundwater diffusion into this matrix will fill interconnected porosity by water and may expose individual fuel particles to this pore water. The fuel kernel, whose the corrosion rate is slow [5], is protected by the SiC coating, with corrosion rates in the range of 1/10000 per year. This means that it will take about 10000 yrs until the SiC coating is destroyed. The corrosion of SiC does not result in the complete dissolution of SiC but in the formation of solid reaction products. The formation of these reaction products may be one of the reasons why corrosion rates of SiC decrease with time.

The nature of the corrosion products is not known yet. In the present study it is attempted to estimate the kind of corrosion products both by performing a literature evaluation and by geochemical modeling.

2 Literature study

SiC is very stable both in air and in water. However this does not mean that it does not react within these media (oxidation, dissolution). Instead reaction rates may be very slow. Both solid and gaseous reaction products may form. At first the reaction in air, then in water will be described.

2.1 Oxidation at room temperature

V. Médout-Marère et al. [6] have shown clearly that SiC oxidizes relatively rapidely to SiO2 even at room temperature. Structure of the oxidized surface is more similar to quartz than to bulk SiC. There is a homogeneous surface layer of SiO_2, which increases in thickness with temperature. The SiO_2 layer is proably denser than quartz as observed from adsorption energies. The formation of a very dense SiO_2 type surface is explained by the more closer Si-Si distance in SiC as compared to SiO_2. It has been shown that passively oxidized SiC surface contains both hydrophobic and hydrophilic sites [7]. This is different to a quartz surface, which essentially only contains hydrophilic sites. The mechanism of oxidation has been revealed by Guerfi et al. [8] studying surface site properties. The properties of the surface sites on oxidized SiC are different that that of pure silica polymorphs The authors explained the presence of hydrophobic groups by an intermediate step in oxydation: formation of oxy-carbide surface surface sites of a generic stoichiometry SiOxCy. Further oxydation enhaces hydrophyllic character of the surface sites. Oxydation is assocated to increase of quantity of acidic surface groups. It is interesting to note that the oxydised layer can be removed by NaOH solutions. In this sense the SiO_2 surface on SiC behaves like normal SiO_2.

2.2 Corrosion in water

A detailed study of corrosion products formed in aqueous solution has been performed by Imai et al. [9]. Even though the experimental conditions (acid solution, temperature of 120°C) are quite different than those expected for geological disposal, the data are relevant since reaction

product formation will probably not depend on pH (SiO_2 is stable between pH 0 and 13) and since the key effect of high temperature is the acceleration of the chemical dissolution reactions.

Figures 1 and 2 show the results of surface analyses of oxidized SiC. It can be seen that an about 4 nm thick SiO_2 layer is formed after 3 hours. The high-resolution image in Figure 2 shows that the transition between SiC and SiO_2 occurs within a single monolayer of SiC without presence of any spacing. This indicates that the chemical transformation from SiC to SiO_2 rather is a solid state transformation reaction than a reaction product formed by a dissolution/precipitation mechanism.

Figure 1: Cross-sectional TEM image of the SiO_2 layer formed on the 4H-SiC(0 0 0 1) Basal plane using the NAOS method for 3 h. The layer with darker contrast on the SiC Basal plane is due to the SiO_2 layer

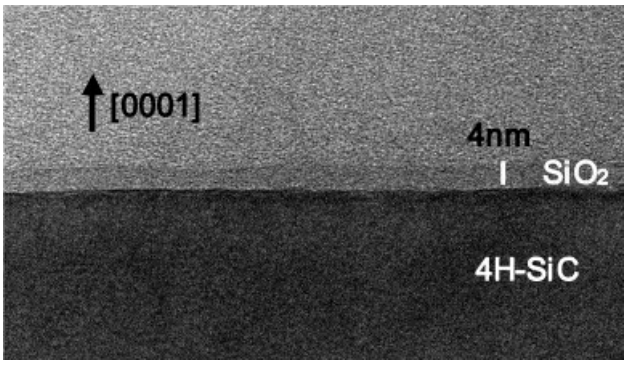
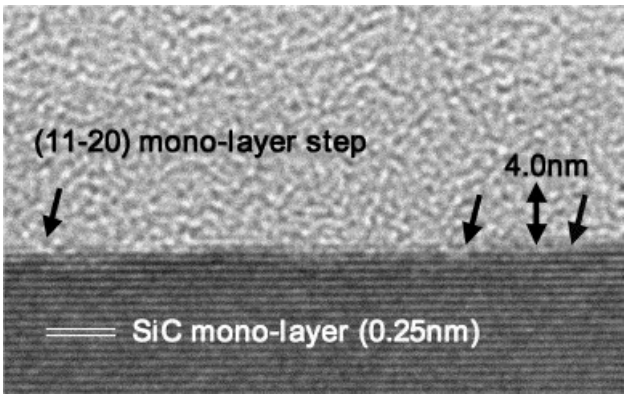
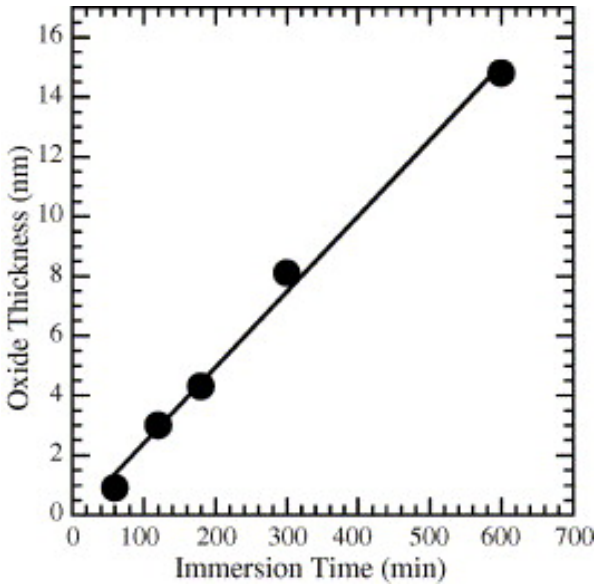


Figure 2: HR-TEM image of the SiO2/4H-SiC(0 0 0 1) interface. (1 1 −2 0) SiC monolayer steps are indicated by the arrows.



The kinetics of formation of SiO_2 on the surface of SiC in acid aqueous solutions indicates a linear rate law for the first 700 hours (Figure 3).

Figure 3: Plot of the SiO2 thickness formed on the 4H-SiC(0 0 0 1) substrate using the NAOS method vs. the immersion time in HNO3 at 121°C



2.3 Conclusions from literature study

SiO2 forms on SiC both in air and in water. The SiO2/SiC interface is dense and may probably be considered as diffusion barrier. From the constant oxidation rate we learn that diffusion of oxidants in SiO2 is not rate limiting (is sufficiently fast for up to 4 nm thickness of the SiO2 layer). It is likely that the reactivity at the SiO2/SiC interface might play key role. Dissolution of SiC would than be a 2 step mechanism:
(1) Oxidation of SiC to SiO2, (2) Dissolution of SiO2. If this mechanism could be confirmed one could use data on the dissolution mechanism of SiO2 to understand SiC dissolution. The dissolution mechanism of SiO2 is well known. The first step is the dissolution with constant rate. Thereafter in a second step an equilibrium with the aqueous solution is obtained and this corresponds to a stop of the dissolution reaction. It is very important to study the potential equilibrium between the SiO2 surface on SiC and the aqueous solution. If this mechanism can be validated experimentally, life times much longer than 10000 years may be achieved for the SiC coating.

3 Geochemical and thermodynamic modelling

3.1 Calculation tools

Stability diagrams (phase diagrams) as well as Eh/pH diagrams were calculated with the code HSC [10] using the as delivered thermodynamic database of heat capacity values, enthalpies et free energies of formation of key solid phases, gases and aqueous species. These diagrams allow identifying thermodynamically stable phases for a given set of geochemical conditions in a disposal scenario. So one can calculate under which conditions SiC is thermodynamically stable, hence, under which condition, no reaction is expected. On the other hand, if a solid phase is thermodynamically instable it shall become transformed into the more stable phase, but it may nevertheless in certain cases still take tens of thousands of years before this transformation may occur.
A detailed reaction path is calculated by the geochemical code PHREEQC [11]. The reaction path of a solid phase like SiC in contact to an aqueous phases like groundwater is calculated

assuming the stepwise dissolution of SiC in groundwater. The dissolved fraction of SiC leads to formation of aqueous carbon and Si species in water. Which aqueous species forms depends on the geochemical conditions. When concentrations of aqueous species supersede the solubility of a solid phase, this phase is assumed to precipitate, thus decreasing the solution concentrations of the involved species. The precipitated solid phase may be considered as a secondary solid reaction product. In reality however, transition between the primary reacting phase (SiC) and the secondary phase may occur without passing into solution. Finally, if there are gases, which may be formed from given aqueous species, the reaction path calculation considers that this gas is formed under equilibrium conditions. Reaction path calculations calculate as well the evolution of pH and in certain cases; an initially formed secondary phase is calculated to redissolve in favor of the precipitation of another one.

3.2 Stability of SiC under repository conditions

The stability field boundaries for SiC were calculated as a function of temperature and partial pressure of CO2. The calculations were performed both for a hydrogen saturated repository (log p O2= -83) and a repository under anoxic and slightly reducing conditions (log p O2 = -60). Results are shown in the figures 4 and 5.

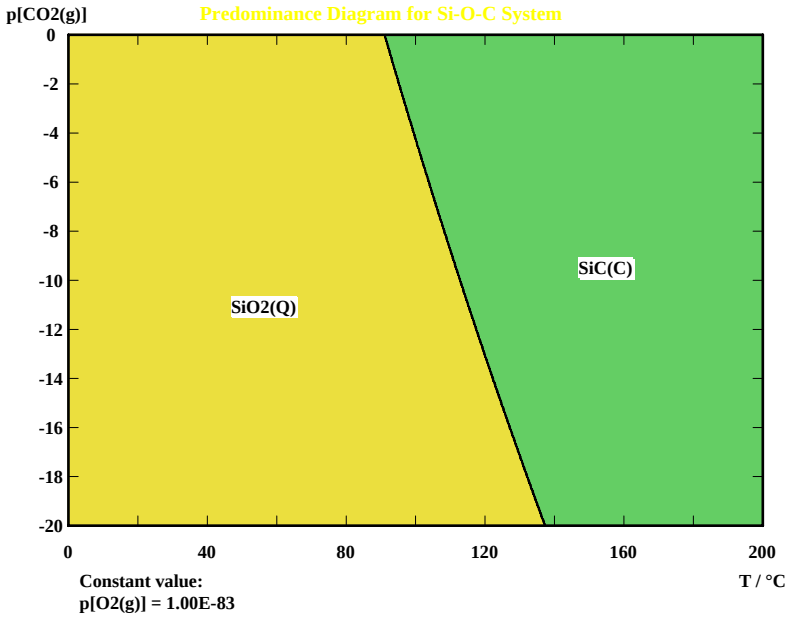


Figure 4: HSC calculations of the stability field of SiC as a function of temperature and carbonate partial pressure (attention: logarithmic unit for Y-axis) at log pO2 = -83.

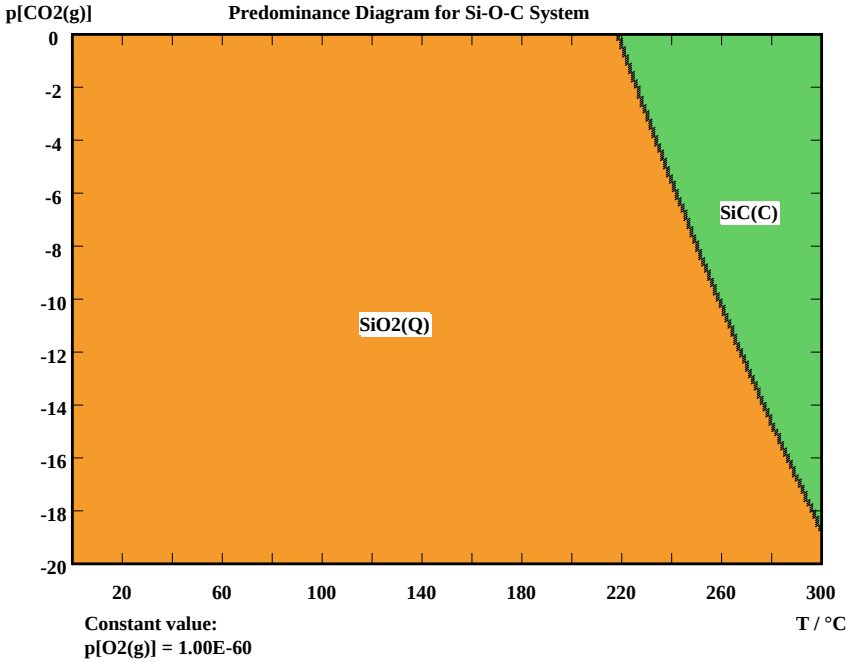


Figure 5: HSC calculations of the stability field of SiC as a function of temperature and carbonate partial pressure (attention: logarithmic unit for Y-axis) at log pO2 = -60.

Figure 6 show the stability field of SiC both as a function of oxygen and CO2 partial pressure.

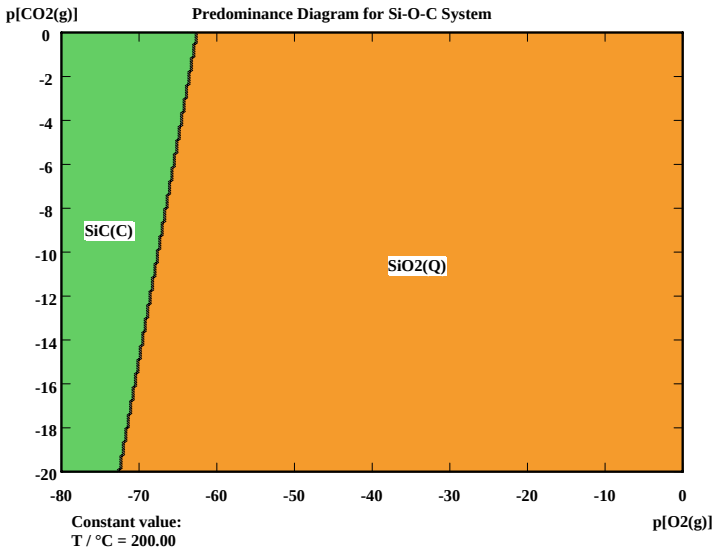


Figure 6: HSC calculations of the stability field of SiC as a function of oxygen and carbonate partial pressure (attention: logarithmic unit for X- and Y-axis) at a fixed temperature of 200°C

The results in the figures 4-6 show that SiC stability increases with temperature with partial pressure of CO2 and decreases with the partial pressure of dissolved oxygen. The principal transformation product is calculated to be SiO2. It shall be mentioned that current European repository concepts involve log pCO2 values between –2 and – 4. Temperatures are lower than 100°C. Under these conditions, SiC is never stable thermodynamiquement. Transformation into SiO2 is expected even under hydrogen saturated-conditions.

3.3 Stability of SiC and secondary phases as seen by the use of Eh/pH diagrams

The calculated Eh/pH diagrams are given in the figure 7 to 10 for 25°C and in the figures 11-14 for 300¨C. In some calculations gaseous methane (CH4) was excluded from formation, to simulate for example the absence of a free gas phase in a repository in which all void spaces are saturated with ground water. Figures 7, 9, 11 and 13 show the distribution in Eh/pH space of Si containing solid and aqueous species while the figures 8, 10, 12 and 14 show the corresponding carbon containing species. A total pressure for carbon containing species (CO_2 or CH4) of 1 bar was assumed. Maximum Si concentrations in the aqueous phase were assumed to be 10^{-3} M, a typical value for natural water conditions.

The results show absence of any overlap of the stability field of water with that of SiC even for temperatures as high as 300°C and hydrogen saturated conditions (lower stability field boundary of water. Compared to the calculations performed in chapter 3.2 we see here that additional to SiO2 two additional phases further limit the stability field of SiC: CH4 and graphite C. Under reducing conditions, as well a series of organic reaction products like acetate or oxalate is expected to be formed.

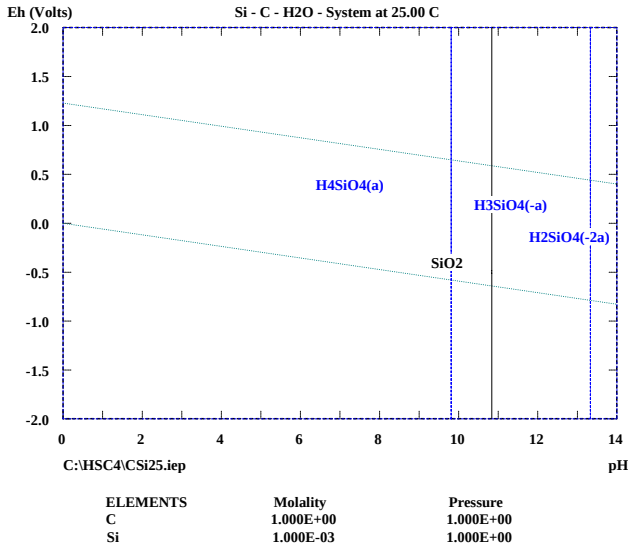


Figure 7: HSC calculated Eh/pH diagram for the Si-C-H2O system at 25°C showing the distribution of Si containing species. (blue: aqueous species, black: solids or gases). CH4 formation is allowed. Lower dashed line is the stability boundary for water against hydrogen formation, the higher dashed line indicates the stability of water against oxygen formation. The vertical black line at pH 10-11 indicates the stability of SiO2 against dissolution.

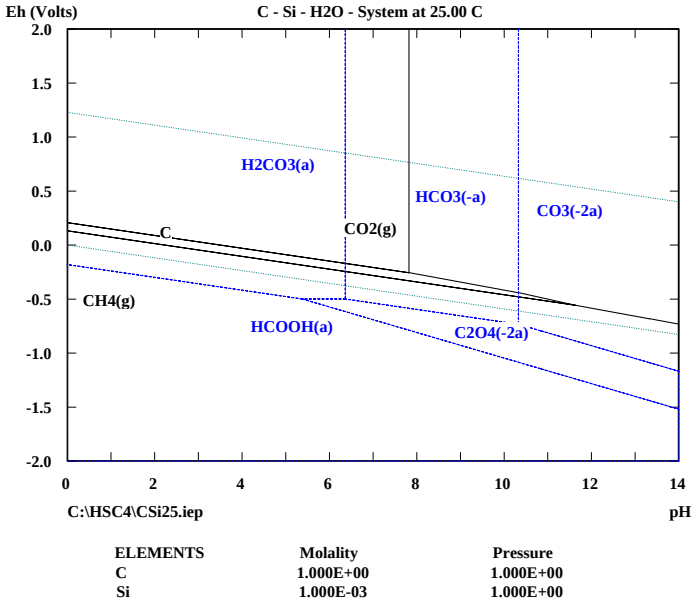


Fig. 8: same calculation as in figure 7 but carbon species are shown. The vertical black line at pH 8 indicates that at the right of the line equilibrium CO2 pressures are lower than 1 atm

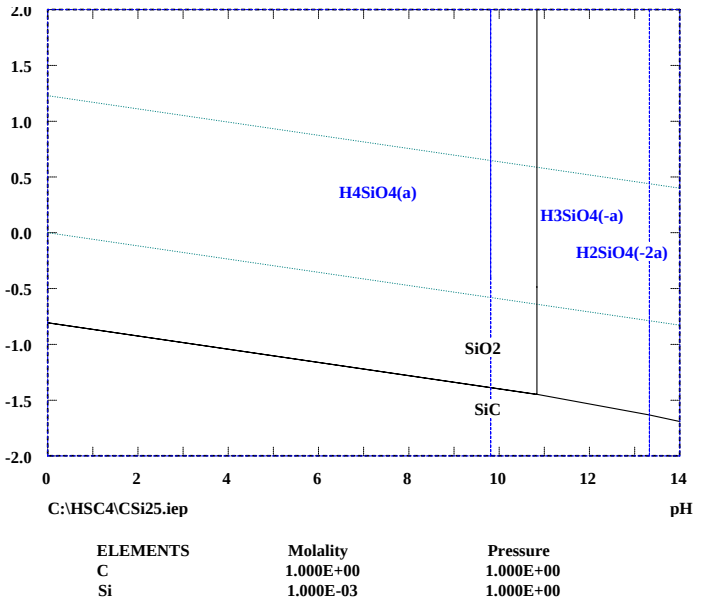


Figure 9 HSC calculated Eh/pH diagram for the Si-C-H2O system at 25°C showing the distribution of Si containing species. (blue: aqueous species, black: solids or gases). CH4 formation is prevented. Lower dashed line is the stability boundary for water against hydrogen formation, the higher dashed line indicates the stability of water against oxygen formation. The vertical black line at pH 10-11 indicates the stability of SiO2 against dissolution.

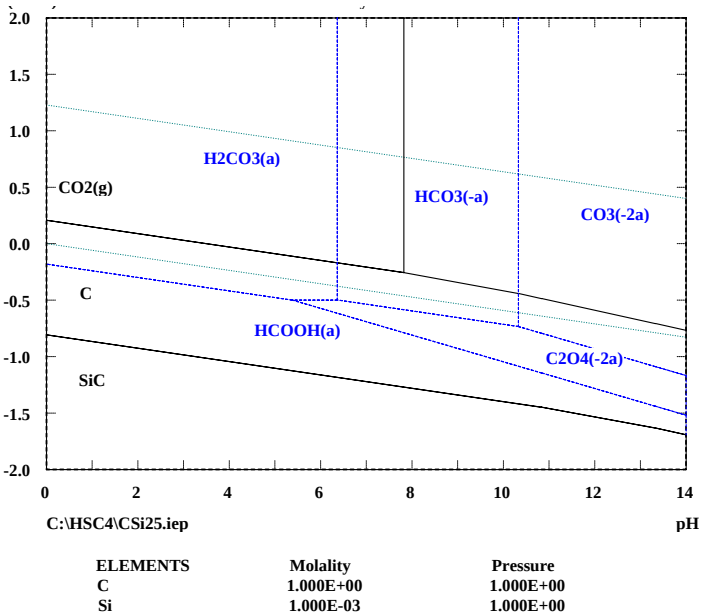


Figure 10, same calculation as in Figure 9 but C containing species are shown. The vertical black line at pH 8 indicates that at right equilibrium CO2 pressures are lower than 1 atm

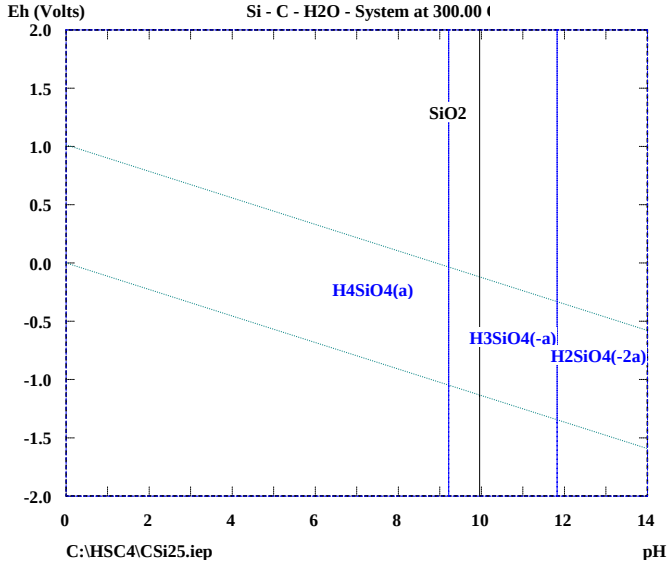


Figure 11: HSC calculated Eh/pH diagram for the Si-C-H2O system at 300°C showing the distribution of Si containing species. (blue: aqueous species, black: solids or gases). CH4 formation is allowed. Lower dashed line is the stability boundary for water against hydrogen formation, the higher dashed line indicates the stability of water against oxygen formation. The vertical black line at pH 10 indicates the stability of SiO2 against dissolution.

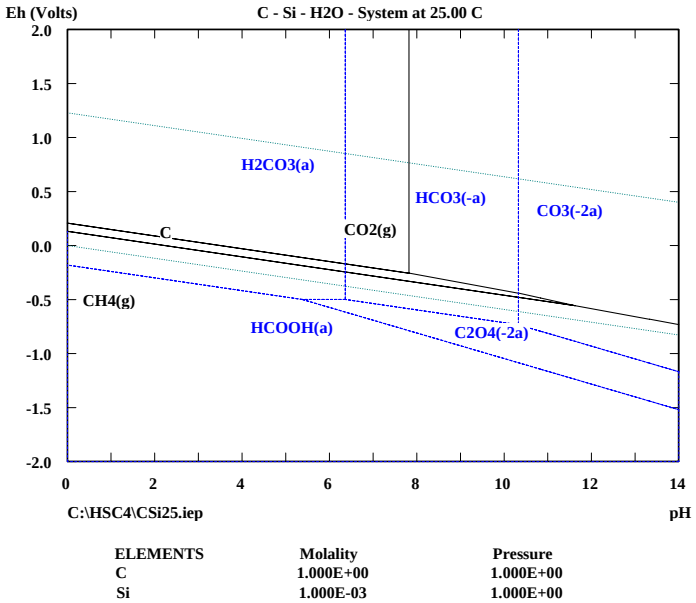
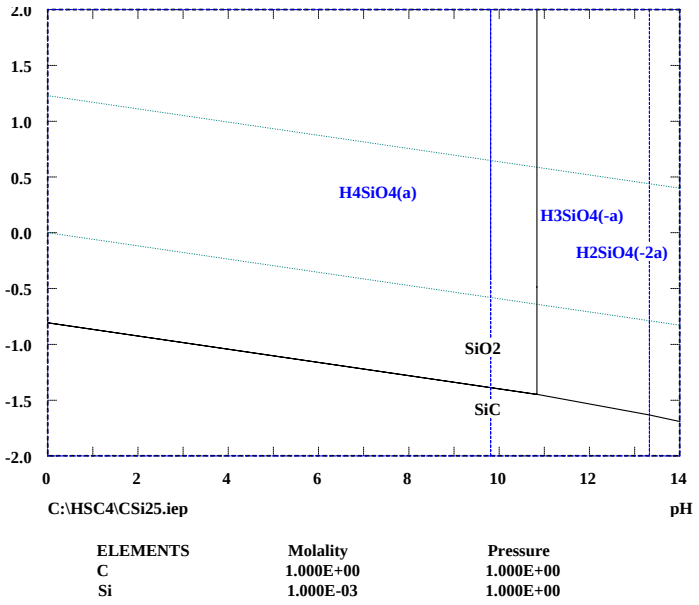
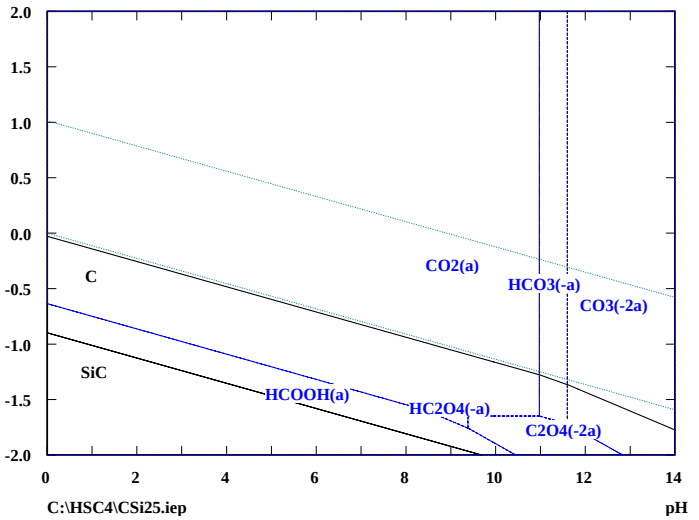


Fig. 12: same calculation as in figure 11 but carbon species are shown. The vertical black line at pH 8 indicates that at the right of the line equilibrium CO2 pressures are lower than 1 atm



ELEMENTS	Molality	Pressure
C	1.000E+00	1.000E+00
Si	1.000E-03	1.000E+00

Figure 13 HSC calculated Eh/pH diagram for the Si-C-H2O system at 300°C showing the distribution of Si containing species. (blue: aqueous species, black: solids or gases). CH4 formation is prevented. Lower dashed line is the stability boundary for water against hydrogen formation, the higher dashed line indicates the stability of water against oxygen formation. The vertical black line at pH 11 indicates the stability of SiO2 against dissolution.



ELEMENTS	Molality	Pressure
C	1.000E+00	8.463E+01
Si	1.000E-03	8.463E+01

Figure 14, same calculation as in Figure 13 but C containing species are shown. The vertical black line at pH 8 indicates that at right equilibrium CO2 pressures are lower than 1 atm

3.4 Geochemical modelling of the dissolution reaction of SiC in groundwater

The calculated reaction path for SiC in typical clay groundwater is given in Figure 15 not considering oxidation of carbon (reducing conditions) whereas Figure 16 shows the respective results allowing for oxidation of carbon.

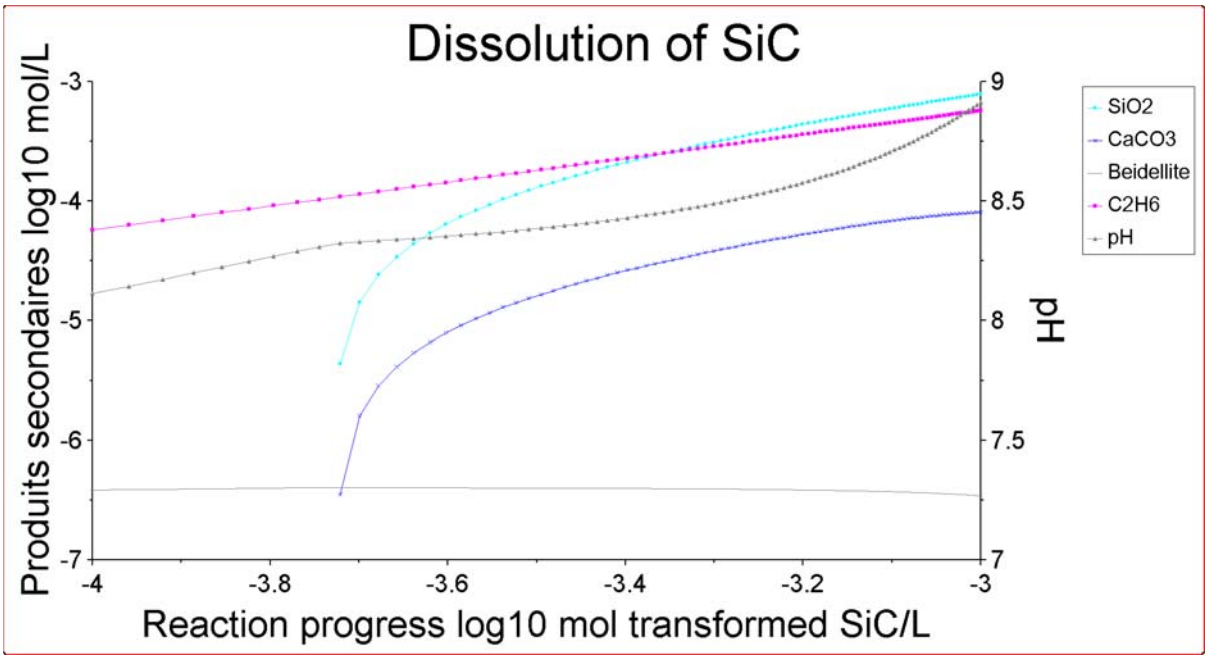


Fig. 15 Results of geochemical modeling of the dissolution reaction of SiC with clay groundwater under reducing conditions, not allowing for carbon oxydation.

The results show in absence of C oxidation an evolution of pH with reaction progress from an initial value of 8.2 to a final value of 8.9. The reduction of pH is probably beneficial for radionuclide retention since retention of most radionuclides is stronger at this higher pH. The precipitation of calcite is a direct consequence of the increase of pH. After having dissolved about $10^{-3.5}$ moles of SiC par liter of solution, SiO2 becomes supersaturated and will from at the surface of SiC in quantities proportional to the quantity of dissolved SiC. Ethane (C2H6) is calculated to form as organic reaction product. Beidelite (a clay mineral) is calculated to remain saturated all the time.

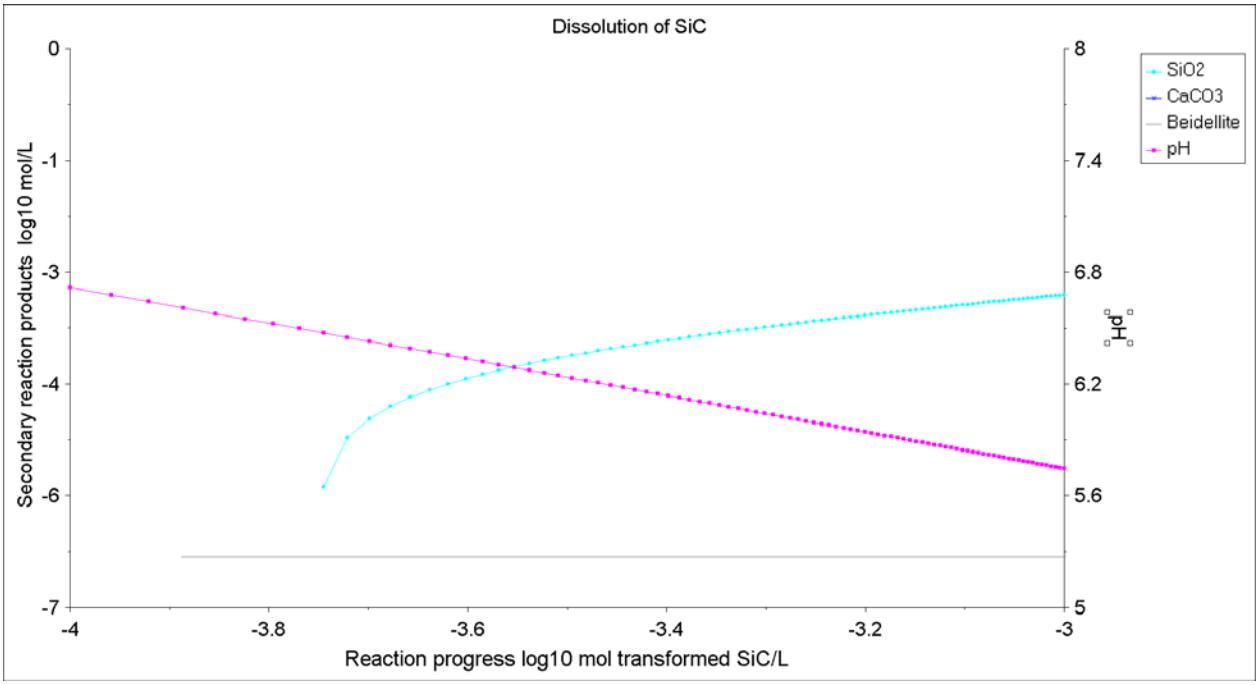


Fig. 16 Results of geochemical modeling of the dissolution reaction of SiC with clay groundwater under reducing conditions, allowing for carbon oxydation.

In case carbon oxidation is allowed (for example simulating an effect of radiolysis), SiO2 is also expected to be formed as principal reaction product. Carbonate species will form from SiC leading to an acidification of the solution. Calcite (CaCO3) cannot form under these conditions. The decreased pH may strongly increase radionuclide mobility (decrease retention), however, if reaction rates are very slow, buffer effects may stabilize the pH. On the other hand, in the pore water of a graphite matrix, the buffer capacity might be very low. What effect prevails can only be determined in an overall geochemical model combining kinetic and geochemical constraints.

4 Conclusions

The geochemical calculations reproduce and explain the observation form literature studies: SiC is unstable in water under all conditions and SiO2 is expected to be the principal solid reaction product. The known high stability of SiC in water is in consequence probably the consequence of the formation of a protective SiO2 layer. Literature data have shown that SiC forms a very tight layer on the surface of SiC. This indicates the formation of a dense protective layer, but more work on reaction cinetics on SiC dissolution is necessary to confirm this hypothesis.

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