CHEMICAL STABILITY OF LOW MOLECULAR WEIGHT ORGANIC COMPOUNDS IN THE CEMENTITIOUS NEAR FIELD OF A REPOSITORY FOR RADIOACTIVE WASTE

E. Wieland, J. Tits, B. Z. Cvetković, D. Kunz, T. Thoenen

Paul Scherrer Institut, Laboratory for Waste Management, CH-5232 Villigen PSI, Switzerland

Introduction

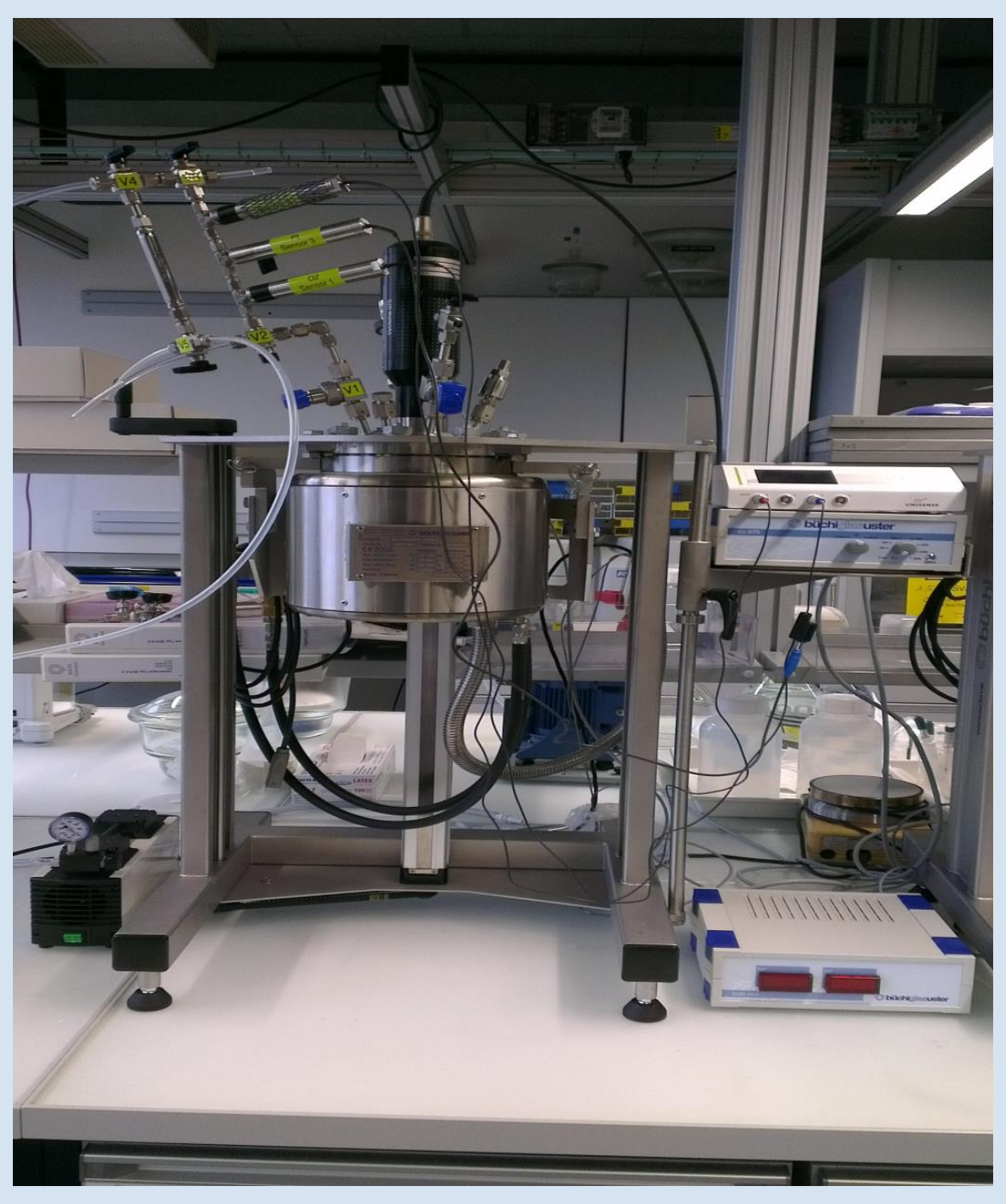
^{14}C-containing low molecular weight (LMW) organic molecules released during the corrosion of activated steel could be chemically unstable under the hyperalkaline, reducing conditions of a cement-based repository for low- and intermediate-level radioactive waste (L/ILW). In case of complete thermodynamic equilibrium, decomposition of LMW organics is predicted while the predominant species are CH_4 and CO_2 (and its bases) [1]. However, complete thermodynamic equilibrium is rarely achieved in the C-H-O system at moderate temperatures. In case partial thermodynamic equilibrium (metastability) prevails, it is still unclear what organic compounds will predominate in the repository. Note that temperatures up to 80˚C and H_2 partial pressures up to 100 atm [2] can be reached in the near-field of a L/ILW repository [2].

Preliminary experiments showed that in a gas-tight reactor at room temperature under anoxic conditions (1 atm N_2), Na-formate (HCOONa) is stable over a time period of three months both in Milli-Q water and in $Ca(OH)_2$ solution (pH=12.5). Formate is a LMW organic molecule produced during corrosion of activated steel.

The present study aims to investigate the stability of Na-formate under conditions anticipated in the cementitious near-field of a L/ILW repository. The effects of pH, temperature and H_2 partial pressure on the formate stability have been studied. This poster shows first results.

Experimental method

Laboratory pressure reactor (Versoclave Büchi AG)



Specifications:

- Volume: 500 ml
- Overpressure of max. 10 bar
- Gas-tight over long periods of time
- Online digital pressure control
- Sampling and refilling of liquid and gas phase without opening the reactor

Chemicals: ^{13}C-labelled HCOONa solutions spiked with $H^{14}COONa$

Analysis: Aqueous phase: IC-MS, TOC and liquid scintillation counting (LSC)
Gas phase: GC-MS

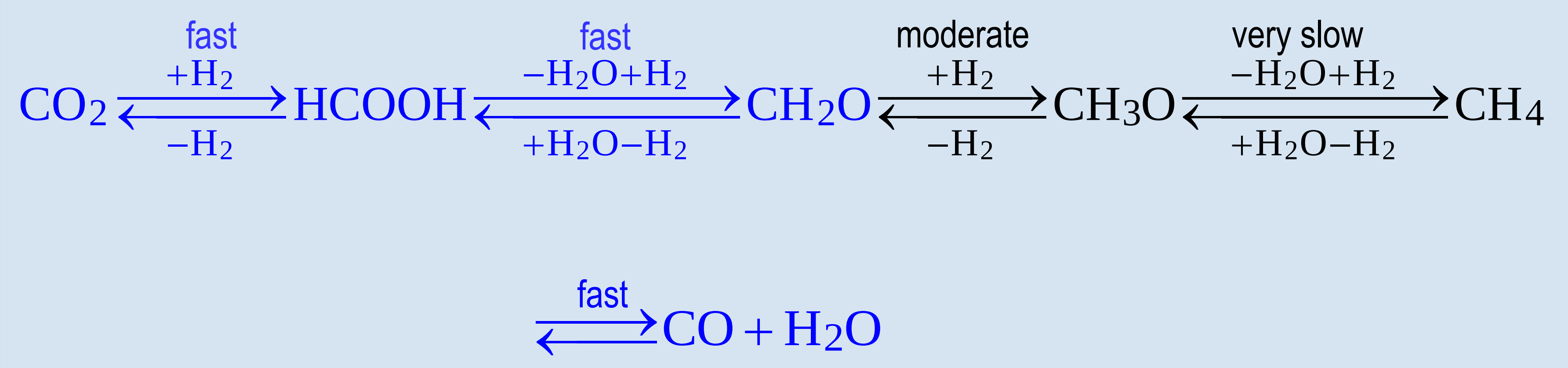
Experimental set-up and conditions

- Initial concentrations: 50 and 300 μM $H^{13}COONa$
- Chemical conditions: 1) Milli-Q H_2O
  2) Artificial cement porewater (ACW_{eq}-II): 2 g L^{-1} CaO equilibrated for 2 days followed by filtration (pH = 12.5, $[Ca]_{tot}$ = 0.02 M)
- Temperature: 150˚C (elevated temperature to accelerate the reaction kinetics)
- Atmosphere: 2 atm N_2+3.5 atm H_2O vapour (T=150˚C)
  2 atm forming gas (95% N_2/5% H_2)+3.5 atm H_2O vapour (T=150˚C)
- Catalyst: Stainless steel reactor surface
- Reaction time: up to 135 days
- Sampling: Liquid phase: 5 mL transferred into a fluid sampling tube
  Gas phase: 45 mL transferred into a gas collecting tube
  Volume of fluid and gas pressure were adjusted after sampling.

Experimental results

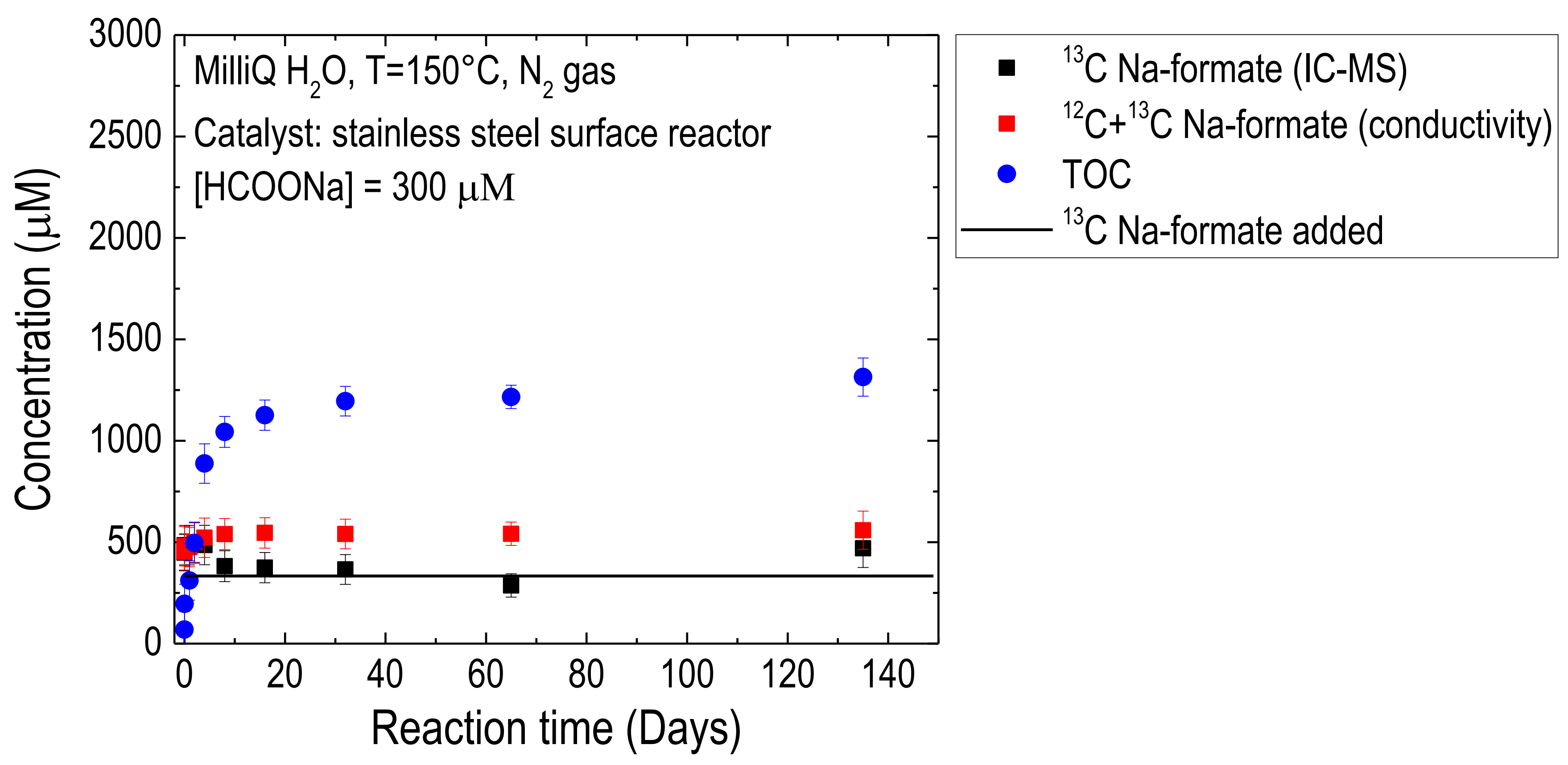
Stability experiments with Na-formate

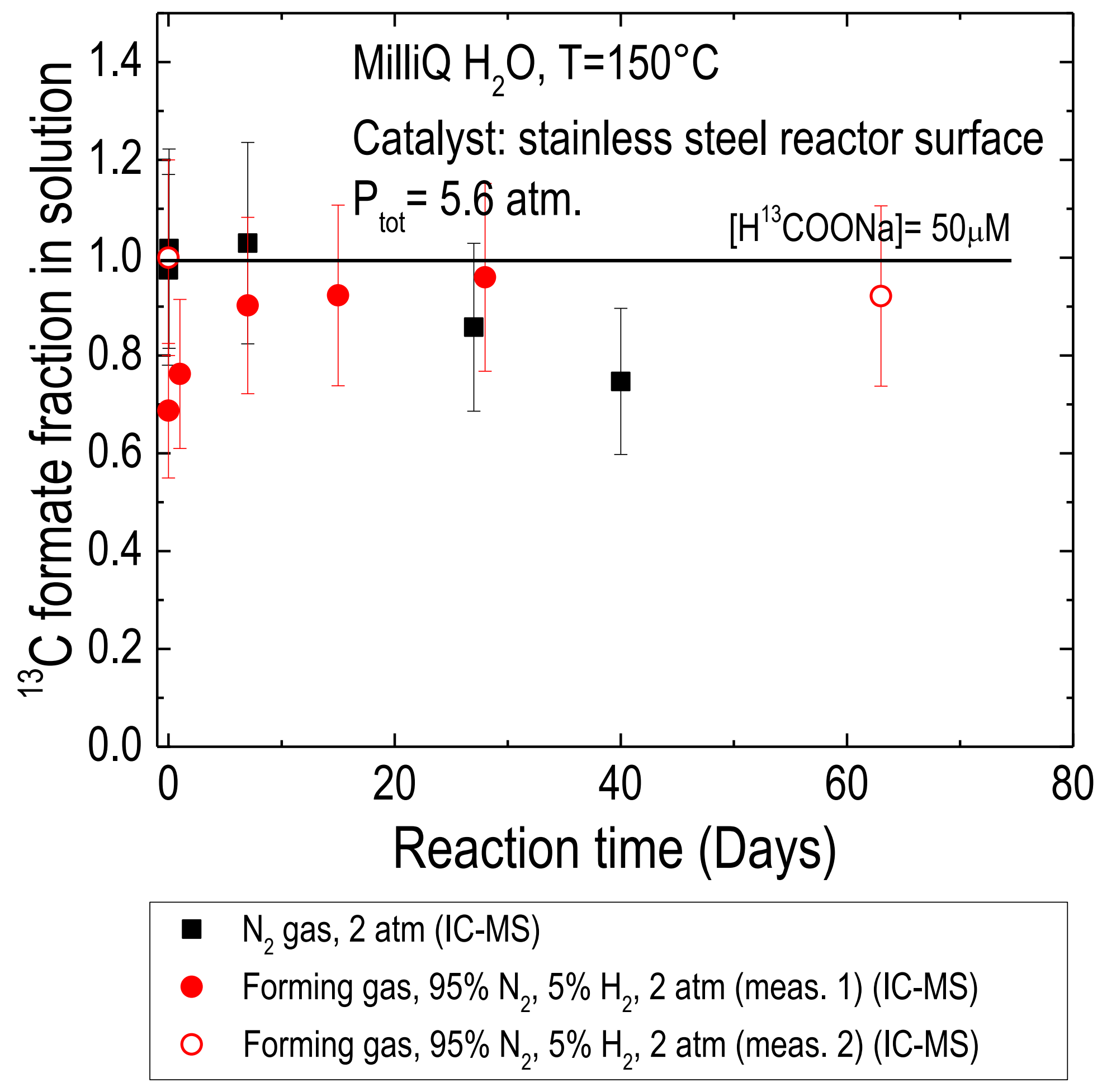
HCOONa redox kinetics [3]

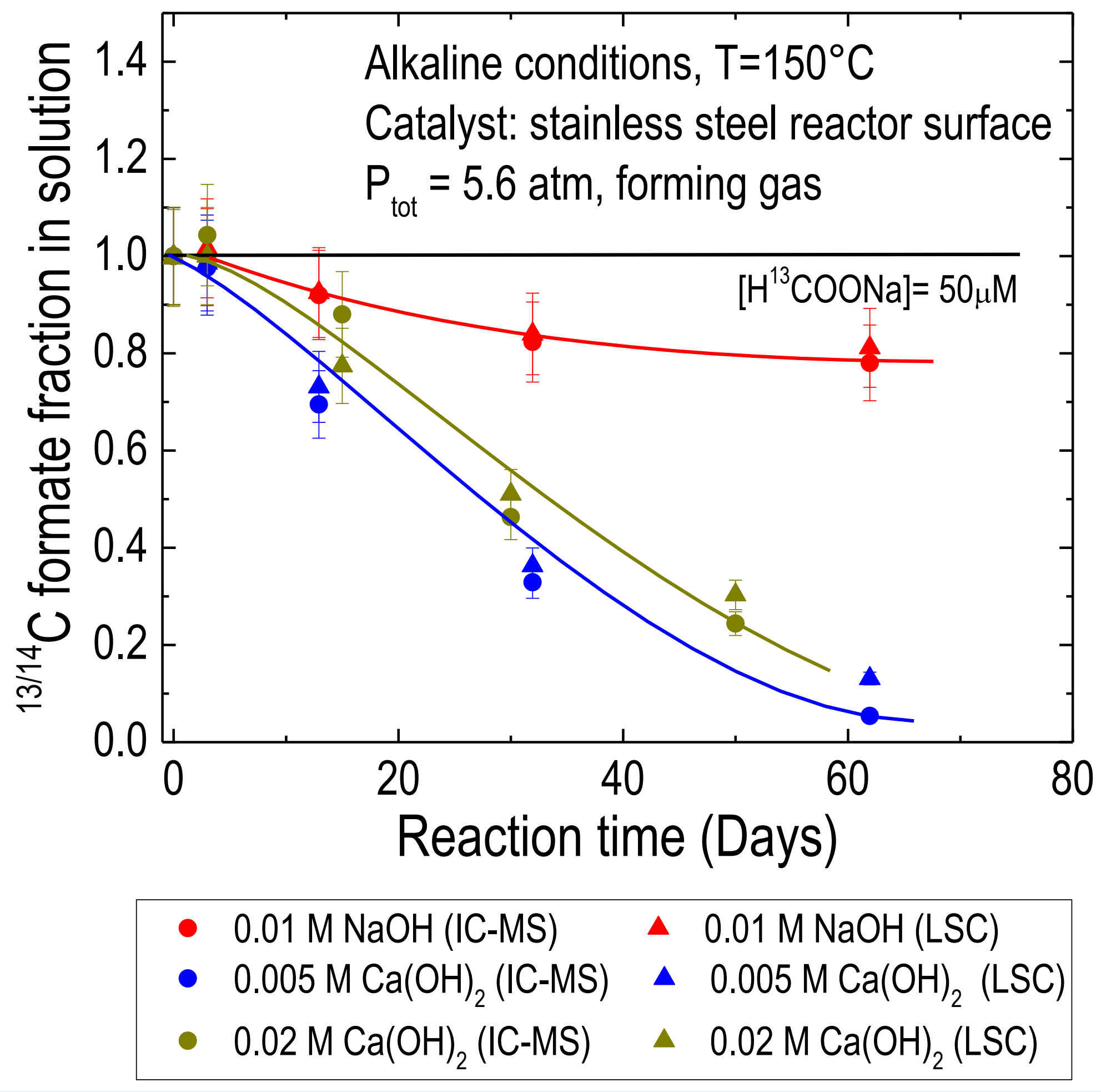


$$CO_2 \underset{-H_2}{\overset{\text{fast}}{\underset{}{\xrightleftharpoons{+H_2}}}} HCOOH \underset{+H_2O-H_2}{\overset{\text{fast}}{\xrightleftharpoons{-H_2O+H_2}}} CH_2O \underset{-H_2}{\overset{\text{moderate}}{\xrightleftharpoons{+H_2}}} CH_3O \underset{+H_2O-H_2}{\overset{\text{very slow}}{\xrightleftharpoons{-H_2O+H_2}}} CH_4$$

$$\xrightleftharpoons{\text{fast}} CO + H_2O$$







- Presence of organic contaminants (including formate) requires the use of ^{13}C-labelled HCOONa.
- Stability of formate in Mill-Q water was observed at high temperature and elevated H_2 partial pressure in line with previous experiments with N_2.
- Formate disappears completely from solution within a period of 2 months at T=150˚C and 0.1 atm H_2 partial pressure in ACW:
  - no $^{13/14}C$-bearing compounds other than formate detected in the liquid phase during the degradation experiment;
  - no $^{13/14}C$-bearing compounds detected in the gas phase during the degradation experiment.
- ^{14}C activity was detected in the fluid and gas phase after acid wash of the closed reactor for one day.

➞ **oxidation of $HCOO^-$ and precipitation as Fe/$Ca^{13}CO_3$? - HCOOH → CO_2 + H_2 → Fe/$CaCO_3$**

➞ **precipitation of $Ca(HCOO)_2$? - Very soluble compound even at elevated temperature**

➞ **precipitation of $Ca(OH)_2$ and $HCOO^-$ sorption onto $Ca(OH)_2$? – black surface precipitate on steel (magnetite?) rather than white precipitate was observed**

Summary

HCOONa is stable in Milli-Q water for at least 3 months at temperatures up to 150˚C and pressure of 5.6 atm in anoxic (N_2 atmosphere) and reducing conditions (5.6 atm, P_{H_2} = 0.1 atm).

Na-formate concentration decreases with time in ACW (pH=12.5) under the same experimental conditions (150˚C, 5.6 atm, P_{H_2} = 0.1 atm). Chemical process not yet resolved. Tentative explanation: $H^{13}COONa$ oxidation + Fe/$Ca^{13}CO_3$ precipitation. **Next step:** Experiments to determine the critical experimental parameters by varying H_2 partial pressures and temperature and identify reaction products to check mass balance.

References

[1] Wieland E. & Hummel, W. 2015. Mineral. Mag. 79, 1275-1286. [2] Xu, T. , Senger, R., Finsterle, S. 2008. Applied. Geochem., 23, 3423-3433. [3] McCollom, T. & Seewald, J.S. 2007. Chem. Rev., 107, 382-401.

Acknowledgments

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