Teacher’s Card

Antisolvent Crystallization

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General Introduction

Critical raw materials (CRM) [1] are used in many products of great importance for today's society such as mobile phones (ex. Sb, Be, Ga, In and Pt), wind turbines (ex. Nd and Dy), solar panels (ex. Ga and In), electric vehicles (ex. La, Ce and Co), energy efficient light sources (In, Ga, Y , Eu) and lightweight alloys that save energy and can be used in the transport industry (ex. Sc and Mg). The supply of these metals is limited, and the needs are expected to increase drastically. There are also geopolitical aspects surrounding the availability of these metals and minerals. Being able to recycle these materials is therefore of great interest.

Crystallization is often used to separate different substances to produce intermediate concentrates or high-quality products. By adding an alcohol to an aqueous solution with a dissolved salt, salts can crystallize due to a reduced solubility in the new solvent mixture. This technique is called antisolvent (or displacement) crystallization and can be used to produce inorganic salts from aqueous solutions.[2] After separation of salt, e.g. distillation can be used to separate the alcohol from the aqueous solution and return these streams to the process. Research is underway on how this can be applied, and it has been shown that antisolvent crystallization can be used to separate rare earth metals from leachates in the recycling of rechargeable nickel metal hybrid batteries (NiMH batteries)[3] or to recover scandium from red mud [4]. The technique can also be applied to recover high quality sulphate salts of Ni, Mn and Co in recycling of lithium-ion batteries.

In this laboratory activity, students will investigate antisolvent crystallization. The laboratory can either be carried out as a demonstration of antisolvent crystallization or as an investigative laboratory / high school project where different solvents and / or salts are examined.

The lab activity is suitable for 14- 18 years old students.

Key words:

Raw Materials; Recycling; Hydrometallurgy; Chemical Engineering; Crystallization

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[1] COM(2020) 474 - Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability – 03/09/2020

[2] Moldoveanu G. A., Demopoulos G. P. (2015) Organic solvent-assisted crystallization of inorganic salts from acidic media, *J. Chem. Technol. Biotechnology*; 90: 686–692, Doi: 10.1002/jctb.4355

[3] Korkmaz K., Alemrajabi M., Rasmuson Åke C., Forsberg K. M. (2020). Separation of Valuable Elements from NiMH Battery Leach Liquor via Antisolvent Precipitation. *Separation and Purification Technology*, 234: artikel 115812, Doi: 10.1016/j.seppur.2019.115812

[4] Peters E., Kaya S., Dittrich C., Forsberg K. (2019). Recovery of Scandium by Crystallization Techniques. *Journal of Sustainable Metallurgy*, 5(1): 48- 56. Doi: 10.1007/s40831-019-00210-4

Extended background information

Antisolvent crystallization is a separation technique that can be applied in the laboratory and that is also applied in an industrial scale, e.g., as part of the production of certain pharmaceuticals.

Resource recovery from waste

Todays' society needs a lot of high technology equipment to function, e.g., batteries, electric motors, wind turbines etc. These often contain so called critical or strategic materials. Critical Raw Materials (CRMs) are economically and strategically important while there is a high risk that they will not be accessible for production in the near future. The European commission has put together a list of CRMs for the European Union. The updated list from 2020 contains 30 CRMs[1]. Examples of elements on the list are Li and Co, which are used in lithium-ion batteries and rare earth elements, which are used to produce strong permanent magnets that are needed for e.g., wind turbines.

If CRMs can be recovered from waste products there is less need for them to be mined and supply can be secured. Furthermore, recycling is promoted by the ambition to reduce waste and create a circular economy. There is a need to develop new sustainable processes and techniques to recover CRM from both primary (mining) and secondary (waste including end-of-life equipment) sources.

Crystallization

Crystallization is a technique to separate a substance in solid form (e.g., a salt) from a solution or a melt. This is the opposite of dissolution. When the concentration of the substance in the solution is higher than the saturation value (so called supersaturated) nucleation and crystal growth will proceed until saturation is reached.

Supersaturation can be generated by evaporating the solvent, cooling or heating (depending on the solubility curve as a function of temperature), adding a chemical to create a reaction or by adding a second solvent (antisolvent crystallization). An important part of a crystallization process is the control of the generation of supersaturation. In general, if nucleation occurs at a very high supersaturation many nuclei will form, while if the nucleation occurs at lower supersaturation fewer crystals will form. If the same mass of crystals is formed in a crystallization process the crystals will be larger if the number of crystals is fewer. Often the solution contains impurities that can be incorporated into the growing crystals. In general, the crystals will become purer if they are allowed to grow slowly. However, in an industrial process the crystals can't grow too slowly because it will decrease the productivity of the process and an optimization in productivity and purity must sometimes be found.

The principle of antisolvent crystallization is the addition of a second solvent so that the solubility of the compound to be crystallized will decrease. For example, if ethanol is added to a saturated aqueous solution of manganese sulphate, then crystals of manganese sulphate will form. This is

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because the solubility of manganese sulphate is lower in mixtures of the two solvents water and ethanol than in pure water. Rare earth elements (REE) are the lanthanides (La- Lu in the periodic table) together with Sc and Y. These elements are grouped together because they have very similar properties and are thus difficult to separate from each other. Alcohols are widely used in industry even if care must be taken since alcohols are flammable.

Learning outcomes

By the end of the activity the students will:

- Learn about separation processes applied for recycling of waste.
- Understand the principle of antisolvent crystallization.
- Know how to carry out antisolvent crystallization practically.
- Be aware of the importance of recycling of everyday-life devices.

Key Competence European Framework

Multilingual competence
S1. Ability to understand and interpret concepts, feelings, facts or opinions in oral and written form.
S5. Knowledge of vocabulary, grammar and language.
Mathematical competence and competence in science, technology and engineering
S4. Readiness to address new problems from new areas.
S5. Capacity for quantitative thinking.
Personal, social and learning to learn competence
S2. Identifying available opportunities.
Citizen competence
S1. Ability to effective interaction with other people.
Cultural awareness and expression competence
S1. Ability to turn idea into action.
S3. Ability to plan and manage tasks.
S4. Independence, Motivation and Determination.

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United Nations' Sustainable Development Goals

	1 NO POVERTY 2 ZERO HUNGER Enable access to basic services		10 REDUCED INEQUALITIES Equal access to global expertise
	3 GOOD HEALTH AND WELL-BEING Safe medical devices		11 SUSTAINABLE CITIES AND COMMUNITIES Sustainable urbanization
	4 QUALITY EDUCATION Access to education	✓	12 RESPONSIBLE CONSUMPTION AND PRODUCTION Responsible consumption and production
	5 GENDER EQUALITY Less hardship, more opportunities		13 CLIMATE ACTION Strengthen resilience, reduce disaster impact
	6 CLEAN WATER AND SANITATION Safe and affordable water		14 LIFE BELOW WATER Reduce marine pollution
✓	7 AFFORDABLE AND CLEAN ENERGY Energy – the golden thread		15 LIFE ON LAND Sustainable use of terrestrial ecosystems
	8 DECENT WORK AND ECONOMIC GROWTH Safety of workers and economic growth		16 PEACE, JUSTICE AND STRONG INSTITUTIONS Promote peaceful and inclusive societies
✓	9 INDUSTRY, INNOVATION AND INFRASTRUCTURE Resilient infrastructure and sustainable industrialization		17 PARTNERSHIPS FOR THE GOALS Better access to technology and innovation

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Lab Activity

Overview

The needed materials and the procedure are presented below. The lab can easily be adapted to other chemistries as is indicated in the materials section.

The lab is currently available in English and Swedish, but more languages will be added over time.

Material

Equipment:

2 Erlenmeyer (E) flasks (note the weight), pipette, filtration funnel and filter paper, magnetic stirring bar, magnetic stirrer plate, scale.

Chemicals:

Sulphuric acid (H_2SO_4), manganese sulphate, (or sulphates of K, Mg, Fe or Ce), concentrated ethanol (about 95%)

Procedure

1) Prepare 50 mL of a solution with 1 mol/L of a chosen element (Mn, K, Mg, Fe or Ce) in 100 g/L of H_2SO_4 at room temperature (about 20°C) in an E-flask. Weigh the flask before and after reagent addition. Mark the flask with A (sulphuric acid + element).
2) Fill 100 mL of ethanol in an E-flask. Weigh the flask before and after reagent addition. Mark the flask with B (ethanol).
3) Add a magnet to flask A and put the flask on a magnetic stirrer. Use the pipette and add 0.5 mL of ethanol from flask B to the sulphuric acid solution in flask A while stirring. Observe the solution for a few minutes.
4) Continue to add small portions of the alcohol (B) to the sulphuric acid solution (A) while stirring. Mark how much mass of alcohol is added as a function of time. Continue until a precipitate appears in the flask. Note the time. Continue to add alcohol in portions until an alcohol to initial sulphuric acid solution mass ratio of at least 2 is reached.
5) Filter of the solids.

For deeper investigation the quality of the crystals (e.g., crystal sizes) could be investigated after adding either all antisolvent at one or after adding the antisolvent very slowly dropwise, e.g., using a burette. To assess the quality of the crystals the time for filtration could be measured and compared. It is also possible to carry out the lab using mixtures of elements and investigate how this affects the obtained crystal products. Furthermore, the alcohol can be distilled from the aqueous solution and the alcohol and remaining acidic acid solution could be reused.

Discussion points

a) Why are the crystals forming when adding the alcohol?
Answer: the solubility of the salt in the new solvent mixture is lower.

b) Why is the rate of addition of antisolvent important?
Answer: The number of crystals formed at high supersaturation is higher than at lower supersaturation. Adding all alcohol at once will lead to many small crystals which could be difficult to filter off. Furthermore, the crystals could contain more impurities.

c) Which parameters can be important in an industrial process?
Answer: Stirring rate, rate of antisolvent addition, temperature, …

d) Which unit operations will you combine to build an industrial process to produce the crystals?
Answer: Crystallization, filtration of crystals, drying of crystals, distillation.

e) Could there be any point in adding a more dilute alcohol?
Answer: Yes, then you could generate supersaturation even slower. Furthermore, you can avoid a very high supersaturation locally (at the point of addition), which could otherwise lead to unwanted nucleation locally and a wider size distribution of the final product. A wider size distribution could lead to problems in washing and filtration of the crystals and thus make the product more impure.

f) …

Learning Pathway

Step 1- Time & Activity: 40 min -Teacher gives a short introduction on CRMs and their importance in the transition to a more sustainable society. The teacher also explains the principle of antisolvent crystallization. Furthermore, the teacher informs about the risks of using the chemicals and appropriate protective wear (e.g., goggles and gloves) and procedures in case of accident (according to the local guidelines of handling the chemicals used and the published safety data sheets under the EU's REACH regulation).

Step 2 – Time & Activity: 20 min - Students are divided into groups (maximum 5 students in each group) and read the instructions to understand how to carry out the lab. The teacher answers any questions the students might have and make sure that each group knows how to carry out the lab safely.

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Step 3 – Time& Activity: 90 min – Carry out the lab.D

Step 4 – Time& Activity: 30 min – The points a-e above are discussed in the class.

Evaluation

Possible questions for assessing the learning of some key concepts:

1. What are CRMs?
2. Why are CRMs so important?
3. Indicate at least three CRMs and examples of applications?
4. What is the principle of antisolvent crystallization?
5. Propose two different methods to separate a salt dissolved in a solution.
6. Which parameters are important to control in an antisolvent crystallization process and why?

Acknowledgement

KTH thanks Dr. *Marie Danielsson* at House of Science (Vetenskapens hus) in Stockholm (Sweden) for the valuable collaboration in developing and testing this lab. activity.
In addition, KTH thanks EIT Raw Materials for funding the work within the scope of the RM@Schools project.

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