Dissolving Magnets: Etidronic Acid Facilitated Solvation of Magnetite

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1. *Solar Energy Storage Application*

- The Solar Energy Research Facility (SERF) uses 312 mirrors to focus sunlight in one spot that reaches temperatures around 1500℃ (**Figure 1**).

Figure 1. The Valparaiso University Solar Energy Research Facility (SERF).

- The immense temperatures that the SERF can generate are capable of converting solid Rust into solid Magnetite, a reaction that does not happen otherwise. (**2a.**)
- Dissolved magnetite has increased reactivity in solution versus solid Magnetite. (**2b.**)
- Adding small amounts of electricity to the dissolved Magnetite should produce hydrogen fuel and regenerate rust. (**2c.**)
- Hydrogen fuel can be stored or distributed in congruence with energy requirements. (**2d.**)

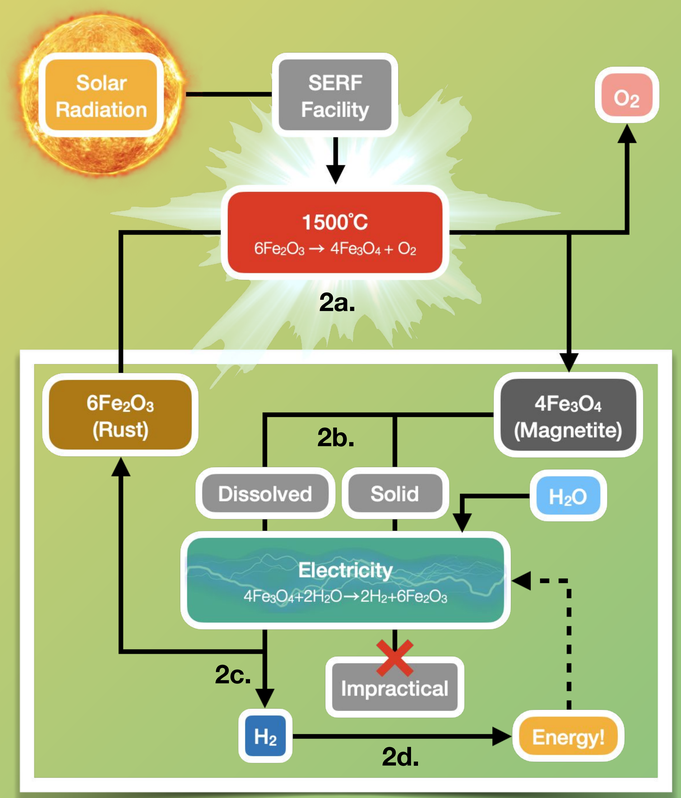


Figure 2. A conceptual scheme of the decoupled solar-electrolysis cycle.

2. *The Dissolution of Magnetite*

Dissolving a material used for household refrigerator magnets (**Figure 3**) is about as easy as it sounds. Typically, this would require using a highly concentrated, strong acid. Unfortunately, this can complicate the recovery of Rust following electrolysis. Etidronic Acid (Hydroxyethylidenediphosphonic Acid a.k.a. HEDP) (**Figure 4**) has demonstrated valuable attributes in this application, facilitating dissolution at milder pH's (**Figure 5**) and allowing the recovery of Rust through control of pH.

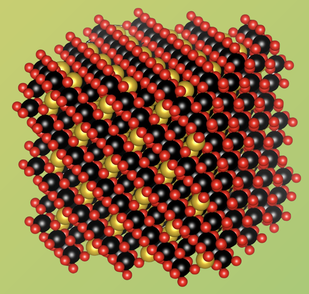


Figure 3. Crystal structure of Magnetite.[2] Energetically valuable Iron (II) is yellow, and lower energy Iron (III) is black.

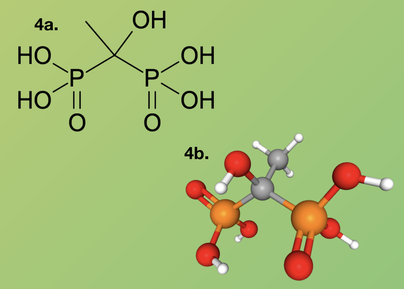


Figure 4. 2-Dimensional (**4a.**) and 3-Dimensional (**4b.**) molecular structures of HEDP.

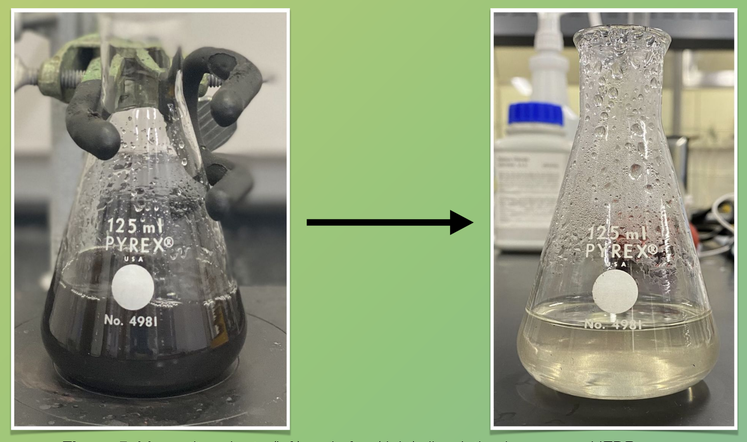


Figure 5. Magnetite prior to (left) and after (right) dissolution in aqueous HEDP.

3. *The Beer-Lambert Law*

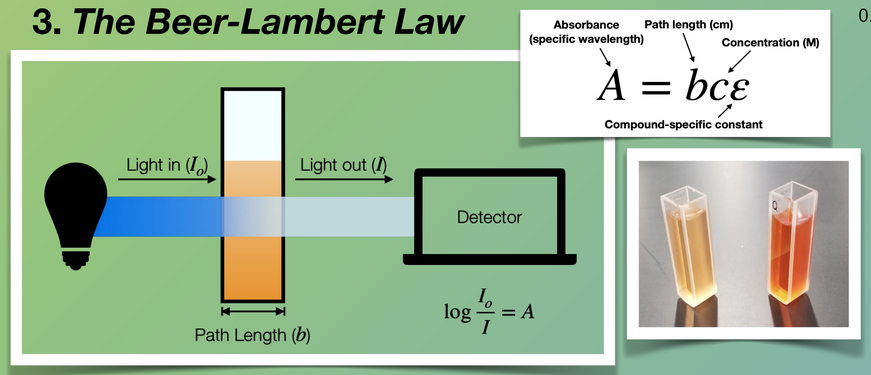


Figure 6. The concentration of Iron calculated by measuring absorbance using UV-VIS Spectroscopy. The Beer-Lambert Law derives concentration based on absorbance values and a known epsilon value.

4. *Sample Preparation: Phenanthroline Assay*

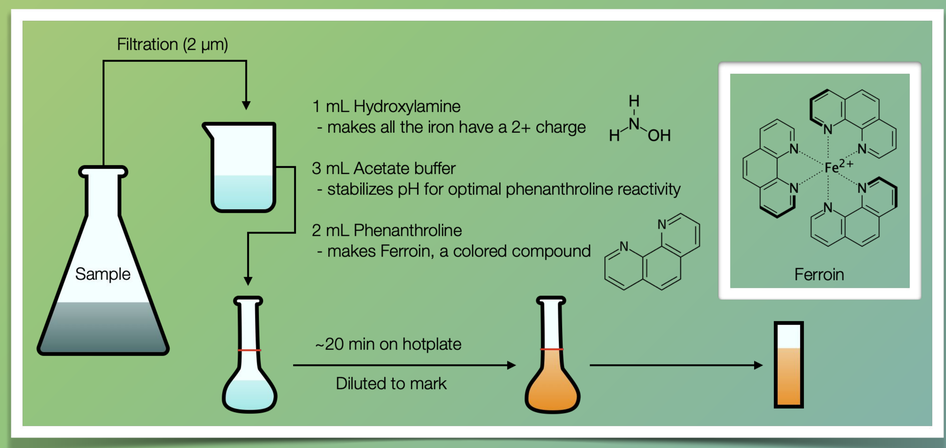
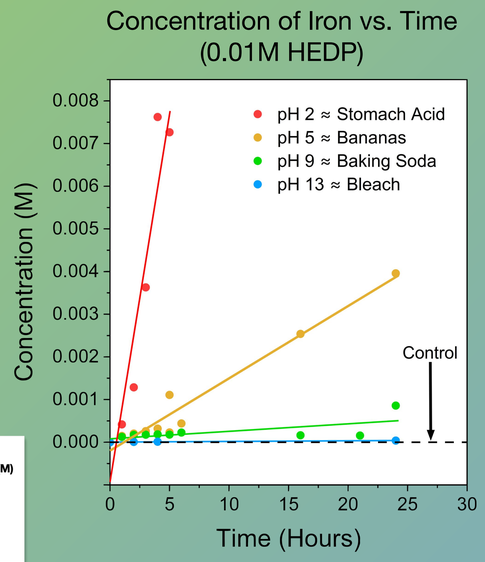


Figure 7. Outlined method for the determination of Iron concentration via phenanthroline assay. This assay converts all Iron in a solution into Ferroin, a red-orange compound with a known epsilon.[3]

5. *Data and Results*



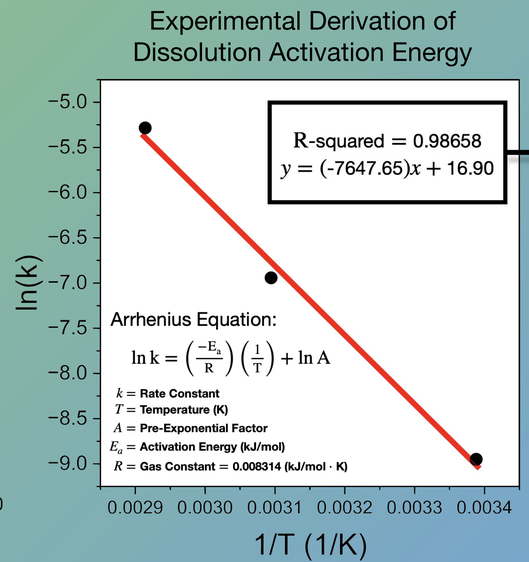


Figure 8. Magnetite dissolution rates at varying pHs (left), and the derivation of the dissolution reaction's activation energy (right). Our reported activation energy of 63.6 kJ/mol coincided with literature values of 71 kJ/mol.[4,5]

$$\frac{E_a}{R} = -7647.65 \rightarrow E_a = 63.6 \frac{kJ}{mol}$$

6. *Future Work*

- Systematically Evaluate:
  - Conditions to produce Hydrogen at different pH's, pressures, and temperatures.
  - Efficiency of rust recovery.
- Investigate the atomic structure of the interaction between HEDP and Iron.
- Analyze the specific arrangement of HEDP on the molecular level in solution.

References

1. Silcox, Rachel; Engerer, Laura K.; Nudehei, Shahin; Smith, Paul; Schoer, Jon; Krenzke, Peter T.; Palumbo, Robert; Venstrom, Luke J. Solar Thermal Decoupled Water Electrolysis Process III: The Anodic Electrochemical Reaction in a Rotating Disc Electrode Cell. *Chemical Engineering Science*. **2020**. *227*. 115885. DOI: 10.1016/j.ces.2020.115885.
2. Fleet, Michael E. The Structure of Magnetite. *Acta Crystallographica B*. **1981**, *37* (4), 917-920. DOI: 10.1107/S0567740881004597
3. Filimonova et al. Optoacoustic Spectroscopy for Real-Time Monitoring of Strongly Light-Absorbing Solutions in Applications to Analytical Chemistry. *Photoacoustics*. **2013**, *1* (3-4), 54-61. DOI: 10.1016/j.pacs.2013.08.002.
4. Gorichev, I. G.; Gorshevna, V. F.; Kiprianov, N. A.; Klyuchnikov, N. G. Kinetic Regularities Shown by the Dissolution of Magnetite in Aqueous Solutions of Hydroxyethylidenediphosphonic Acid. *Kinetica i Kataliz (Engl. Transl.); (United States)*. **1980**, 21 (6), 1013-1016
5. Mikhal'chenko, I. S.; Gorichev, I. G.; Gorsheneva, V. F.; Kiprianov, N. A. Kinetics of Magnetite Dissolution in Aqueous Solutions of Hydroxyethylidenediphosphonic Acid. *J. Appl. Chem. USSR (Engl. Transl.); (United States)*. **1981**, *54* (4), 651-655.