

ST9: Leaching kinetics of Oxides from Battery waste

1 Introduction

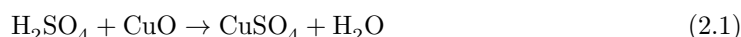
The purpose of this experiment is to obtain an understanding of the kinetics of leaching of electrical vehicle battery waste. In this experiment the leaching kinetics of mixed metal oxides, in this case copper(II) oxide and iron (III) oxide, and graphite, in the presence of sulphuric acid, are going to be studied. The kinetics will be tracked by removing a small volume from the reaction mixture, before analyzing it using UV-Vis spectrophotometer. The temperature, the concentration of H_2SO_4 , and the solid/liquid ratio will be held at a constant, whilst the percentage of metal oxides and graphite will differ. The leaching process will be studied as a function of these parameters, and modelled accordingly.

2 Theory

2.1 Leaching and filtration

Leaching is a heterogeneous reaction which takes place at the interface between a solid and liquid phase.^[1] In this process a soluble part of the solid dissolves into the liquid. The leaching process works by putting a solid matrix with a soluble part into a leachant. After some time has passed, the soluble part will be somewhat or completely dissolved in the leachant, depending on the reaction rate and the leachant can then be filtrated.^[2]

In this experiment, the leaching kinetics of mixed metal oxides and graphite in the presence of sulphuric acid, will be studied. The mixed metal oxides consists of copper(II) oxide (CuO) and iron(III) oxide (Fe_2O_3). The set reaction to be studied will be the reaction between sulphuric acid (H_2SO_4) and copper(II) oxide:



This is because iron(III) oxide and graphite are non-leachable components, and therefore they will not undergo a detectable reaction, whilst copper(II) oxide forms copper sulfate, as seen in reaction 2.1, which has a blue colour.^[2]

The efficiency of the leaching process can be calculated by the following equation:

$$\text{Efficiency} = \frac{m_{\text{solidmixture}} - m_{\text{driedcake}}}{m_{\text{solidmixture}}} \quad (2.2)$$

This shows how much the inorganic acid, H_2SO_4 , is able to dissolve the metal oxide, CuO , at different reaction conditions.

2.2 Shrinking core model(SCM)

There are several methods that can be used to understand the pathway through which the reactions proceed. One of these methods is the shrinking core model (SCM). This model is used to describe situations that occur in heterogeneous liquid-solid reactions, in which spherical solid particles are being consumed, either by dissolution or by reaction in a liquid. As a result, the amount of the material being consumed is “shrinking.”^[3]

The different ways the particles react at the surface are:

- The soluble part of the solid shrinks until it disappears while the reaction progresses. This process is shown in figure 2.1 (a).
- The soluble part of the solid reacts and produces an insoluble product whereby the reacting core shrinks while the particle does not change in size. This process is shown in figure 2.1 (b).
- 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. This process is shown in figure 2.1 (c).^[2]

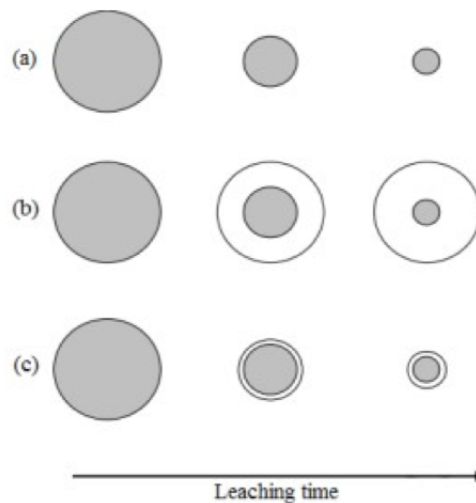


Figure 2.1: Different reaction pathways in the shrinking core model^[2]

All leaching processes include both diffusion and surface reaction. However the overall kinetics may be dominated by only one of these, and thus the kinetics of leaching is divided into two different processes: reaction-controlled or diffusion-controlled. This is important when calculating the rate constants because the calculations are different for the two processes. The calculations are shown in section A.

2.3 UV-Vis spectrophotometer

A UV-Vis spectrophotometer measures the absorbance of an optically active species, which can then be quantified using the Beer-Lambert's law:

$$A = \epsilon l C, \quad (2.3)$$

here A is the absorbance, ϵ is the absorptivity of the species, l is travel length of the light, and C is the concentration of the species. Thus the law states that the quantity of light absorbed by the substance is proportional to the concentration of the substance and the path length of light travelling through the solution. However the formula can not be used directly to obtain the metal sulphate concentration in this experiment, because the molar absorptivity ϵ for the species is not known. Thus, a calibration curve must be used instead.

3 Experimental Procedure

In this experiment, reaction kinetics will be studied. This will be carried out by differing one experimental condition, while keeping the others constant to see how it will affect the reaction rate. There will be performed two experiments where the mixture of metal oxides and graphite will differ. The parameters and compositions are shown in table 3.1

Tabell 3.1: Reaction data

Experiment	Solid/Liquid Ratio [g/L]	T [C°]	$C_{H_2SO_4}$	CuO, Fe_2O_3 , graphite [%]
1	20	25	0.1	40 + 40 + 20
2	20	25	0.1	30 + 40 + 30

3.1 Procedure

Prior to the experiments all glassware and magnets need to be cleaned, to assure accurate measures. Chemicals should also be pre-measured to the correct amount, shown in table 3.2

Tabell 3.2: Amounts of chemicals

Experiment	H_2O (DI)[mL]	H_2SO_4 [mL]	CuO [g]	Fe_2O_3 [g]	graphite [g]
1	250	250	2	2	1
2	250	250	1.5	2	1.5

3.1.1 Leaching

1. Place the glass reactor on the stirring plate, using clamps to secure it from moving during the experiment.
2. Water outlets must be connected to the reactor jacket and to the water bath. Then set the temperature for the water bath.
3. Attach the condenser to the reactor using clamps, and make sure it is secure prior to turning on the water flow to the condenser.
4. While the temperature stabilizes, prepare the materials needed for the leaching experiment (10 glass vials, filter tips, syringes).
5. Add 2.5 mL deionized water to the vials.
6. When the temperature has stabilized at the set value, add the solid material.
7. Then 250 mL of sulfuric acid is added to the reactor, and the stirring plate should be turned on as soon as some acid is added.
8. Start the stopwatch.
9. Stirring speed set to 500 rpm.
10. Use a thermometer to measure the temperature at each timepoint: 30 sec, 1 min, 1.5 min, 3 min, 4.5 min, 6 min, 7.5 min, 10 min, 20 min, 30 min.
11. Samples of 2.5 mL are to be taken at these ten time points, using a pipette, and added to 2.5 mL of deionized water to stop the reaction.
12. Filter the sample (5 mL) by using 0.45 μ m filter tips.
13. While taking the samples, measure and record the temperature inside the reactor, as well as the temperature of the reactor jacket.

14. When 30 minutes have passed, turn off the water bath, water flow in condenser, and stirring plate.
15. Use the Buchner funnel setup and vacuum filtration to filter the remaining solution through the filter paper.

3.1.2 Uv-Vis Spectrophotometer

- On the right side of the equipment, turn the switch.
- While the Uv-Vis is initializing, prepare the 10 samples in chronological order.

3.2 Experimental time table

Tabell 3.3: Data from experiment 1

Sample	t [s]	A [$\text{Lmol}^{-1}\text{cm}^{-1}$]	C [mol L^{-1}]	V [L]	n [mol]	X
1	30					
2	90					
3	180					
4	270					
5	360					
6	450					
7	600					
8	900					
9	1200					
10	1800					

Tabell 3.4: Data from experiment 2

Sample	t [s]	A [$\text{Lmol}^{-1}\text{cm}^{-1}$]	C [mol L^{-1}]	V [L]	n [mol]	X
1	30					
2	90					
3	180					
4	270					
5	360					
6	450					
7	600					
8	900					
9	1200					
10	1800					

4 Risk analysis

This experiment has some risk associated with aspects like spillage of hot solution, burn injuries and wounds from broken glass. However these risks are fairly unlikely and/or have small consequences. The biggest risks for this experiment involve handling of the different chemicals, and the most dangerous component is sulphuric acid.^[4] The hazards associated with each chemical are shown in Table 4.1:

Tabell 4.1: The hazards associated with each chemical in this experiment^[4]

Chemical	Hazards
Sulphuric acid	Danger May be corrosive to metals Causes severe skin burns and eye damage
Copper sulfate	Warning Harmful if swallowed Causes skin irritation Causes serious eye irritation Very toxic to aquatic life with long lasting effects
Copper(II) oxide	Warning Very toxic to aquatic life with long lasting effects
Iron(III) oxide	Not a hazardous substance
Graphite powder	Not a hazardous substance

Trondheim, 9. september 2021

Referanser

- [1] Leaching theory and kinetics. http://wiki.biomine.skelleftea.se/wiki/index.php/Leach_kinetics, 2008. Hentet 08.09.2021.
- [2] Katharina Zürbes. St9: Leaching kinetics of oxides from battery waste. URL https://folk.ntnu.no/preisig/HAP_Specials/Felles_lab/Experiments/ST9_battery_waste.pdf.
- [3] W14A The Shrinking Core Model. http://websites.umich.edu/~elements/5e/14chap/expanded_ch14_A.pdf. Hentet 08.09.2021.
- [4] Gøril Flatberg. Detailed risk report, 2020. Hentet 08.09.21 .

A Calculations for the rate constant

The kinetic equations for the shrinking core model for reaction controlled process and diffusion controlled process are shown in equation A.1 and A.2 respectively:

$$1 - (1 - X)^{\frac{1}{3}} = k_c t \quad (\text{A.1})$$

$$1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}} = k_d t \quad (\text{A.2})$$

Here are k_c and k_d the rate constants for reaction controlled process and diffusion controlled process respectively. X is the conversion factor, defined by:

$$X = \frac{n}{n_0} \quad (\text{A.3})$$

Here n is the number of moles reacted, and n_0 is the amount of moles fed.

B Volume of H_2SO_4

The sulphuric acid used in the experiment was 98% concentrated, which gives a molarity of 18.4 mol/L. Using this principle, $C_1 \cdot V_1 = C_2 \cdot C_2$, gives the following expression.

$$X_{\text{H}_2\text{SO}_4} \cdot 18.4 \frac{\text{mol}}{\text{L}} = 0.250 \text{L} \cdot 0.1 \frac{\text{mol}}{\text{L}} \quad (\text{B.1})$$

$$X_{\text{H}_2\text{SO}_4} = \frac{0.250 \text{L}}{18.4 \text{mol/L}} \cdot 0.1 \frac{\text{mol}}{\text{L}} \text{H}_2\text{SO}_4 = \underline{\underline{1.36 \text{mL}}} \quad (\text{B.2})$$

C Calculations for CuO , Fe_2O_3 and graphite

The volume of H_2SO_4 is 0.25 L, and the S/L ratio is 20. The total weight of all the solids is therefore:

$$S = 20 \cdot L = 20 \cdot 0.25 = \underline{5g} \quad (\text{C.1})$$

The percentages of the mixed metal oxides and graphite differ from experiment 1 and 2, and are given in table 3.1. The mass of each component in both experiments is given in table C.1

Tabell C.1: Data from experiment 2

	$\text{m}_{\text{CuO}}[g]$	$\text{m}_{\text{Fe}_2\text{O}_3}[g]$	$\text{m}_{\text{graphite}}[g]$
Experiment 1	2	2	1
Experiment 2	1.5	2	1.5