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Sorption of Zirconium on Quartz

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Zirconium in Radioactive Waste

The long-living radionuclide ^{93}Zr (half-life 1.61 million years) is generated in the reactors by

- neutron activation
- fission of uranium and plutonium (yield 6.3%)

The aim of this work

Determination of the mechanism and parameters of zirconium sorption on α-quartz

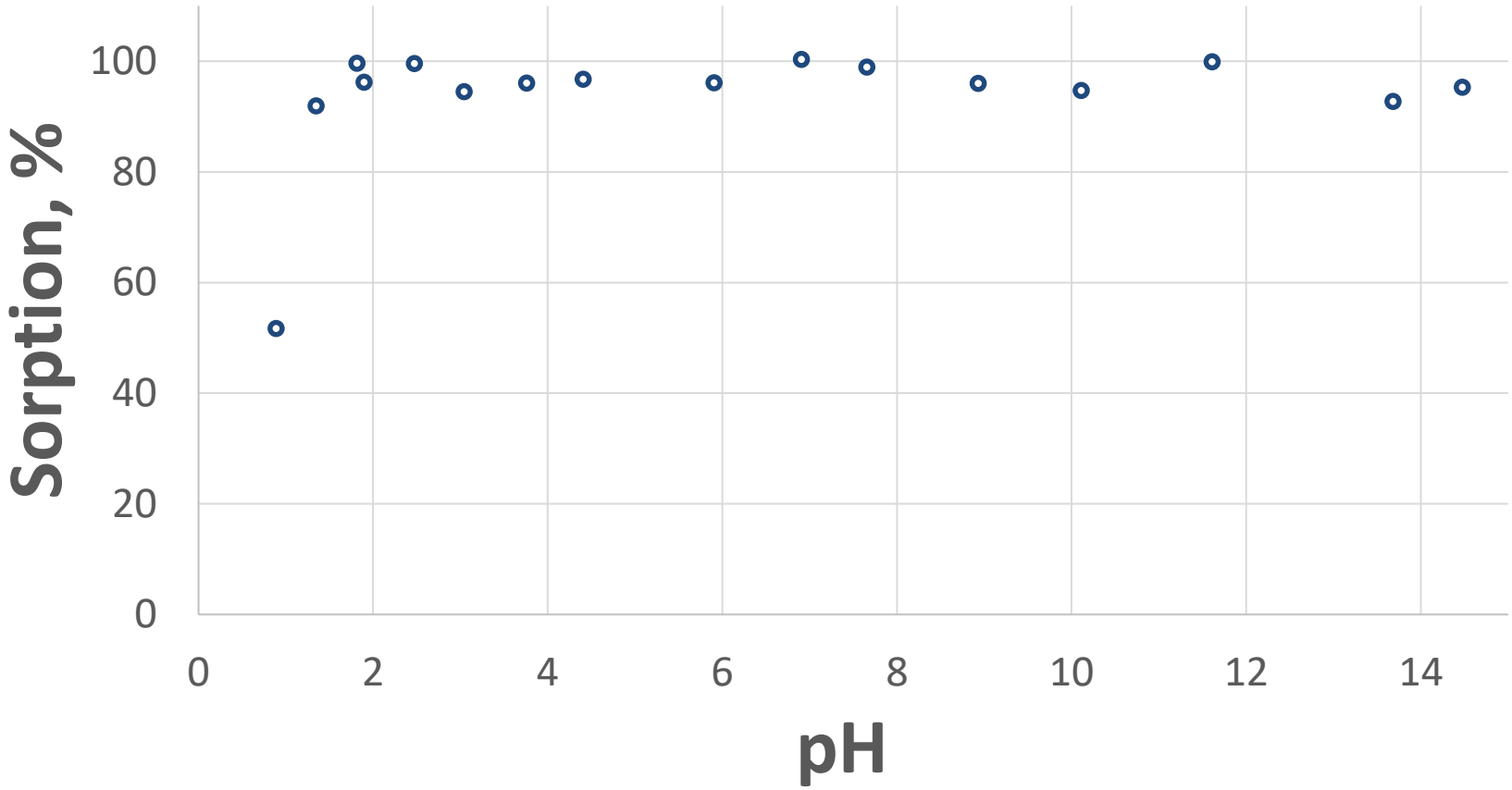
Experimental Part

Initial solutions

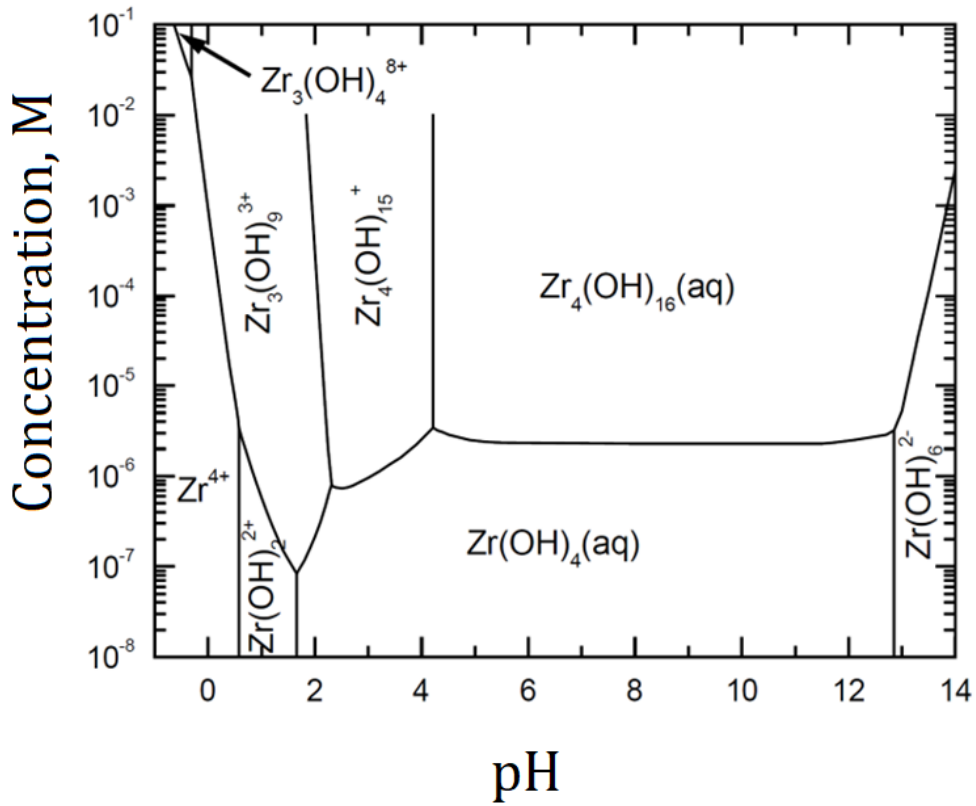
10^{-7} M $ZrOCl_2$ in 0.1 M $NaClO_4$

Method of analysis

ICP-MS



Modeling – Aq. Solutions of Zr(IV)

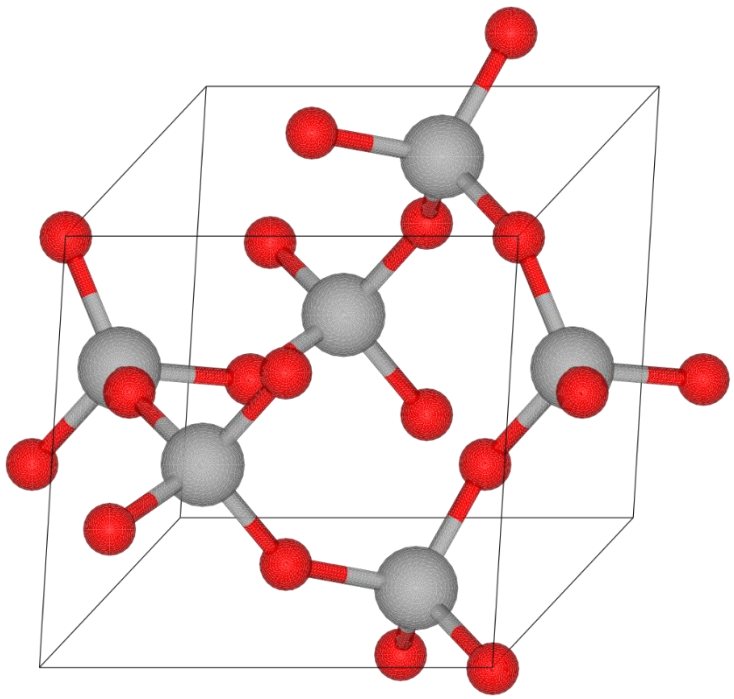


The main equilibria at concentrations 10^{-7} M and lower are

$$Zr(OH)_2^{2+} + 2H_2O \leftrightarrow Zr(OH)_4 + 2H^+, \qquad \mathrm{pK} = 3.17$$

$$Zr(OH)_4 + 2H_2O \leftrightarrow Zr(OH)_6^{2-} + 2H^+, \qquad \mathrm{pK} = 26.81$$

Modeling – Structure of α-Quartz



SiO_2

Trigonal crystal system

Point group D_3

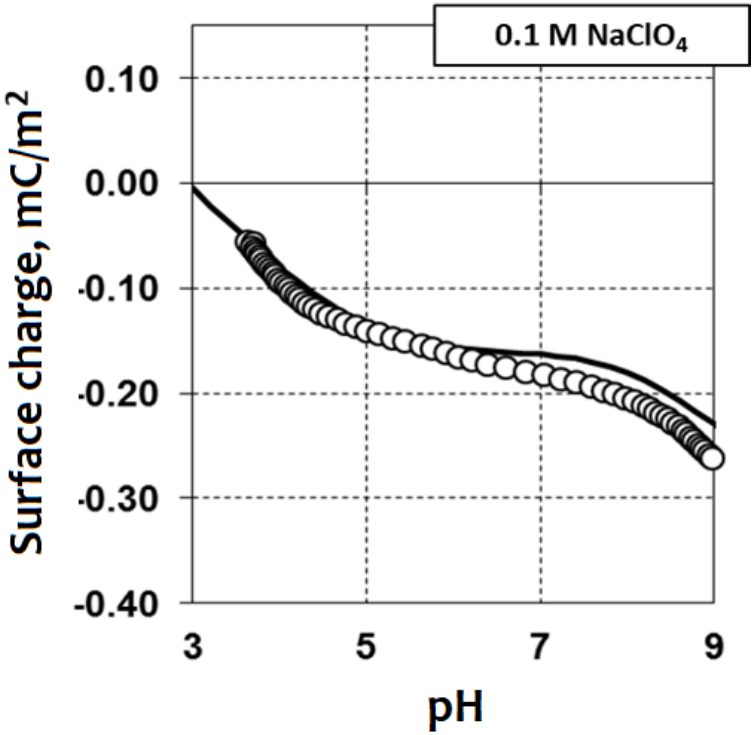
Unit cell parameters

a = 4.90 Å, c = 5.39 Å

Z = 3

Modeling – Surface of Quartz

The surface is hydrolyzed



Equilibia established at the boundary of the aqueous phase and quartz

$$\equiv Si - OH + H^+ \leftrightarrow \equiv Si - OH_2^+, \quad \text{pK} = \text{-1.0}$$

$$\equiv Si - OH \leftrightarrow \equiv Si - O^- + H^+, \quad \text{pK} = 4.0$$

Calculations – Stable Forms

Determination of the most stable configurations and thermodynamic constants through Gibbs free energy calculation with B3LYP / def2-SVP and CPCM

$(\equiv Si-O-)_2H_3^+ + Zr(OH)_2^{2+} \leftrightarrow (\equiv Si-O-)_2Zr(OH)_2 + 3H^+,$ pK=177.7

$(\equiv Si-O-)_2H_3^+ + Zr(OH)_4 \leftrightarrow (\equiv Si-O-)_2Zr(OH)_2 + H^+ + 2H_2O,$ pK=-27.0

$2(\equiv Si-OH) + Zr(OH)_2^{2+} \leftrightarrow (\equiv Si-O-)_2Zr(OH)_2 + 2H^+,$ pK=-24.8

$2(\equiv Si-OH) + Zr(OH)_4 \leftrightarrow (\equiv Si-O-)_2Zr(OH)_2 + 2H_2O,$ pK=-28.0

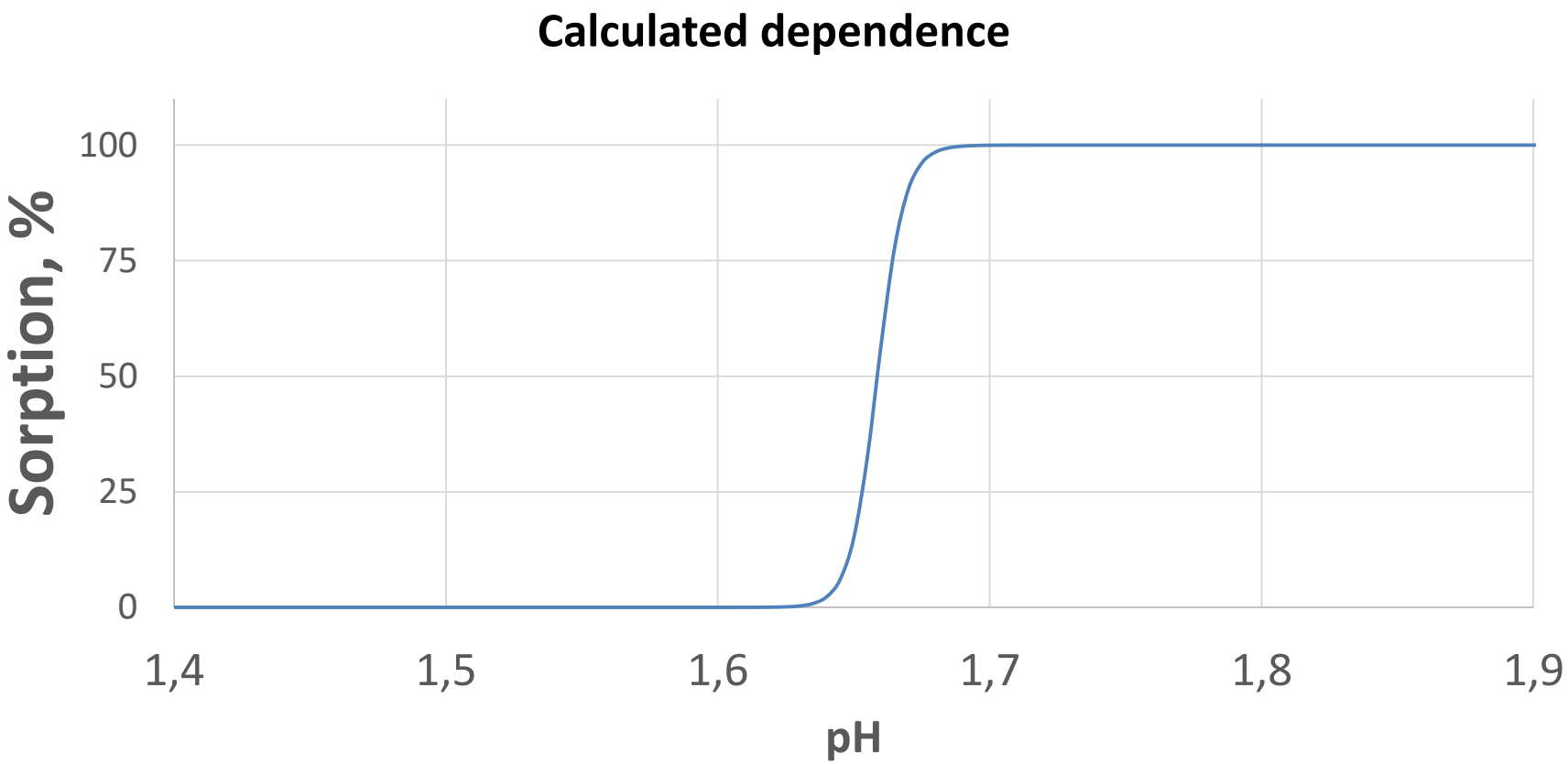
$2(\equiv Si-OH) + Zr(OH)_6^{2+} + 2H^+ \leftrightarrow (\equiv Si-O-)_2Zr(OH)_2 + 4H_2O,$ pK=-54.9

$(\equiv Si-O-)_2H^- + Zr(OH)_2^{2+} \leftrightarrow (\equiv Si-O-)_2Zr(OH)_2 + H^+,$ pK=-28.8

$(\equiv Si-O-)_2H^- + Zr(OH)_4 + H^+ \leftrightarrow (\equiv Si-O-)_2Zr(OH)_2 + 2H_2O,$ pK=-32.0

$(\equiv Si-O-)_2H^- + Zr(OH)_6^{2+} + 3H^+ \leftrightarrow (\equiv Si-O-)_2Zr(OH)_2 + 4H_2O,$ pK=-58.9

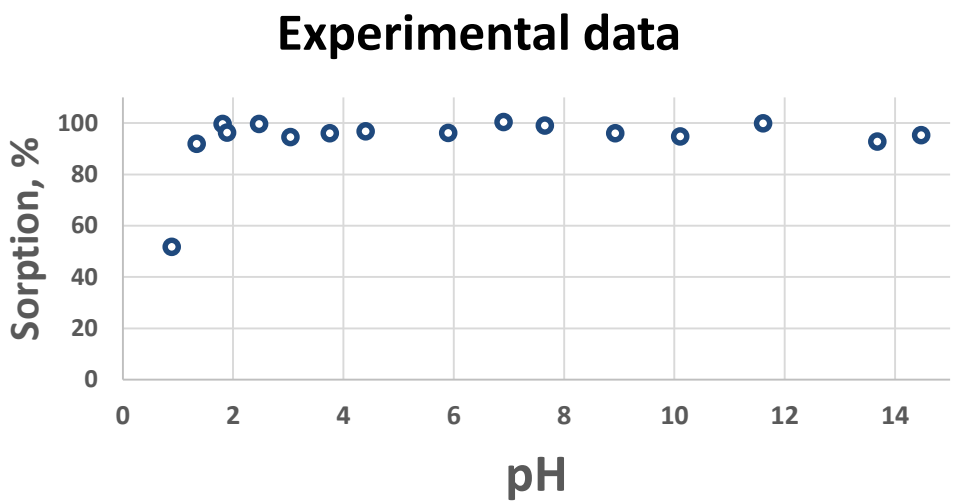
Calculations – Results



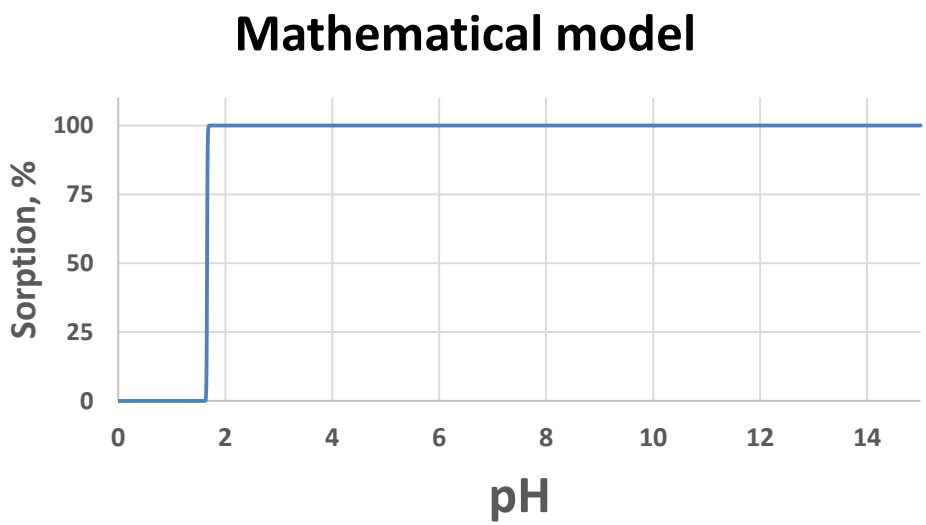
$$2(\equiv Si - OH) + Zr^{4+} + 2H_2O \leftrightarrow (\equiv Si - O-)_2Zr(OH)_2 + 4H^+$$

pK = -25.8

Summarizing the Results



Sorption 50% – pH 0.9



Sorption 50% – pH 1.65

Conclusions

1. Data on the sorption of zirconium on quartz were obtained for the first time.
2. The sorption is almost 100% at pH > 1.8.
3. A mathematical model was constructed and can be improved.
4. There still is a lot of work, and we are doing that.