FellesLab 2021

ST9: Leaching kinetics of Oxides from Battery waste

Katharina Zürbes
(Katharina.zurbes@ntnu.no, Phone number: 452two4036)

1. Introduction

Norway has the highest electrical vehicle (EV) fraction of new car sales in the world. Lithium-ion batteries (LIBs) have a long lifetime, between eight to ten years, but eventually the batteries will reach end of life. Proper recycling then becomes an obvious requirement. The batteries used in EVs contain several valuable metals. For a sustainable economy, these metals need to be recovered and recycled. For this purpose, metals such as cobalt (Co), nickel (Ni), manganese (Mn), iron (Fe) and other valuable metals need to be recovered using a variety of hydrometallurgical and/or pyrometallurgical routes. In this experiment, you will study one of the hydrometallurgical routes called leaching. You will get an understanding of the kinetics of leaching of EV battery waste. In industrial recycling processes, after discharging, dismantling and pre-treating, car batteries are crushed and the resultant powder is first subjected to a leaching step. Here, inorganic acids such as sulphuric acid, hydrochloric acid and often a reducing agent, such as hydrogen peroxide is used. Although this experiment was initially planned to use battery waste directly, it was later re-designed with other metal oxides since several of the oxides present in battery waste produce carcinogenic end products after leaching. Therefore, in this experiment, you will study the leaching kinetics of mixed metal oxides (copper (II) oxide and iron (III) oxide) and graphite (anode component in batteries) in the presence of sulphuric acid.

The kinetics will be tracked by removing a small volume from the reaction mixture and analyzing it using UV-Vis spectrophotometer. Reactions parameters like temperature, concentration, solid/liquid ratio will be altered, and the leaching process will be studied as a function of these parameters and modelled accordingly.

2. Theory

Leaching is a process where a soluble part of a solid dissolves into a liquid through a reaction at the interface between solid and the liquid. A well-known example of how leaching process works is making tea using a tea bag. Consider tea bag as a solid matrix, tea leaf as the soluble part and hot water as a leachant. In this setup, green tea is extracted from the tea bag into the water and after few minutes, the color and taste of the hot water (liquid phase) has changed.

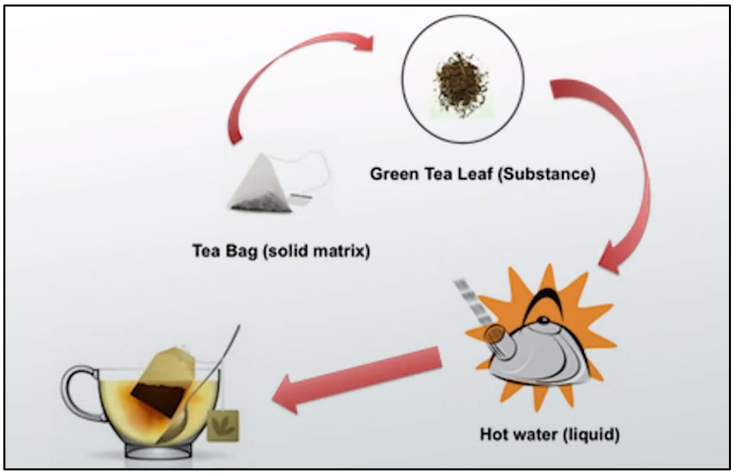

Figure 1: A simple example of leaching process

To understand the pathway through which the reactions proceed, several models have been developed. The models, like the shrinking core model described below, help in optimizing the process and design equipment that can achieve efficient leaching at industrial scale.

2.1. Shrinking Core Models (SCM)

One of the widely used models to study leaching kinetics is called shrinking core model. In heterogeneous liquid-solid reactions, spherical solid particles are being consumed either by dissolution or reaction in a liquid. The different ways that reaction occur at the particle surface are:

- Fig 1(a): The soluble part of the solid shrinks until it disappears as the reaction progresses.
- Fig 1(b): The soluble part of the solid may also react to produce an insoluble product whereby the reacting core shrinks while the particle does not change in size
- Fig 1(c): The soluble part of the solid reacts and a gelatinous and intermediate layer forms around the surface of the particle while the unreacted core shrinks.

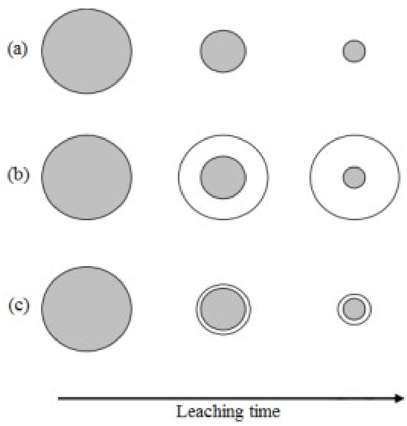

Figure 2: Different reaction pathways in the shrinking core model [1]

The kinetics of leaching can either be reaction-controlled (the surface reaction) or diffusion-controlled (diffusion of the solvable part away from the particle surface). All leaching processes include both diffusion and surface reaction, but the overall kinetics may be dominated by one of these. The equations to calculate the rate constants of these two processes are described in section 2.3.

2.2. Reactions

Copper (II) oxide reacts with sulfuric acid:

$$H_2SO_4 + CuO \rightarrow CuSO_4 + H_2O$$

The forming copper sulfate ($CuSO_4$) is blue. Iron (III) oxide and graphite are the non-leachable components and will therefore not undergo a detectable reaction.

2.3. Calculations

The kinetic equations [2] for the shrinking core model are given below:

$$1 - (1 - X)^{1/3} = k_c t \qquad \text{Eq. 1, reaction controlled}$$

$$1 - (\frac{2}{3})X - (1 - X)^{2/3} = k_d t \qquad \text{Eq. 2, diffusion controlled}$$

Where k_c is rate constant for reaction-controlled process and k_d is rate constant for diffusion-controlled process and t is the time. X is the conversion factor and defined as follows:

$$X = \frac{n}{n_0} \qquad \text{Eq. 3}$$

It can be described as the number of moles of a compound that reacted (n) divided by the amount of the moles that were fed (n_0).

2.4. UV-Vis spectrophotometer:

A UV-Vis spectrophotometer measures the absorbance of an optically active species, which can be quantified using the Beer-Lambert's law. This law states that the quantity of the light absorbed by the substance in a solvent is directly proportional to the concentration of the substance and the path length of light travelling through the solution. Hence, the absorbance A is given by:

$$A = \varepsilon l C \qquad \text{Eq. 4}$$

Here, ε is absorptivity of the species, l is path length and C is the concentration of the species.

Note: Remember that in this experiment, this formula can not be used to directly obtain the metal sulphate concentration, since we do not know its molar absorptivity (ε) of the species. Therefore, a calibration curve needs to be used instead.

2.5. Efficiency

After the leaching process, the percentage of dissolution of metal (copper) oxide in the leaching agent (H_2SO_4) solution is calculated by the following equation:

$$Efficiency = \frac{The\ initial\ weight\ of\ the\ solid\ mixture - \ weight\ of\ the\ dried\ cake}{The\ initial\ weight\ of\ of\ the\ solid\ mixture} \times 100 \qquad \text{Eq. 5}$$

It shows the efficiency of the leaching process, to know how much the inorganic acid is able to dissolve CuO from the metal mixture at the different reaction conditions (see parameters below).

3. Experiment

3.1. Objective:

Each group will study the effect of one experimental condition on the reaction kinetics. The different experimental conditions that will be studied are given in Table 1.

Table 1: Reaction parameters

Experimental condition	Solid/Liquid Ratio z(S/L) (g/L)	Temperature, T (ºC)	Concentration of Sulphuric Acid x, (M)	Mixed metal oxides % and and graphite (copper (II) oxide and iron (III) oxide) and graphite
Range	20	25	0.1	40%+40%+20%
	30	40	0.15	50%+30%+30%
	50	50	0.2	40%+20%+40%
	80	60	0.3	30%+40%+30%

When varying one reaction parameter, the other parameters used are highlighted. For instance, if a group works on understanding the effect of temperature, they should use S/L ratio 30, and 0.2 M Sulphuric acid and mixed metal percentage should be 40%+40%+20% for copper (II) oxide and iron (III) oxide and graphite, respectively.

3.2. Before Experiment: Work Plan

The students are expected to deliver a work plan to the lab assistant before being allowed to enter the lab. It is to be submitted at **least 3 working days** in advance. The work plan is submitted to katharin.zurbes@ntnu.no

- Read the risk assessment for the experiments.
- Learn about the chemicals used and the process, especially their hazards and safety.
- Prepare a work plan that should contain:

  1. Theory about leaching and filtration, diffusion controlled and reaction-controlled processes, shrinking core model in **your own words**. Cite the references you're using! This section can then also be used in your final report.
  2. The parameters to be studied (you will get information about this in advance of your experiment).
  3. Experimental time plans including calculations for solution preparation (mass of metal mixed metal oxides, volume H_2S0_4 and water, etc)

4. Remember that each group will perform 2 experiment by varying the study parameter. So be prepared for two measurements.
5. Understanding leaching kinetic models and how you will get information about the kinetics of the reaction using graphs.
6. Section about the risks involved. What is the most dangerous component?

3.3. Experiment Procedure

- Calibration

As mentioned in section 2.4, a fitted linear regression curve should be used for data obtained from UV-Vis measurements. Figure 3 shows the calibration curve when measuring the absorbance of different concentrated $CuSO_4$ solutions at wavelength 800 nm. y is the absorbance (A) measured with the UV-vis Spectrophotometer and x is the concentration of the species (C), here the concentration of copper sulfate. The linear fit for the presented datapoints for calibration provides the following equation:

$$Abs = 11.86 \times C$$

As you can see, there is limited data for the calibration curve for higher concentration of copper sulfate (>0.02 M). Therefore, the calibration range needs to be expanded. For this purpose, the absorbance (A) should be measured with the UV-Vis Spectrophotometer for different concentration of copper sulfate (C: mol/lit). The students are provided with prepared solutions with different concentrations.

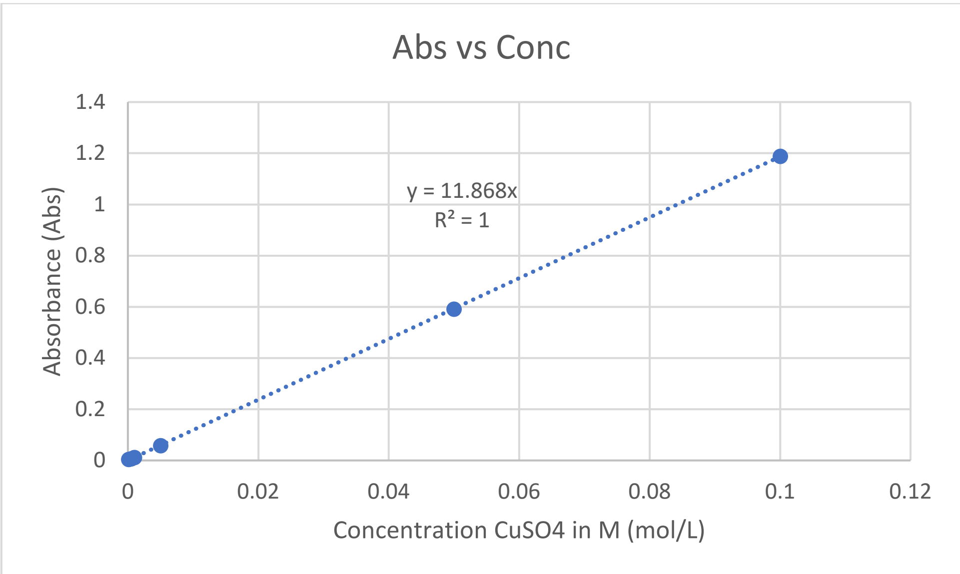

Figure 3: preliminary Calibration Curve

- Experiment setup

Make sure all the glassware and the magnets used are clean. Prepare a sufficient amount of chemicals depending on the reaction conditions you'll test. Always use nitrile gloves while working with the chemicals. Inspect the setup for any damages or leaks and ensure all the connections are proper.

1. **Materials**

    a. Prepare 250 ml (0.25 L) of x (M) Sulphuric acid solution.
    b. Weight out graphite, copper (II) oxide and iron (III) Oxide to reach (S/L) ratio.

2. **Methods**
    a. Setup the glass reactor on the stirring plate. Clamp it to ensure that the reactor is safely placed on the stirrer.
    b. Connect the water outlets to the reactor jacket and set the water bath temperature T (make sure that you have connected the correct outlets for the water bath).
    c. Connect and clamp the condenser to ensure that it is safely placed in the reactor and turn on water flow.
    d. As you wait for the temperature to stabilize, prepare your materials for the leaching experiments (10 glass vials, filter tips, syringes)
    e. Add 2.5 ml of DI water in the vials.
    f. Once the temperature has stabilized at the set value, put the magnetic stirrer in the reactor and add the solid materials.
    g. Add 250 mL of x (M) Sulphuric acid into the reactor and turn on the stirrer plate when you have added some acid. Then close the reactor.
    h. Start the stopwatch.
    i. Set the stirring speed to 500 rpm.
    j. Measure the temperature with a Thermometer at different timepoints.
    k. Take samples of 2.5 ml after different time intervals i.e. 30 sec, 1 min, 1.5 min, 3 min, 4.5 min, 6 min, 7.5 min, 10 min, 20 min and 30 min respectively with pipette in the prepared small vials. Add the different samples into 2.5ml of DI water. This is done to quench the reaction.
    l. Filter the 5ml sample using 0.45µm filter tips.
    m. While taking the samples, check and measure the temperature inside the reactor and note down the temperature of water in the reactor jacket as well.
    n. After 30 min, turn off the water bath, water flow in condenser and stirrer plate.
    o. Filter, using a filter paper, the remaining solution in the reactor by using a Buchner funnel setup and vacuum filtration.

Figure 4: Representative image of the setup

3. **Characterization of Samples**

a. The kinetic samples are characterized using UV-Vis spectrophotometer.
b. For each sample, the absorbance will be measured for a single wavelength – 800nm.
c. Switch on the UV-Vis Spectrophotometer (on the right side) and wait for initializing
d. Meanwhile, prepare your sample in cuvettes (10 sample taken from different time)

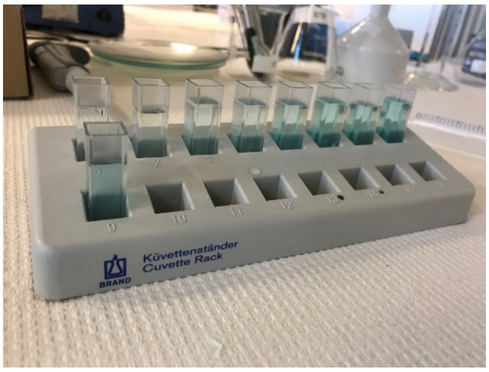

Figure 5: Cuvettes for measurement of absorbance with the UV-Vis Spectrophotometer

e. The procedure to use the instrument:

- Press: Fixed
- Select: Fixed 800 + Continue
- Give your Measurement set a comprehensive name
- Insert a blank solution (Cuvette filled with MQ water)
- Press Blank
- Insert sample
- Press Measure
- Repeat the last two steps for all your samples (give them a good name!)
- After all measurements are done click on the three dots in the upper right corner
- Select Export, a USB stick will be used to transfer the data

The Data from the (UV-Vis) measurements will be sent to the students by the end of the experiment day. If the data was not sent, please give a reminder 😉

NOTES: Handling of cuvettes

- Only touch the sides of the cuvettes, not the 'windows' through which the beam will pass
- Check for PS/dust inside the cuvettes
- Use gloves to hold cuvettes (to avoid fingerprints).
- While filling the cuvettes, avoid spillage of the solution on the outer side of the cuvettes.
- While filling the cuvettes, avoid presence of air bubbles in the sample.
- Before inserting the cuvettes in the holders, dry them (from all the sides) with Kimtech wipes.

4. The filter cake will be let kept for drying and the weight of the dried cake will be taken the next day.

3.4. After the experiment

1. Turn off the water bath and remove the magnetic stirrer and the temperature probe.
2. Carefully dispose off the waste and wash all the glassware properly.
3. **Remove the water circulations and clean the reactor for the next experiment**
4. Make sure the lab and the fume hood are clean for the next group.

3.5. Waste handling

- Solutions of H_2SO_4 are disposed in the container marked with Inorganic Acids Waste!
- Dried cakes are disposed in normal waste bin after defuming overnight.
- Glass vials have to be washed with water and thrown clean into Glass Waste!
- Gloves, papers and filters can be thrown into normal waste bin!

4. Report Guidelines

The initial report should be submitted within a week after performing the experiments. The initial report should be complete with discussions, references, figures etc. After the feedback from the supervisor, the group will have one more week to address the feedback and submit the final version.

- Short introduction and theory (from the work plan) followed by the experimental work done
- Results with calculations and graphs.
- Discussion about the results and relationships between the different experimental parameters.
- Discussion about the experimental error and its effect on the final results.
- Literature references.
- An appendix with detailed calculations, risk assessment and copies from the lab journal.

The report should address the following questions. The answers should be through understanding the process and explained using the data and results. The report should not directly answer the three questions, rather be evidence supported discussion.

- Plot the conversion as a function of time (t) and use appropriate curve fit to the obtained data. Tip: have a look at Section 2.3.
- Find the rate constants $k_c$and k_d using plot X-t. Determine and discuss if the process is a diffusion controlled or reaction-controlled pathway.
- Calculate and compare the leaching efficiency and leaching kinetics as a function of the parameter studied. Give reasons for the results obtained.
- How would you improve the experiment?
- Attach the (excel) file with raw data and calculations and plots when sending the final version of the report.

References

1. Othusitse, Nhlanhla, and Edison Muzenda. "Predictive models of leaching processes: A critical review." *7th International Conference on Latest Trends in Engineering & Technology (ICLTET'2015), Irene, Pretoria (South Africa)*. 2015.

2. Nayl, A. A., et al. "Acid leaching of mixed spent Li-ion batteries." *Arabian Journal of Chemistry* 10 (2017): S3632-S3639.

3. Habbache, N., N. Alane, S. Djerad, and L. Tifouti. "Leaching of copper oxide with different acid solutions." Chemical Engineering Journal 152, no. 2-3 (2009): 503-508.