



Barium Ferrate for In-Situ Chemical Oxidation of BTEX Contaminants

Christine Herrmann, Karin Hauff, Norbert Klaas

VEGAS, University of Stuttgart



Barium Ferrate - History

Iron known in oxidation state 0, +2 and +3

~ 1720: „purple by-product in some strongly alkaline solutions”

~ 1840: First publications mentioning iron in oxidation state +6

....

~ 2000: intensive research on BaFeO_4 for use in energy storage (batteries)

(also known: Fe^{4+} and Fe^{5+} , reports on Fe^{7+} and Fe^{8+})

Barium Ferrate

Why is it interesting?

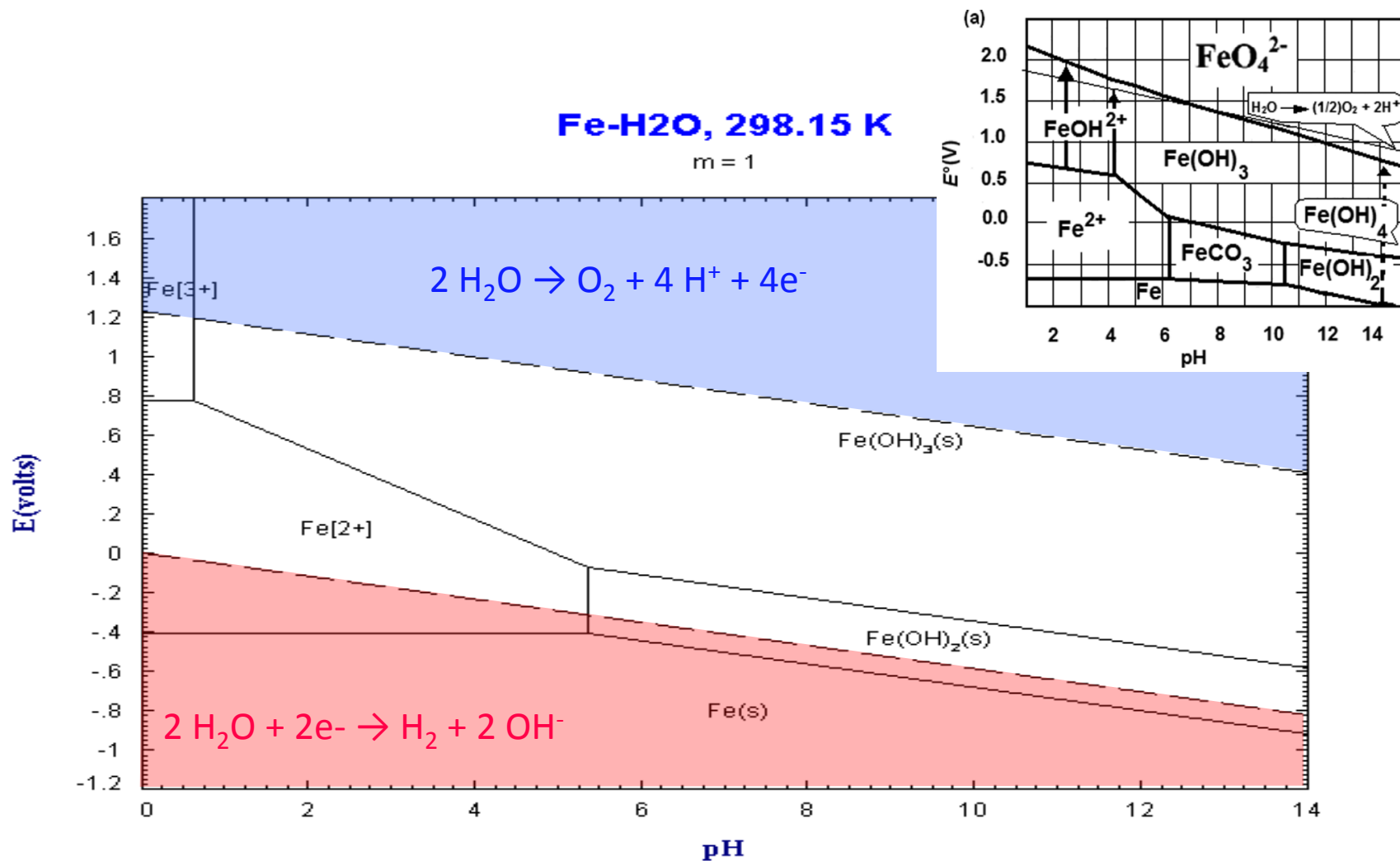


- Very strong oxidant
- Non-toxic

| Oxidant | Reaction | E^0 , V |
|--------------|---|-----------|
| Permanganate | $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$ | 1.68 |
| | $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ | 1.51 |
| Ozone | $\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$ | 2.08 |
| Ferrate (VI) | $\text{FeO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- \rightarrow \text{Fe}^{3+} + 4\text{H}_2\text{O}$ | 2.20 |
| | $\text{FeO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Fe}(\text{OH})_3 + 5\text{OH}^-$ | 0.7 |

- **Barium** ferrate offer slow-release properties
→ Creation of a depot-effect in the aquifer

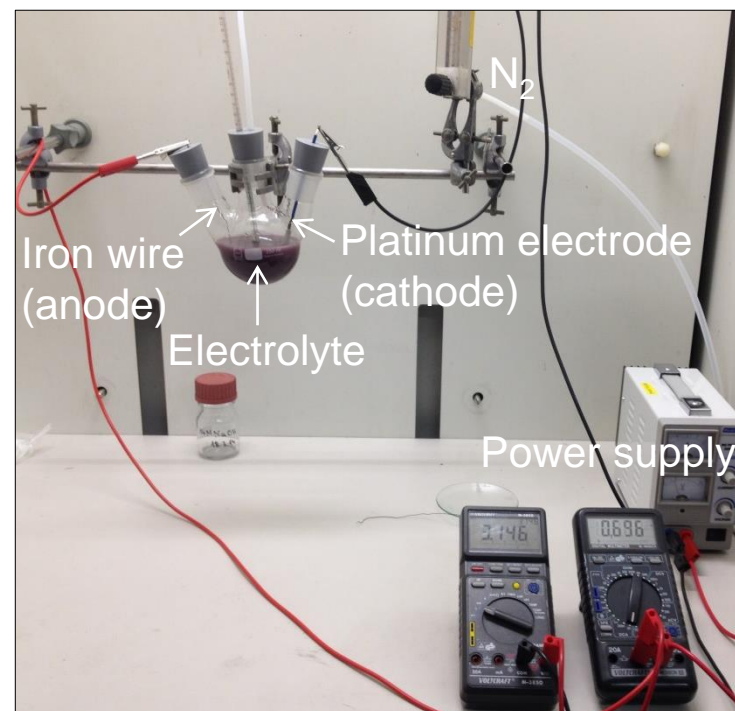
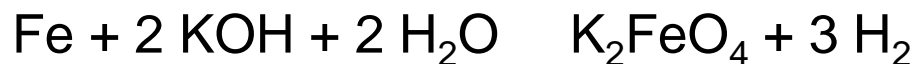
Pourbaix-Diagramm of Iron



Preparation of ferrates(VI) – Step 1

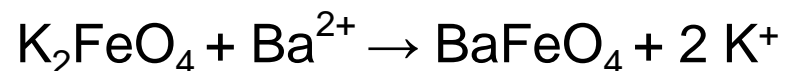
- Dry oxidation, wet oxidation or electrochemically
- Electrochemical preparation: shorter synthesis time, reduced costs
- Ex-situ synthesis route seems to be most promising

1) Electrolysis

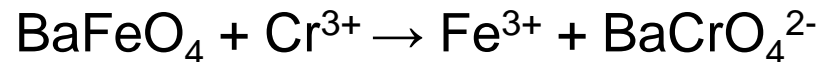


Preparation of ferrates(VI) – Step 2

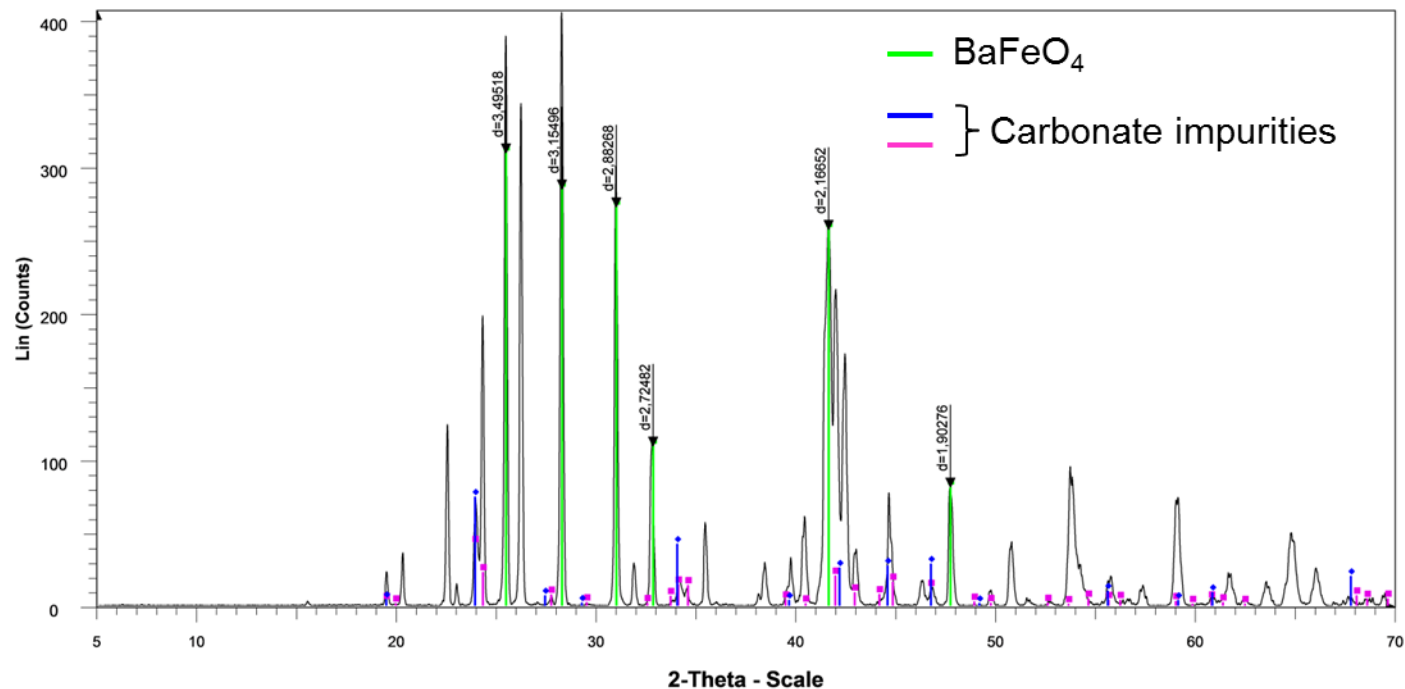
2) Precipitation of FeO_4^{2-} and purification



3) Characterization by titrimetric chromite analysis and X-ray diffraction



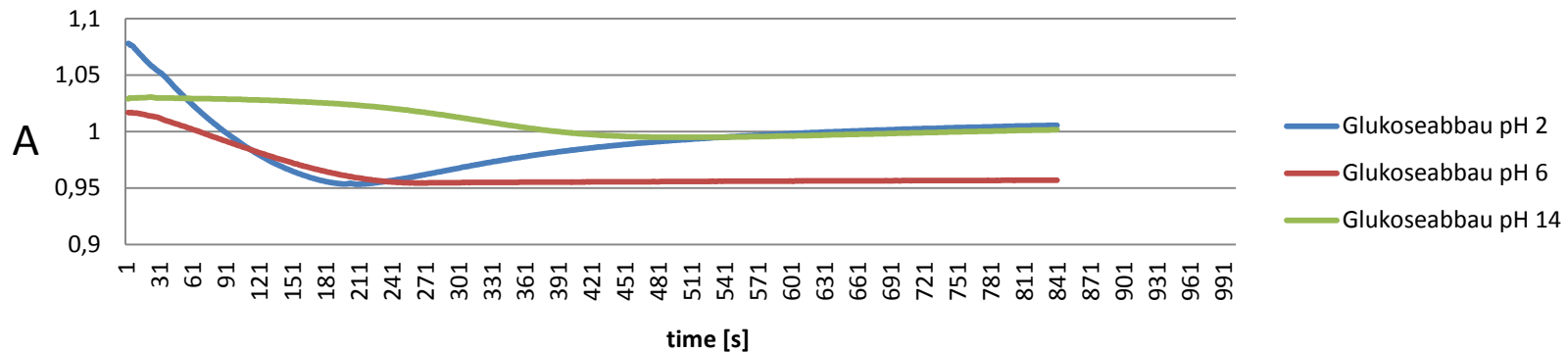
→ Main impurities are carbonate species.



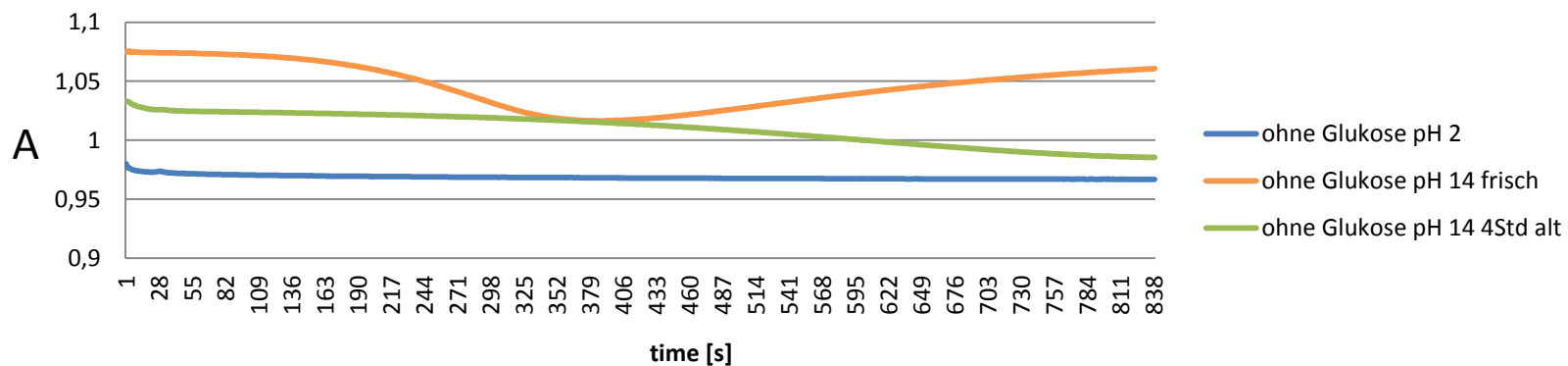
Reactivity of BaFeO₄

Aqueous glucose solution + Ferrat
Photometric tracking of reaction at pH 2 and 6 (H₂SO₄)

Glucose degradation



Stability in aqueous solution



Batchtests for Assessing the Reactivity

Model contaminant: toluene

($n_{\text{Ferrate}}/n_{\text{Toluene}} \sim 1.5/1$)

- Batch test (resting vials):
 c/c_0 approx. 45% after 2 weeks
(independent of pH-Wert?)

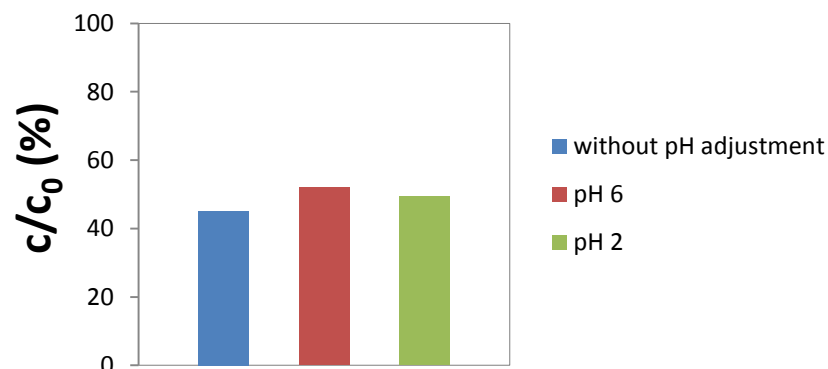
(c_0 : ~200 mg/L)

- Batch test with shaking:
pH 2 and 6 (H_2SO_4)

3 weeks

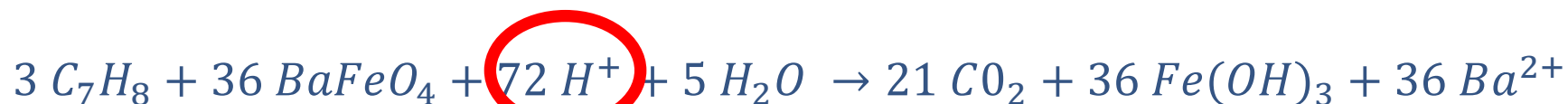
(c_0 : ~65 mg/L)

Toluene concentration



no improvement!

Disappointing Results?



- a) Low concentration of FeO_4^{2-} due to the low solubility of $BaFeO_4$
- b) Neutral conditions do not favor the reaction

Not disappointing but challenging!

→ We are using $BaFeO_4$ to stimulate the microbial degradation of HC by providing an electron acceptor

(here the lower concentrations will be beneficial)



Thank you!



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