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Investigation of the organic anion production by helium ion irradiation of calcite suspensions in water

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Context

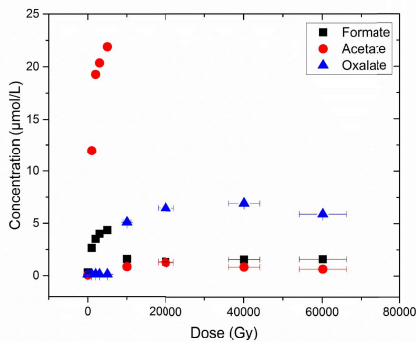
This study deals with the deep geological storage of long-lived radioactive wastes. In particular, among the options available, the use of concrete has been extensively studied. However, the presence of radionuclides in the waste container will however induce radiolysis phenomena on the concrete and the cement matrix. The carbonation of portlandite $\text{Ca}(\text{OH})_2$ in calcite CaCO_3 is a natural phenomenon occurring in every concrete depending on the storage conditions, and especially in the nuclear waste storage conditions [1]. The radiation chemical behavior of calcite is not well documented yet [2]. It is thus difficult to predict the evolution of chemical properties of concrete under irradiation, if the latter was carbonated.

« Healthy » cement : Portlandite $\text{Ca}(\text{OH})_2$ $\xrightarrow{\text{Carbonatation}}$ Calcite CaCO_3
Impact of ionizing radiation on calcite?

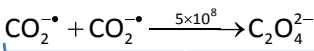
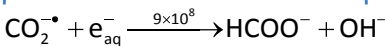
- Helium ion irradiation of calcite samples
- ARRONAX cyclotron (Nantes) \rightarrow Energy 60,7 MeV
- Focus on the organic ions produced by the irradiation

Irradiation of calcite suspensions in water

Organic anions production vs. dose

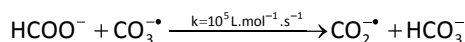
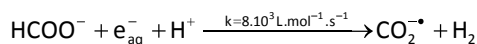
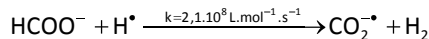
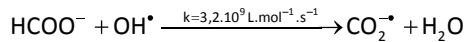


Reaction with a radical from water radiolysis
 \rightarrow Lower dose needed

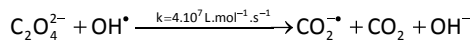


Reaction between two carbonate radicals
 \rightarrow Needs to accumulate a higher dose

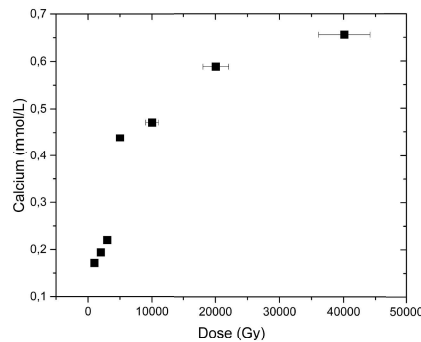
\rightarrow Formate consumption [3]



\rightarrow Oxalate stabilization



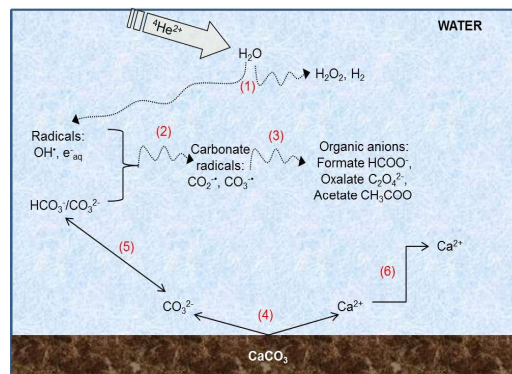
Calcium concentration in water vs. dose



As dose increases:

- \rightarrow Same pH and $[\text{CO}_3^{2-}] \sim$ constant
- \rightarrow $[\text{Ca}^{2+}] \nearrow$
- \rightarrow Difference with calcium carbonate solutions
- \rightarrow Calcite acts as a carbonate ion supply, thus providing calcium accumulation in the medium

Summary of the radiolytic dissolution of calcite



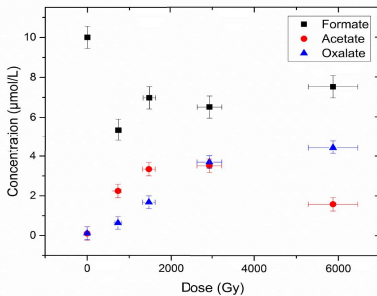
1. Water radiolysis (with helions)
2. Consumption of carbonate ions by radicals from water radiolysis
3. Organic anions formation from carbonate radicals reactions with either themselves or radicals from water radiolysis
4. Lack of carbonate ions \rightarrow CaCO_3 dissolution
5. Carbonate acid-base equilibrium
6. Calcium ion diffusion in the medium

Questions:

- \rightarrow Where does acetate come from?
- \rightarrow Are formate and acetate directly responsible for oxalate formation?

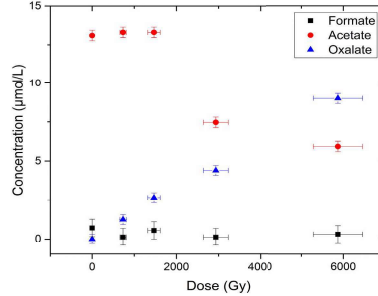
Irradiation of organic anions solutions in water

Formate solution



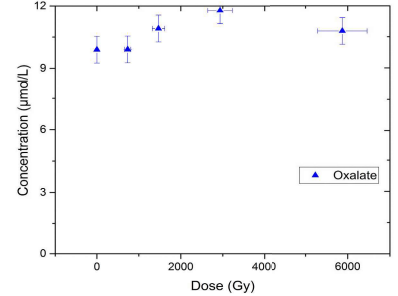
- \rightarrow Decrease of formate concentration vs. dose
- \rightarrow Formation of acetate and oxalate
- \rightarrow Decrease of acetate concentration at higher dose \rightarrow Conversion to oxalate

Acetate solution

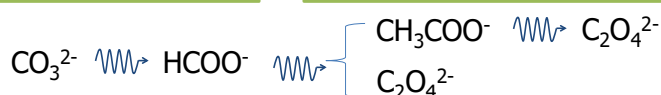


- \rightarrow Decrease of acetate concentration vs. dose
- \rightarrow Formation of oxalate
- \rightarrow No formate in solution

Oxalate solution



- \rightarrow Stable oxalate concentration vs. dose



Further work:

- \rightarrow Influence of pH and carbonate/carboxylate concentration?
- \rightarrow Influence of oxygen on the mechanism?
- \rightarrow Radiolytic yields and rate constants determination

[1] M. Thierry, *PhD*, Ecole nationale des ponts et chaussées (2005)

[2] G. Albarrán *et al*, *Radiat. Phys. Chem.* (1994) **43**, 307

[3] T.E. Eriksen, *J. Nucl. Mater.* (2012) **375** (3), 331