



# Formation and stability of $^{14}\text{C}$ -containing organic compounds in alkaline iron-water systems: preliminary assessment based on a literature survey and thermodynamic modelling

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## ABSTRACT

Carbon-14 is an important radionuclide in the inventory of radioactive waste and is considered to be a key radionuclide in performance assessment. In Switzerland, the  $^{14}\text{C}$  inventory in a cement-based repository for low- and intermediate-level radioactive waste is mainly associated with activated steel (~85%). Anaerobic corrosion of the activated steel will determine the time-dependent release of  $^{14}\text{C}$ -bearing compounds from the cementitious near field into the host rock. The present study was carried out to provide an overview on the current state of the art knowledge regarding the carbon speciation during the anaerobic corrosion of activated and non-activated iron/steel and to critically assess the capability of thermodynamic modelling to predict  $^{14}\text{C}$  speciation in anoxic alkaline conditions. Previous experimental work showed the presence of oxidized and reduced hydrocarbons during corrosion in iron-water systems in anoxic (near neutral to alkaline) conditions which appears to be inconsistent with the negative redox potential of the system. The capability of thermodynamic modelling to predict the carbon speciation in these conditions was found to be limited due to uncertainties associated with the concept of metastability in the C–H–O system.

**KEYWORDS:** repository, corrosion, organics, thermodynamics, carbon-14.

## Introduction

CARBON-14 has been identified as an important radionuclide in the inventory of radioactive waste (e.g. Johnson and Schwyn, 2008; Yim and Caron, 2006) and as a key radionuclide in radiological assessments (Nagra, 2002; Nuclear Decommissioning Authority, 2012). The half-life of  $^{14}\text{C}$  is sufficiently long (5730 y) for its release to be of relevance after repository closure. Carbon-14 is of specific concern due to its potential presence as either dissolved or gaseous species in the disposal facility

and the host rock, the high mobility of dissolved compounds in the geosphere caused by weak sorption onto minerals under near neutral conditions, and eventually because it can be incorporated in the human food chain. The importance of  $^{14}\text{C}$  in the safety case further arises from specific assumptions that are being made regarding the rate of release from potential sources, the speciation upon release and the mobility of the different forms of carbon in the cementitious near field (Johnson and Schwyn, 2008).

In light water reactors (LWR)  $^{14}\text{C}$  is the product of mainly  $^{14}\text{N}$  activation ( $^{14}\text{N}(n,p)^{14}\text{C}$ ) (Yim and Caron, 2006). The main source of  $^{14}\text{C}$  in low- and intermediate-level radioactive waste in Switzerland are activated metallic nuclear fuel components and reactor core components as well as spent filters and

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ion exchange resins used in the LWRs for the removal of radioactive contaminants in a number of liquid processes and waste streams. Carbon-14 production from carbon impurities ( $^{13}\text{C}(\text{n},\gamma)^{14}\text{C}$ ) in metals is negligible as the  $^{13}\text{C}$  content and the capture cross-section of  $^{13}\text{C}$  for thermal neutrons are very low. Transmutation of  $^{17}\text{O}$  in  $\text{H}_2\text{O}$  ( $^{17}\text{O}(\text{n},\alpha)^{14}\text{C}$ ) as well as dissolved  $^{14}\text{N}$  and  $^{13}\text{C}$  (as bicarbonate and organic compounds) in reactor coolant is another possible source of  $^{14}\text{C}$ . Compilations of the activity inventories reveal, however, that in the already existing and future arising of radioactive waste in Switzerland, the  $^{14}\text{C}$  inventory is mainly associated with activated steel (~85%) while the  $^{14}\text{C}$  portions from nuclear fuel components (e.g. Zircaloy) and waste from the treatment of reactor coolants are much smaller.

Carbon-14 can be released in a variety of organic and inorganic chemical forms depending on the nature of the waste material and the chemical conditions of the near field. Carbon-14 will decay within a disposal facility if the carbon-14-bearing compounds are retained by interaction with the materials of the engineered barrier. Inorganic carbon, i.e.  $^{14}\text{CO}_2$  (and its bases), is expected to precipitate as calcium carbonate within a cement-based repository or undergo  $^{14}\text{CO}_3^{2-}$  isotopic exchange with solid calcium carbonate (e.g. Allard *et al.*, 1981; Bayliss *et al.*, 1988; Pointeau *et al.*, 2003) and therefore inorganic  $^{14}\text{C}$  has only a negligibly small impact on dose release. By contrast, gaseous species containing  $^{14}\text{C}$ , such as  $^{14}\text{CH}_4$  and  $^{14}\text{CO}$ , could form and migrate with bulk gas from the near field into the host rock.

Low molecular weight (LMW) oxygenated  $^{14}\text{C}$ -bearing organic compounds, e.g. acetate, formate, acetaldehyde, formaldehyde, methanol and ethanol are expected to form in the course of steel corrosion (see section 2). Studies on the uptake of these compounds by mortar indicate weak interaction (Matsumoto *et al.*, 1995) while stronger uptake was observed on cement paste (Yamaguchi *et al.*, 1999; Sasoh, 2008a). New sorption studies with the same organic compounds confirmed the earlier findings of Matsumoto *et al.* (1995) that LMW oxygenated hydrocarbons sorb only weakly to cement paste (Wieland, 2014). This further implies that dissolved  $^{14}\text{C}$  mainly contributes to dose in its organic form, i.e.  $^{14}\text{C}$ -bearing LMW organics.

Knowledge of the speciation of  $^{14}\text{C}$  in the cementitious near field is essential for more detailed assessments of the long-term impact of  $^{14}\text{C}$  on dose release. To this aim, an experimental programme on the formation of  $^{14}\text{C}$ -containing

species generated in the course of the anaerobic corrosion of activated steel has been recently launched in Switzerland. In the framework of this programme the present study was carried out aiming at (1) providing an overview on the current state of the art knowledge regarding the carbon speciation during the anaerobic corrosion of activated and non-activated iron/steel in conditions relevant to the cementitious near field of a repository for radioactive waste, and (2) critically assessing the capability of thermodynamic modelling to predict  $^{14}\text{C}$  speciation under these conditions.

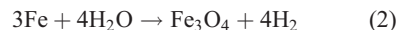
## Chemical form of carbon and carbon-14 released during iron/steel corrosion

### Chemical conditions

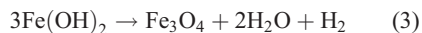
The redox conditions in a cement-based repository (pH of porewater typically >11) were described in detail elsewhere (Wersin *et al.*, 2003). Residual oxygen is depleted rapidly in the early phase of the repository and therefore, the conditions will remain reducing in the long term where the redox potential is largely influenced by steel corrosion. The Eh-pH diagram for the  $\text{Fe}^0\text{-H}_2\text{O}$  systems (Ning *et al.*, 2014) indicates a negative redox potential at the iron-water interface in anoxic conditions and the presence of ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) forming according to anaerobic corrosion (Evans and Wanklyn, 1948; Jelinek and Neufeld, 1982; Marsh and Taylor, 1988):



Magnetite may preferentially form either by direct reaction:



or through the Schikorr reaction, particularly at temperatures above 50°C to 60°C (Grauer *et al.*, 1991) as  $\text{Fe}_3\text{O}_4$  has similar thermodynamic stability to  $\text{Fe}(\text{OH})_2$ :



In the simplified view of the complex array of reactions that are likely to occur in practice (e.g. Smart, 2009) magnetite is considered to be the thermodynamically most stable corrosion product under the expected reducing conditions of a repository for radioactive waste, and therefore, the main corrosion product forming in contact

with water in anoxic alkaline conditions. Siderite ( $\text{FeCO}_3$ ) may form in near neutral and moderately alkaline conditions (pH 6–11) and the presence of carbonate (Agrawal *et al.*, 2002). Electrochemical measurements of corroding carbon steel in anoxic, carbonate containing artificial groundwater were consistent with the formation of  $\text{Fe}^{2+}$  (Smart *et al.*, 2002), indicating control of the redox potential at the steel surface by the  $\text{Fe}^0/\text{Fe}^{2+}$  couple. Furthermore, the formation of hydrocarbons from the reduction of aqueous  $\text{CO}_2$  is thermodynamically possible in the  $\text{Fe}^0\text{-H}_2\text{O-CO}_2$  system although the reaction is kinetically unfavourable and therefore extremely slow (Hardy and Gillham, 1996).

The rate of  $^{14}\text{C}$  release from activated steel components will be determined by the rate of steel corrosion in anoxic alkaline conditions and the chemical form of  $^{14}\text{C}$  in the activated steel. On the basis of the above considerations and on the assumption of complete thermodynamic equilibrium predominant formation of reduced hydrocarbons is expected in these conditions, e.g. the formation of  $\text{CH}_4$ , while oxygenated hydrocarbons, e.g. carboxylic acids, aldehydes and alcohols, are expected to be only minor species (see following section on thermodynamic modelling).

### Evidence from experimental studies

Information on the chemical form of carbon released during corrosion of irradiated metals, such as Zircaloy and irradiated steel, is available from research carried out in the framework of the Japanese disposal programme for radioactive waste (Yamaguchi *et al.*, 1999; Kaneko *et al.*, 2003; Sasoh, 2008*b,c*; Noshita, 2008; Kani *et al.*, 2008; Yamashita *et al.*, 2014; Takahashi *et al.*, 2014). Additional information is available from corrosion studies with non-irradiated iron powders carried out in connection with the development of clean-up techniques for chlorinated hydrocarbons using zero-valent iron (Hardy and Gillham, 1996; Campbell *et al.*, 1997; Deng *et al.*, 1997; Agrawal *et al.*, 2002).

Yamaguchi *et al.* (1999) investigated the chemical form of  $^{14}\text{C}$  species produced from leach tests on irradiated Zircaloy cladding hull specimens in a stainless steel container placed in a remote-handling shielded cell using a simulated groundwater equilibrated with cementitious materials. The gaseous and liquid phases were analysed for  $^{14}\text{C}$ -bearing compounds, i.e.  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{CH}_4$  in the gas phase, and the organic and inorganic  $^{14}\text{C}$

chemical forms in the liquid phase, by separating the chemical forms by acidic oxidative treatment. An absence of gaseous  $^{14}\text{C}$  species was observed, while in the liquid phase the total amount of  $^{14}\text{C}$  was bound in the organic fraction after 3 months. The portion of inorganic  $^{14}\text{C}$  increased to 80% after 5 months at the expense of organic  $^{14}\text{C}$ . Inorganic carbon in solution is expected to be either  $\text{H}^{14}\text{CO}_3^-$  or  $^{14}\text{CO}_3^{2-}$  depending on pH while no further details were reported on the chemical forms of the organic compounds. Yamashita *et al.* (2014) re-assessed the results from the study of Yamaguchi *et al.* (1999) by conducting leach tests on two different irradiated Zircaloy claddings. A substantial amount of  $^{14}\text{C}$  was detected in the form of gaseous species in the early phase of the experiment ( $\leq 9$  months) while predominant formation of organic compounds was reported in the long run ( $> 9\text{--}24$  months). The authors distinguished inorganic from organic carbon but provided no further information on the organic compounds that had formed.

Detailed speciation studies in systems containing corroding metals were undertaken by Kaneko *et al.* (2003), Sasoh (2008*b,c*), Noshita (2008) and recently by Takahashi *et al.* (2014). Kaneko *et al.* (2003) identified formic ( $\text{HCOOH}$ ) and acetic acids ( $\text{CH}_3\text{COOH}$ ), formaldehyde ( $\text{HCHO}$ ), methanol ( $\text{CH}_3\text{OH}$ ) and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) as the main chemical forms in leach solutions in contact with non-irradiated carbides ( $\text{ZrC}$ ,  $\text{Fe}_3\text{C}$ ), which were used as a surrogate for hull and end pieces. It was assumed that carbon exists in the form of carbide or atomic carbon in Zircaloy. Sasoh (2008*c*) continued the experimental approach developed by Kaneko *et al.* (2003) using non-irradiated zirconium and carbon steel powders as well as irradiated stainless steel, which were subjected to a leaching process in solution (with unreported composition) at pH 8 and 12.5. Total carbon and the fractions of organic and inorganic carbon were determined in the liquid phase. Furthermore, the gas phase was analysed. The author determined only a small portion of carbon in the gas phase ( $< 0.01\%$ ). The liquid phase contained both organic and inorganic carbon. While the inorganic carbon fraction corresponds to  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$ , respectively, formate and acetate were identified as the main organic compounds both in the groundwater type (pH 8) and alkaline (pH 10 and 12.5) leach solutions. For some materials, such as irradiated steel, formaldehyde, acetaldehyde, methanol, ethanol and propanol were also identified as minor species. Note that a significant portion of organic carbon (25%) could not be identified in the leach solution in contact

with activated steel. Sasoh (2008b) further studied the chemical stability of the above-mentioned organic compounds (except propanol) in near neutral and alkaline conditions (the leach solutions from the irradiated stainless steel) over the time period of 12 months. The author observed a gradual but very small decrease in the concentration of acetate while no change in the concentrations of the other oxygenated hydrocarbons, i.e. formate, formaldehyde, ethanol and methanol, was observed. Note that the possible formation of gaseous species was not checked by Sasoh (2008b). Takahashi *et al.* (2014) recently presented an overview of the organic compounds detected in the framework of the Japanese research programme and the corresponding analytical procedures that have been used to identify these compounds.

Exposing  $^{14}\text{C}$ -labelled organic compounds (i.e. formate, acetate, formaldehyde, methanol, ethanol) dissolved in alkaline solution and groundwater under anoxic conditions to gamma ray irradiation ( $^{60}\text{Co}$  source) caused the decomposition of these organic compounds, which was interpreted in terms of an oxidation reaction by OH radicals generated during irradiation (Noshita, 2008). Kani *et al.* (2008) carried out irradiation tests with organic compounds under similar experimental conditions (i.e. anoxic, alkaline) and observed the conversion of carboxylic acids, aldehydes and alcohols to carbon dioxide ( $\text{CO}_2$ ) by the effect of OH radicals.

In summary, the Japanese studies suggest predominant formation of oxidized hydrocarbons during iron/steel corrosion, in particular the formation of carboxylic acids, aldehydes and alcohols, along with smaller portions of  $\text{CO}_2$ , while the formation of gaseous, reduced hydrocarbons was rarely observed.

These findings contrast with those published from laboratory studies that were carried out in connection with the development of *in situ* remediation techniques for groundwater contaminated with chlorinated aliphatic compounds (Hardy and Gillham, 1996; Campbell *et al.*, 1997; Deng *et al.*, 1997; Agrawal *et al.*, 2002). Hardy and Gillham (1996) identified ten volatile hydrocarbons up to C5, including methane, ethane, ethene, propane, propene, and butene, as products of  $\text{CO}_2$  reduction by iron powders in simulated groundwater-type solutions at pH 6. Note that the possible presence of dissolved carbon species was not checked. Campbell *et al.* (1997) showed that hydrocarbons form in an iron-water system under conditions similar to those used by Hardy and

Gillham (1996) both in Ar-purged ( $\text{CO}_2$ -free) and  $\text{CO}_2$ -amended water and concluded that carbon impurities bound in iron were the source of carbon rather than  $\text{CO}_2$  dissolved in water. Finally, Deng *et al.* (1997) investigated hydrocarbon formation in an iron-water system at low and high aqueous carbonate concentrations using various commercial iron products with a wide range of carbon contents. The authors confirmed the formation of volatile hydrocarbons up to C5 and also concluded that iron is the carbon source as the addition of carbonate to the systems did not influence hydrocarbon formation. Note that also Deng and co-workers did not analyse the liquid phase for dissolved carbon species.

Thus, the results from the above studies are consistent with regards to the type of hydrocarbons formed and the concentration range, but they disagree regarding the carbon source. Hardy and Gillham (1996) and Deng *et al.* (1997) proposed that a Fischer-Tropsch process involving the reduction of carbon along with the building of hydrocarbon chains was responsible for the formation of hydrocarbons. In addition, the main source of hydrogen was water in both cases, thus suggesting reduction of water in the course of the process. In contrast to Hardy and Gillham (1996), who considered dissolved carbonate as carbon source, Deng *et al.* (1997) proposed that iron carbide present in the iron fillings react through processes similar to those that occur in Fischer-Tropsch synthesis. This causes the formation of hydrocarbons in metallic iron-water systems.

In summary, the above studies indicate predominant formation of volatile, reduced hydrocarbons during iron/steel corrosion, in particular alkanes and alkenes. Note that the liquid phase was not analysed for dissolved organic carbon species in any of these studies.

The range of carbon species that have been identified in the various studies discussed in brief in this section are listed in Table 1, illustrating the very different chemical nature of the species identified. Both oxidized and reduced hydrocarbons have been observed in iron-water systems in anoxic (near neutral to alkaline) conditions. This appears to be inconsistent with the negative redox potential of anoxic iron-water systems. To complete the picture, the following thermodynamic calculations were carried out with the aim of assessing carbon speciation under alkaline, reducing conditions and testing the predictive capability of thermodynamic modelling of the carbon (C–H–O) system.

TABLE 1. Carbon species expected to be formed as a result of iron/steel corrosion.

Alkane/alkene <sup>1</sup>	Alcohols/aldehydes <sup>2</sup>	Carboxylic acids <sup>3</sup>	Carbonate <sup>4</sup>
Methane (CH <sub>4</sub> )	Methanol (CH <sub>3</sub> OH)	Formate (HCOO <sup>-</sup> )	CO <sub>2</sub>
Ethane (C <sub>2</sub> H <sub>6</sub> )	Ethanol (C <sub>2</sub> H <sub>5</sub> OH)	Acetate (CH <sub>3</sub> COO <sup>-</sup> )	CO <sub>3</sub> <sup>2-</sup>
Ethene (C <sub>2</sub> H <sub>4</sub> )	Propanol (C <sub>3</sub> H <sub>7</sub> OH)	Propanoate (C <sub>2</sub> H <sub>5</sub> COO <sup>-</sup> )	(CO)
Propane (C <sub>3</sub> H <sub>8</sub> )	Formaldehyde (CH <sub>2</sub> O)	Butanoate (C <sub>3</sub> H <sub>7</sub> COO <sup>-</sup> )	
Propene (C <sub>3</sub> H <sub>6</sub> )	Acetaldehyde (C <sub>2</sub> H <sub>4</sub> O)	Malonate (CH <sub>2</sub> (COO <sup>-</sup> ) <sub>2</sub> )	
Butane (C <sub>4</sub> H <sub>10</sub> )	Propionaldehyde (C <sub>3</sub> H <sub>6</sub> O)	Oxalate (C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> )	
Butene (C <sub>4</sub> H <sub>8</sub> ) <sup>5</sup>			
Pentene (C <sub>5</sub> H <sub>10</sub> ) <sup>5</sup>			

<sup>1</sup> Hardy and Gillham (1996), Deng *et al.* (1997), LES (2014).

<sup>2</sup> Kaneko *et al.* (2003), Sasoh (2008b), Sasoh (2008c), LES (2014).

<sup>3</sup> Kaneko *et al.* (2003), Sasoh (2008b), Sasoh (2008c), LES (2014).

<sup>4</sup> Kaneko *et al.* (2003), Noshita (2008).

<sup>5</sup> Including isomers (e.g. cis-2-pentene, trans-2-pentene) (Hardy and Gillham, 1996; Deng *et al.*, 1997).

### Thermodynamic modelling

Complete stable redox equilibrium is seldom achieved in the C–H–O system, at least at moderate temperatures. This circumstance makes possible the spectacularly rich organic chemistry of carbon, and eventually the very existence of life on Earth. The concept of metastable states in water-rock-organic systems greatly enhances the possibilities for analysis of the distribution of organic compounds in groundwaters and in hydrothermal solutions as functions of temperature, pressure, and redox conditions using the well-established apparatus of chemical thermodynamics. Because of the great interest in the effects of organic compounds on a variety of geochemical processes, Helgeson, Shock and co-workers have put a tremendous effort in building a consistent thermodynamic database for organic species (Shock and Helgeson, 1990; Schulte and Shock, 1993; Shock, 1995; Amend and Helgeson, 1997; Helgeson *et al.*, 1998; Plyasunov and Shock, 2000a,b; Plyasunova *et al.*, 2004).

For the present study, thermodynamic data for the aqueous organic species containing from one to five carbon atoms have generally been taken from this database (Table 2). The only exceptions are data for oxalate species which were taken from a more recent NEA review (Hummel *et al.*, 2005). The data for water, dissolved CO<sub>2</sub> and carbonate species are CODATA Key Values (Cox *et al.*, 1989), commonly used in both the Helgeson and Shock databases and the NEA reviews. Organic compounds in the solid or gaseous state were not

considered in the present study. The equilibrium concentrations of 39 dissolved species (Table 2) in the system C–H–O were computed as a function of pe and pH at 25°C for a concentration of total dissolved carbon, C<sub>t</sub> = 10<sup>-3</sup> mol · kg<sup>-1</sup><sub>H<sub>2</sub>O</sub> using the code *PhreePlot* (Kinniburgh and Cooper, 2004) (<http://www.phreeplot.org>).

The predominant dissolved species in the case of complete thermodynamic equilibrium are CO<sub>2</sub>(aq), HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and methane, CH<sub>4</sub>(aq) (Fig. 1). All other organic species occur at trace concentrations only or are thermodynamically unstable. The maximum equilibrium concentrations of these other organic species do not exceed 10<sup>-8</sup> M, i.e. five orders of magnitude below the total dissolved organic carbon, and they are reached in a very small pe range at the methane/carbonate species boundary. Outside this small pe range the organic species quickly become thermodynamically unstable (Fig. 2).

At pH 12 the speciation is rather simple; the trace organic species found are formate HCOO<sup>-</sup> > acetate CH<sub>3</sub>COO<sup>-</sup> ≈ ethane C<sub>2</sub>H<sub>6</sub>(aq), which are below a concentration of 10<sup>-9</sup> M, i.e. much less than the ppm level of total dissolved organic carbon (Fig. 2).

These results are not new. In one of the first theoretical papers on this subject Thorstenson (1970) established the predominance of methane and carbonate species in the C–H–O system with boundaries that are very similar to the ones shown in Fig. 2. Considering the less reliable thermodynamic database available in 1970, the results of Thorstenson (1970) and our study are consistent.

As already mentioned, complete stable redox equilibrium is seldom achieved in the C–H–O

TABLE 2. Thermodynamic database for modelling the C–H–O system at 25°C and 1 bar. Values in bold face are taken from the cited references; all other values are recalculated from these values.  $\Delta_f G^\circ$  is the standard molar Gibbs energy of formation from the elements in their reference state,  $\Delta_r G^\circ$  is the molar Gibbs energy of the reaction and  $\log_{10} K^\circ$  is the equilibrium constant of the reaction, logarithmic.

Species Name	Species Formula	$\Delta_f G^\circ$ cal·mol <sup>-1</sup>	$\Delta_r G^\circ$ kJ·mol <sup>-1</sup>	Ref.	Reaction	Stoichiometry		$\Delta_r G^\circ$ kJ·mol <sup>-1</sup>	$\log_{10} K^\circ$
						CO <sub>2</sub> (aq)	H <sub>2</sub> O(l)		
			<b>4.184</b>	3	cal → J				
Methane	CH <sub>4</sub> (aq)	<b>-8234</b>	-34.451	1	CO <sub>2</sub> (aq) + 8H <sup>+</sup> + 8e <sup>-</sup> = CH <sub>4</sub> (aq) + 2H <sub>2</sub> O(l)	-1	2	-122.761	21.507
Ethane	C <sub>2</sub> H <sub>6</sub> (aq)	<b>-3886</b>	-16.259	1	2CO <sub>2</sub> (aq) + 14H <sup>+</sup> + 14e <sup>-</sup> = C <sub>2</sub> H <sub>6</sub> (aq) + 4H <sub>2</sub> O(l)	-2	4	-192.879	33.791
Propane	C <sub>3</sub> H <sub>8</sub> (aq)	<b>-1963</b>	-8.213	1	3CO <sub>2</sub> (aq) + 20H <sup>+</sup> + 20e <sup>-</sup> = C <sub>3</sub> H <sub>8</sub> (aq) + 6H <sub>2</sub> O(l)	-3	6	-273.143	47.852
n-Butane	C <sub>4</sub> H <sub>10</sub> (aq)	<b>36</b>	0.151	1	4CO <sub>2</sub> (aq) + 26H <sup>+</sup> + 26e <sup>-</sup> = C <sub>4</sub> H <sub>10</sub> (aq) + 8H <sub>2</sub> O(l)	-4	8	-353.089	61.858
n-Pentane	C <sub>5</sub> H <sub>12</sub> (aq)	<b>2130</b>	8.912	1	5CO <sub>2</sub> (aq) + 32H <sup>+</sup> + 32e <sup>-</sup> = C <sub>5</sub> H <sub>12</sub> (aq) + 10H <sub>2</sub> O(l)	-5	10	-432.638	75.794
Ethylene	C <sub>2</sub> H <sub>4</sub> (aq)	<b>19450</b>	81.379	1	2CO <sub>2</sub> (aq) + 12H <sup>+</sup> + 12e <sup>-</sup> = C <sub>2</sub> H <sub>4</sub> (aq) + 4H <sub>2</sub> O(l)	-2	4	-95.241	16.685
l-Propene	C <sub>3</sub> H <sub>6</sub> (aq)	<b>17910</b>	74.935	1	3CO <sub>2</sub> (aq) + 18H <sup>+</sup> + 18e <sup>-</sup> = C <sub>3</sub> H <sub>6</sub> (aq) + 6H <sub>2</sub> O(l)	-3	6	-189.995	33.285
l-Butene	C <sub>4</sub> H <sub>8</sub> (aq)	<b>20310</b>	84.977	1	4CO <sub>2</sub> (aq) + 24H <sup>+</sup> + 24e <sup>-</sup> = C <sub>4</sub> H <sub>8</sub> (aq) + 8H <sub>2</sub> O(l)	-4	8	-268.263	46.997
l-Pentene	C <sub>5</sub> H <sub>10</sub> (aq)	<b>22470</b>	94.014	1	5CO <sub>2</sub> (aq) + 30H <sup>+</sup> + 30e <sup>-</sup> = C <sub>5</sub> H <sub>10</sub> (aq) + 10H <sub>2</sub> O(l)	-5	10	-347.536	60.885
Ethyne	C <sub>2</sub> H <sub>2</sub> (aq)	<b>51890</b>	217.108	1	2CO <sub>2</sub> (aq) + 10H <sup>+</sup> + 10e <sup>-</sup> = C <sub>2</sub> H <sub>2</sub> (aq) + 4H <sub>2</sub> O(l)	-2	4	40.488	-7.093
l-Propyne	C <sub>3</sub> H <sub>4</sub> (aq)	<b>47880</b>	200.330	1	3CO <sub>2</sub> (aq) + 16H <sup>+</sup> + 16e <sup>-</sup> = C <sub>3</sub> H <sub>4</sub> (aq) + 6H <sub>2</sub> O(l)	-3	6	-64.600	11.317
l-Butyne	C <sub>4</sub> H <sub>6</sub> (aq)	<b>50030</b>	209.326	1	4CO <sub>2</sub> (aq) + 22H <sup>+</sup> + 22e <sup>-</sup> = C <sub>4</sub> H <sub>6</sub> (aq) + 8H <sub>2</sub> O(l)	-4	8	-143.914	25.213
l-Pentyne	C <sub>5</sub> H <sub>8</sub> (aq)	<b>52160</b>	218.237	1	5CO <sub>2</sub> (aq) + 28H <sup>+</sup> + 28e <sup>-</sup> = C <sub>5</sub> H <sub>8</sub> (aq) + 10H <sub>2</sub> O(l)	-5	10	-223.313	39.122
Methanol	CH <sub>3</sub> OH(aq)	<b>-42050</b>	-175.937	1	CO <sub>2</sub> (aq) + 6H <sup>+</sup> + 6e <sup>-</sup> = CH <sub>3</sub> OH(aq) + H <sub>2</sub> O(l)	-1	1	-27.107	4.749
Ethanol	C <sub>2</sub> H <sub>5</sub> OH(aq)	<b>-43330</b>	-181.293	1	2CO <sub>2</sub> (aq) + 12H <sup>+</sup> + 12e <sup>-</sup> = C <sub>2</sub> H <sub>5</sub> OH(aq) + 3H <sub>2</sub> O(l)	-2	3	-120.773	21.158
l-Propanol	C <sub>3</sub> H <sub>7</sub> OH(aq)	<b>-41910</b>	-175.351	1	3CO <sub>2</sub> (aq) + 18H <sup>+</sup> + 18e <sup>-</sup> = C <sub>3</sub> H <sub>7</sub> OH(aq) + 5H <sub>2</sub> O(l)	-3	5	-203.141	35.589
l-Butanol	C <sub>4</sub> H <sub>9</sub> OH(aq)	<b>-38840</b>	-162.507	1	4CO <sub>2</sub> (aq) + 24H <sup>+</sup> + 24e <sup>-</sup> = C <sub>4</sub> H <sub>9</sub> OH(aq) + 7H <sub>2</sub> O(l)	-4	7	-278.607	48.809
l-Pentanol	C <sub>5</sub> H <sub>11</sub> OH(aq)	<b>-38470</b>	-160.958	1	5CO <sub>2</sub> (aq) + 30H <sup>+</sup> + 30e <sup>-</sup> = C <sub>5</sub> H <sub>11</sub> OH(aq) + 9H <sub>2</sub> O(l)	-5	9	-365.368	64.009
Formaldehyde	CH <sub>2</sub> O(aq)	<b>-26130</b>	-109.328	2	CO <sub>2</sub> (aq) + 4H <sup>+</sup> + 4e <sup>-</sup> = CH <sub>2</sub> O(aq) + H <sub>2</sub> O(l)	-1	1	39.502	-6.920
Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O(aq)	<b>-33470</b>	-140.038	2	2CO <sub>2</sub> (aq) + 10H <sup>+</sup> + 10e <sup>-</sup> = C <sub>2</sub> H <sub>4</sub> O(aq) + 3H <sub>2</sub> O(l)	-2	3	-79.518	13.931
Propanal	C <sub>3</sub> H <sub>6</sub> O(aq)	<b>-32730</b>	-136.942	2	3CO <sub>2</sub> (aq) + 16H <sup>+</sup> + 16e <sup>-</sup> = C <sub>3</sub> H <sub>6</sub> O(aq) + 5H <sub>2</sub> O(l)	-3	5	-164.732	28.860
Butanal	C <sub>4</sub> H <sub>8</sub> O(aq)	<b>-28720</b>	-120.164	2	4CO <sub>2</sub> (aq) + 22H <sup>+</sup> + 22e <sup>-</sup> = C <sub>4</sub> H <sub>8</sub> O(aq) + 7H <sub>2</sub> O(l)	-4	7	-236.264	41.392
Pentanal	C <sub>5</sub> H <sub>10</sub> O(aq)	<b>-27020</b>	-113.052	2	5CO <sub>2</sub> (aq) + 28H <sup>+</sup> + 28e <sup>-</sup> = C <sub>5</sub> H <sub>10</sub> O(aq) + 9H <sub>2</sub> O(l)	-5	9	-317.462	55.617
Formic acid	HCOOH(aq)	<b>-88982</b>	-372.301	1	CO <sub>2</sub> (aq) + 2H <sup>+</sup> + 2e <sup>-</sup> = HCOOH(aq)	-1	0	13.669	-2.395
Acetic acid	CH <sub>3</sub> COOH(aq)	<b>-94760</b>	-396.476	1	2CO <sub>2</sub> (aq) + 8H <sup>+</sup> + 8e <sup>-</sup> = CH <sub>3</sub> COOH(aq) + 2H <sub>2</sub> O(l)	-2	2	-98.816	17.312
Propanoic acid	C <sub>2</sub> H <sub>5</sub> COOH(aq)	<b>-93430</b>	-390.911	1	3CO <sub>2</sub> (aq) + 14H <sup>+</sup> + 14e <sup>-</sup> = C <sub>2</sub> H <sub>5</sub> COOH(aq) + 4H <sub>2</sub> O(l)	-3	4	-181.561	31.808

(continued)

TABLE 2. (contd.)

Species Name	Species Formula	$\Delta_f G^\circ$ cal·mol <sup>-1</sup>	$\Delta_f G^\circ$ kJ·mol <sup>-1</sup>	Ref.	Reaction	Stoichiometry		$\Delta_f G^\circ$ kJ·mol <sup>-1</sup>	log <sub>10</sub> K <sup>o</sup>
						CO <sub>2</sub> (aq)	H <sub>2</sub> O(l)		
Butanoic acid	C <sub>3</sub> H <sub>7</sub> COOH(aq)	<b>-91190</b>	-381.539	1	4CO <sub>2</sub> (aq) + 20H <sup>+</sup> + 20e <sup>-</sup> = C <sub>3</sub> H <sub>7</sub> COOH(aq) + 6H <sub>2</sub> O(l)	-4	6	-260.499	45.637
Pentanoic acid	C <sub>4</sub> H <sub>9</sub> COOH(aq)	<b>-89210</b>	-373.255	1	5CO <sub>2</sub> (aq) + 26H <sup>+</sup> + 26e <sup>-</sup> = C <sub>4</sub> H <sub>9</sub> COOH(aq) + 8H <sub>2</sub> O(l)	-5	8	-340.525	59.657
Formate	HCOO <sup>-</sup>	<b>-83862</b>	-350.879	1	CO <sub>2</sub> (aq) + H <sup>+</sup> + 2e <sup>-</sup> = HCOO <sup>-</sup>	-1	0	35.091	-6.148
Acetate	CH <sub>3</sub> COO <sup>-</sup>	<b>-88270</b>	-369.322	1	2CO <sub>2</sub> (aq) + 7H <sup>+</sup> + 8e <sup>-</sup> = CH <sub>3</sub> COO <sup>-</sup> + 2H <sub>2</sub> O(l)	-2	2	-71.662	12.555
Propanate	C <sub>2</sub> H <sub>5</sub> COO <sup>-</sup>	<b>-86770</b>	-363.046	1	3CO <sub>2</sub> (aq) + 13H <sup>+</sup> + 14e <sup>-</sup> = C <sub>2</sub> H <sub>5</sub> COO <sup>-</sup> + 4H <sub>2</sub> O(l)	-3	4	-153.696	26.926
Butanoate	C <sub>3</sub> H <sub>7</sub> COO <sup>-</sup>	<b>-84610</b>	-354.008	1	4CO <sub>2</sub> (aq) + 19H <sup>+</sup> + 20e <sup>-</sup> = C <sub>3</sub> H <sub>7</sub> COO <sup>-</sup> + 6H <sub>2</sub> O(l)	-4	6	-232.968	40.814
Pentanoate	C <sub>5</sub> H <sub>9</sub> COO <sup>-</sup>	<b>-82600</b>	-345.598	1	5CO <sub>2</sub> (aq) + 25H <sup>+</sup> + 26e <sup>-</sup> = C <sub>5</sub> H <sub>9</sub> COO <sup>-</sup> + 8H <sub>2</sub> O(l)	-5	8	-312.868	54.812
Oxalic acid	C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> (aq)	-170264	<b>-712.384</b>	3	2CO <sub>2</sub> (aq) + 2H <sup>+</sup> + 2e <sup>-</sup> = C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> (aq)	-2	0	59.556	-10.434
Hoxalate	C <sub>2</sub> HO <sub>4</sub> <sup>-</sup>	-168354	<b>-704.393</b>	3	2CO <sub>2</sub> (aq) + H <sup>+</sup> + 2e <sup>-</sup> = C <sub>2</sub> HO <sub>4</sub> <sup>-</sup>	-2	0	67.547	-11.834
Oxalate	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	-162556	<b>-680.134</b>	3	2CO <sub>2</sub> (aq) + 2e <sup>-</sup> = C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	-2	0	91.806	-16.084
Bicarbonate	HCO <sub>3</sub> <sup>-</sup>	-140259	<b>-586.845</b>	4	CO <sub>2</sub> (aq) + H <sub>2</sub> O(l) = HCO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	-1	-1	36.265	-6.353
Carbonate	CO <sub>3</sub> <sup>2-</sup>	-126171	<b>-527.900</b>	4	CO <sub>2</sub> (aq) + H <sub>2</sub> O(l) = CO <sub>3</sub> <sup>2-</sup> + 2H <sup>+</sup>	-1	-1	95.210	-16.680
Master species	CO <sub>2</sub> (aq)	-92249	<b>-385.970</b>	4					
	H <sub>2</sub> O(l)	-56678	<b>-237.140</b>	4					
	H <sup>+</sup>		<b>0.000</b>	4					
	e <sup>-</sup>		<b>0.000</b>	4					
	R	<b>8.314510</b>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	3	R · T · ln(10) / 1000 = 5.708042 kJ·mol <sup>-1</sup>				
T	298.15	K							
ln(10)	2.302585			log <sub>10</sub> K = -Δ <sub>r</sub> G <sup>o</sup> / (R · T · ln(10) / 1000) = -ΔG <sub>r</sub> <sup>o</sup> / 5.708042					

References: 1, Shock and Helgeson (1990); 2, Schulte and Shock (1993); 3, Hummel *et al.* (2005); 4, Cox *et al.* (1989).

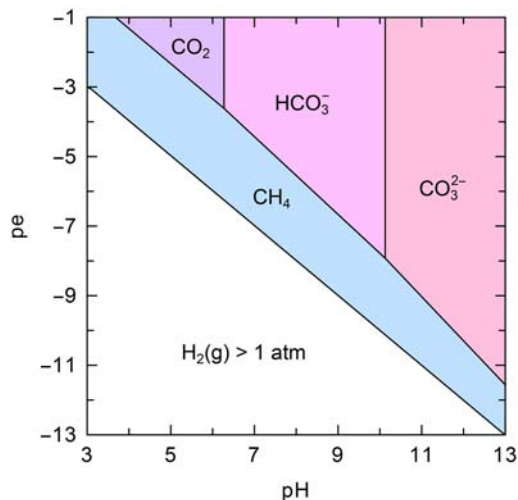


FIG. 1. Predominance diagram of aqueous species for complete thermodynamic equilibrium in the C-H-O system at 25°C. Total dissolved carbon,  $C_t = 10^{-3} \text{ mol} \cdot \text{kg}_{\text{H}_2\text{O}}^{-1}$ .

system. One possibility to calculate partial thermodynamic equilibrium is based on the assumption that dissolved alkanes, i.e. methane, ethane, propane, butane and pentane, are not formed. The results of these calculations are shown in Fig. 3. The predominant dissolved species in this case of partial thermodynamic equilibrium are the

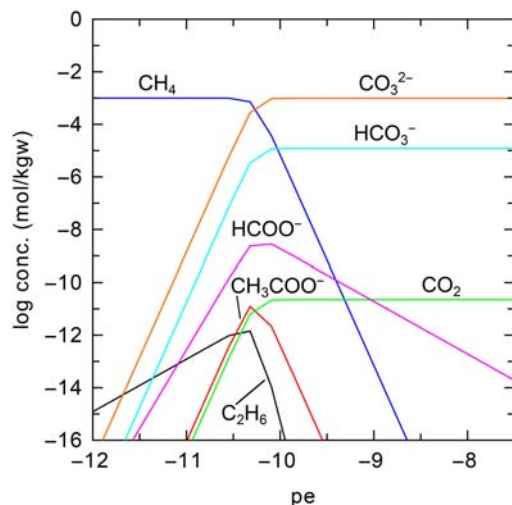
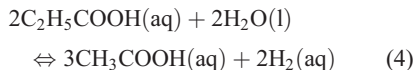


FIG. 2. Aqueous species distribution for complete thermodynamic equilibrium in the C-H-O system at pH 12. Total dissolved carbon,  $C_t = 10^{-3} \text{ M}$ .

carboxylic acids and, at low pH and very reducing conditions, a higher alcohol (Fig. 3). The stability field of these organic species with respect to carbonate is much smaller than the stability field of methane in the case of complete thermodynamic equilibrium (Fig. 1). Especially at high pH, metastable carboxylic acids are in partial thermodynamic equilibrium with carbonate only under the most reducing conditions at the verge of the stability of water (Fig. 3).

At pH 12 the stability range of organic species is restricted to a very narrow range below  $pe = -11$  and the stability of water at  $pe = -12$ . The predominating (metastable) species are acetate  $\text{CH}_3\text{COO}^-$  and propanate  $\text{C}_2\text{H}_5\text{COO}^-$ , with butanoate  $\text{C}_3\text{H}_7\text{COO}^-$  and pentanoate  $\text{C}_4\text{H}_9\text{COO}^-$  in the permille to percent range. Formate,  $\text{HCOO}^-$ , remains a minor species with a maximum concentration of 100 ppm. Above the ppm level, the only other organic species in metastable equilibrium are the alcohols ethanol, 1-propanol, 1-butanol and 1-pentanol.

This type of metastable equilibrium has been used by Shock (1988) to explain the observed high concentrations of acetic acid in sedimentary basins and to account for the systematic variation of acetic and propanoic acid in basinal brines. He suggested that reaction pathways exist that facilitate equilibration of acetic and propanoic acid according to the reaction:



The relative abundance of acetic and propanoic acid can be expressed in terms of the activity of  $\text{H}_2(\text{aq})$  and the equilibrium constant ( $K_{\text{eq}}$ ) for the above reaction as follows:

$$\begin{aligned} \log\{\text{C}_2\text{H}_5\text{COOH}(\text{aq})\} \\ = 3/2 \log\{\text{CH}_3\text{COOH}(\text{aq})\} \\ + \log\{\text{H}_2(\text{aq})\} - 1/2 \log K_{\text{eq}} \quad (5) \end{aligned}$$

Accordingly, a log-log plot of acetic and propanoic acid abundances will define a trend with a characteristic 3/2 slope if (metastable) thermodynamic equilibrium is attained for this reaction at a given temperature, pressure and  $\text{H}_2(\text{aq})$  activity.

A few field data from a single source presented by Shock (1988) suggest a slope of 3/2 and the conclusion that these acetic and propanoic acids are in metastable equilibrium. However, linear regression analyses of a much larger sample of field data for acetic and propanoic acid abundances reported



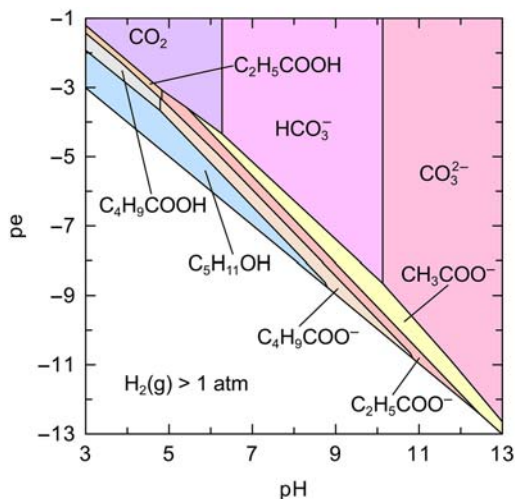


FIG. 3. Predominance diagram of aqueous species for partial thermodynamic equilibrium in the C-H-O system. It is assumed that no alkanes are formed.

by Seewald (2001) indicate slopes near unity, suggesting that the field data may not be consistent with a state of metastable thermodynamic equilibrium.

McCollom and Seewald (2007) report that laboratory experiments have demonstrated the reduction of  $\text{CO}_2$  to methanol via a series of sequential aqueous reactions that produce formic acid and CO as reaction intermediaries (Fig. 4). Each of the reactions that lead to methanol formation is reversible, allowing  $\text{CO}_2$ , CO, formic

acid, methanol and  $\text{H}_2$  to attain states of redox-dependent metastable thermodynamic equilibrium on a laboratory timescale. Relatively rapid reaction kinetics for these single carbon compounds suggest that their abundance may vary systematically as a function of  $\text{CO}_2$  concentration, pH, redox and temperature in hydrothermal systems. Thus, the low measured concentrations of formic acid and methanol in  $\text{CO}_2$ -rich environments may reflect thermodynamic control on their abundance under the prevailing chemical conditions and not the absence of a reaction mechanism necessary for their formation. Note, however, that McCollom and Seewald (2007) also report that complete reduction of  $\text{CO}_2$  to  $\text{CH}_4$  has been observed in laboratory experiments without added catalysts at 200–300°C, but at a substantially slower rate than observed for the formation of other  $\text{C}_1$  compounds, precluding attainment of thermodynamic equilibrium on laboratory time scales. Whether aqueous  $\text{CH}_4$  formation occurs via methanol reduction (Fig. 4) or some other reaction path is presently unknown.

Theoretically, there are an infinite number of possible combinations for assuming kinetic barriers for specific reactions on the one hand while assuming partial equilibria between specific reactive organic carbon species on the other hand. Until now, assumptions about partial equilibrium have been made case by case in the discussions of field observations and experimental studies.

Some field observations and some results from experimental studies have been successfully interpreted in terms of metastable thermodynamic equilibria, for example the high concentrations of

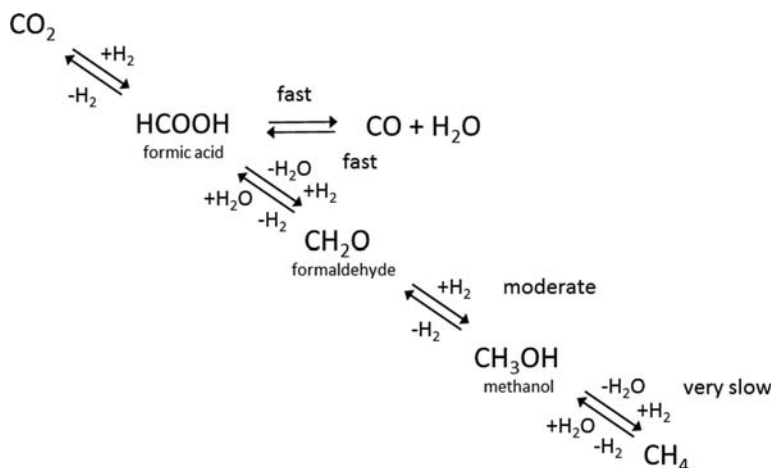


FIG. 4. Reaction scheme for the sequential reduction of  $\text{CO}_2$  to methane (modified from McCollom and Seewald, 2007).

acetic acid observed in some sedimentary basins. Other field observations and experimental results, however, could not be explained in terms of metastable equilibria, for example the relative abundances of acetic and propanoic acids observed in sedimentary basins. If the explanation via metastable equilibria fails then reaction mechanisms and kinetic arguments are used rather than thermodynamic considerations.

Hence, although the concept of metastable states in water-rock-organic systems is very useful to rationalize field observations and experimental findings, it has no predictive capabilities yet.

## Discussion

At present, it is not clear what kind of organic compounds predominantly form during the anaerobic corrosion of iron/steel under hyper-alkaline conditions, i.e. the conditions relevant to the near field of a cement-based repository. In principle, predominant formation of reduced hydrocarbons is expected, such as the formation of alkanes and alkenes, in view of the strongly reducing conditions prevailing at the iron-water interface in alkaline solutions. Nevertheless, experimental evidence has been provided that oxidized species are also present in systems containing corroding iron/steel in contact with alkaline solutions. The presence of oxidized species is conceivable in systems containing irradiated materials due to radiolysis while residual oxygen at the iron-water interface could act as an oxidizing agent in non-irradiated systems. Nevertheless, the reason for the existence of oxidized species and the chemical reactions leading to these compounds are presently not understood. In any case, the number of organic compounds formed in the course of the corrosion process seems to be limited (Table 1), and in particular, all compounds that might form are small molecules up to C5.

Thermodynamic modelling of the C–H–O system, carried out on the assumption of complete thermodynamic equilibrium, reveal that methane and carbonate are the most stable carbon species in reducing, alkaline conditions (Fig. 1) while alkanes, such as ethane, and small carboxylic acids are only minor species (Fig. 2). This finding is consistent with earlier results reported by Thorstenson (1970). However, the picture changes completely on the assumption of partial thermodynamic equilibrium, i.e. by assuming kinetic hindrance of the formation of methane, alkanes

and alkenes. This assumption is justified as complete stable redox equilibrium is seldom achieved in the C–H–O system as evidenced from the type and concentration of organic compounds found in sedimentary basins (Shock, 1988). In these conditions the predominant species are the carboxylic acids and, at low pH and very reducing conditions, a higher alcohol (Fig. 3). However, the assumptions made for modelling partial thermodynamic equilibria are somewhat arbitrary; they are made case by case to explain field observations and interpret experimental studies.

## Conclusions

The current situation concerning carbon speciation in the course of the anaerobic corrosion of iron/steel (activated/irradiated and non-activated/irradiated) is unclear. Neither experimental evidence nor thermodynamic modelling allows well-supported conclusions to be drawn regarding the kind of organic compounds formed. The predictive capability of thermodynamic modelling is limited due to uncertainties associated with the concept of metastability in the C–H–O system. The currently unclear situation requires further experimental investigations into the formation of organic compounds during the anaerobic corrosion of activated and non-activated iron/steel and on the chemical stability of organic compounds in conditions relevant to a cement-based repository.

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