Teachers' Card

Separation of copper and iron: two different approaches

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General Introduction

This module illustrates method to separate metals one from another. This is a very important task in refining primary raw materials as well as recycling. Students are shown that efficient recycling is a fascinating and complex work field that offers many opportunities. What the students should do is a lab activity.

In this module we focus on topics, used during Chemistry:

- Solubility
- Reaction equations
- Qualitative analysis

Further topics

- Law of mass action
- Acid – base reactions
- Equilibri

Key words:

Recycling, Sustainability, Chemistry

Extended background information

We should recycle, especially electric and electronic equipment waste on a very high level, because the world population is increasing rapidly, nearly threefold during the last sixty years, from 2.5 billion people in 1950 to 7.79 billion (2019), while, parallel, the resource consumption per capita accelerated on an even higher rate: Iron ore consumption increased 11-fold, copper ore sextupled, the aluminium consumption increased by a factor of 30 while the world population grew by a factor of three. These numbers indicate that our habitat became a secondary deposit for many metals.

There are a couple of reasons driving the recycling industry. Economic reasons drive the precious metal recovery. Precious metal containing wastes are a valuable good because the concentration of the metals of interest in the end-of-life devices is very often much higher compared to primary ores. Therefore recovery from wastes is much more cost effective than mining for primary minerals.

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In contrast to this example, for many waste streams, for example household waste there is no economic incentive which could trigger recycling activities. But due to ecological and socio-political reasons recycling often makes sense. Mining operations always have a high freshwater demand but unfortunately major deposits are often located in arid areas. Therefore agriculture and livestock breeding compete with mining operation for scarce supplies of freshwater and space. Furthermore the conservation of the environment's natural state is important for the indigenous population in areas where tourism is an important source of income. Will the incentive for mining be decreased by partial supply with secondary products derived from recycled waste? In Germany Steel-, Aluminium- and Glass-Production is up to 50% fed by secondary raw materials. The following simple equation summarizes this idea:

primary mining = total demand – secondary raw materials

But economists argue from a different angle of perspective: While the demand from the highly industrialized countries decreases, the price is lowered as well, sending new demand incentives to buyers who couldn't afford this supply for their purposes before (Rebound effect).

Another reason for increased interest in recycling is a rather selfish one from a general point of view. By depositing waste without further treatment not only valuable materials are lost but hazardous substances are released into the environment uncontrollably. Therefore recycling as a part of an overall waste treatment strategy contributes to the protection of human health and the conservation of an environment suitable to live in.

Long story short: Recycling is useful, more Recycling (in total) would be desirable – but we need to keep good measure. Too much focus on material recovery often is misleading because the high energy and chemicals input in recycling processes are underestimated too easily. For every material, there is an ecological and economical optimum that has to be determined under the given circumstances. If the recovery of a given resource has a higher energy demand and/or has a higher impact on the environment than primary mining, it becomes obsolete or better: It causes more damage than it prevents (Rainer Bunge).

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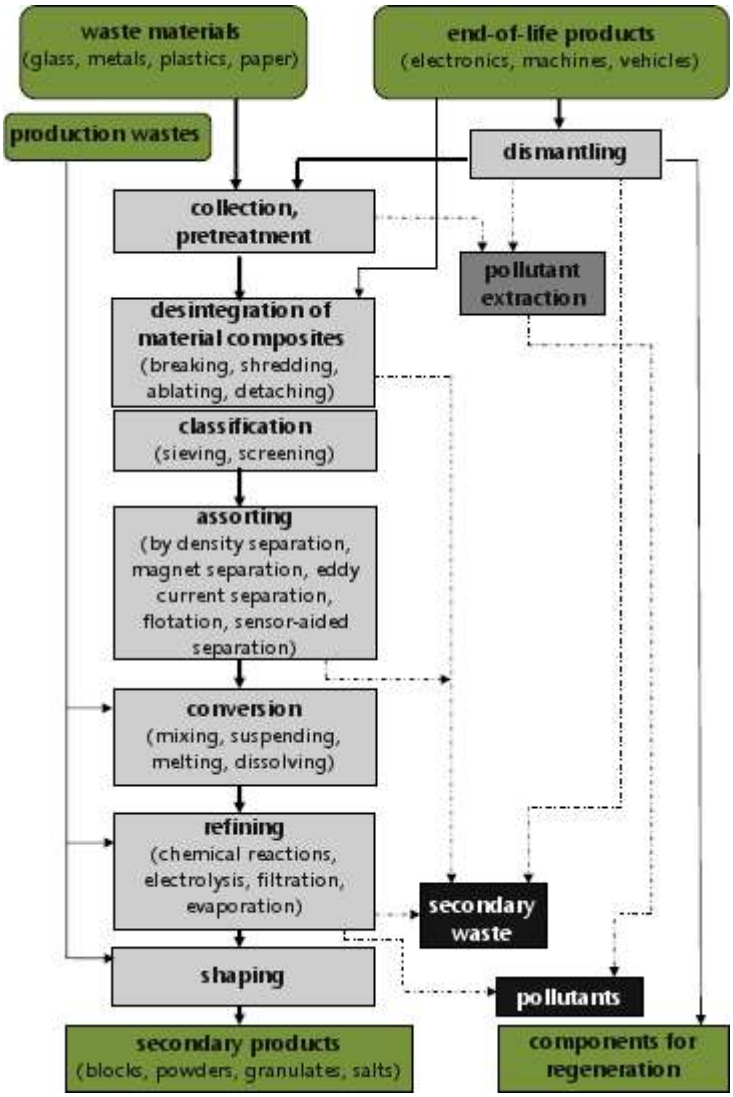

Recycling always aims for the production of secondary raw materials from "wastes" that can compete with primary raw materials in terms of quality and can be manufactured cheaper than or equally to the primary raw materials themselves. During the processing some components of the processed material as well as undesirable impurities and interfering substances make it harder to meet the standards of quality. In all steps of the process special attention has to be paid to these issues. Another objective is the reduction of the environmental impact of the raw material production compared to the primary production. This is an important criterion on the evaluation of recycling processes.

Collection and dismantling are always the first steps in the process chain. An important objective of the dismantling step is the recovery of spare parts and directly reusable components. The

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collection of waste materials (glass, paper) and end-of-life products (electronics, vehicles) can be accomplisheddifferently, distinguished by the logistical approach (e.g. at every home, close to home, regional). On the one hand it is helpful for further processing to have material streams of low complexity or pure materials. On the other hand this increases the costs for logistics dramatically. Compromises have to be made.

Especially in the treatment of end-of-life products like electronic devices, disintegration is highly important. In this step the connections between components and building blocks of the devices as well as connections between different materials are destroyed by breaking, cutting, shredding, ablating or detaching. This is needed to be able to enrich particular substances in separate material streams for further processing.

For this enrichment, the materials mix is separated by the different physical properties of the different substance groups. To achieve the best result in the separation steps, some requirements have to be fulfilled. For example for the density separation, the particles have to have approximately the same size so that differences in density are not compensated by the difference in mass of the particles caused by varying particle sizes. To separate the shredded material in fractions of narrow grain size distributions, classifying techniques such as sieving are used. To meet technical and economical requirements, process parameters such as the design of the sieving machine as well as the retention time can be varied.

Separation techniques include density separation, ferromagnetic separation, eddy-current separation, and electrostatic separation. In this processes, the classified materials are separated into concentrates that are processed further in the conversion step. As an example, one can derive a concentrate of non-ferrous metals from electronics waste by combining magnetic separation and eddy-current separation. First, ferromagnetic materials, containing all sorts of Iron-, Cobalt- or Nickel-alloys are removed by a ferromagnetic separator, next the conductive materials (non-ferrous metals) are separated from the resulting stream by an eddy-current separator. The resulting concentrate mostly consists of copper but precious metals and many metals of technological importance are found in this concentrate. The latter are used in low concentrations but are of crucial importance for the functionality of many modern electronical devices.

The concentrates produced in the last step can be combined with other components and relatively pure waste materials from other sources (e.g. production scraps) and processed in pyro-metallurgical (smelting) processes. Refining processes are used afterwards to separate pure materials from the resulting alloys by utilization of the chemical behaviour of the different metals. In this step, electrolysis, precipitation and leaching, crystallization and ion-exchange processes on solid or liquid phases (solvent extraction) are applied.

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Learning Outcomes

- The student will learn how to handle some chemicals and laboratory equipment
- The student will realise, that recycling helps to safe resources

Key Competence European Framework

Multilingual competence
S1. Ability to understand and interpret concepts, feelings, facts or opinions in oral and written form.
S2. Ability to express concepts, feelings, facts or opinion in oral and written form.
S4. Ability to interact in an appropriate and creative way in any situation.
S5. Knowledge of vocabulary, grammar and language.
S7. Ability to use technical language accordingly to the field of work.
Mathematical competence and competence in science, technology and engineering
S1. Ability to use constructed thinking in order to solve a problem in every situation.
S4. Readiness to address new problems from new areas.
S5. Capacity for quantitative thinking.
S2. Basic skills in ICT
S3. Understanding the role, opportunity and risks related to ICT in everyday life.

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

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	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

Contents – Theoretical principles

Precipitation and leaching

A more or less complex mixture of metal salts can be separated in the pure salts using a sequence of reactions causing some components to precipitate. In case that the resulting precipitate contains more impurities than the target materials, often these impurities can be dissolved again under varied conditions. Another strategy is the precipitation of a mixture, containing the target material and to leach the target material selectively afterwards. This strategy is utilized in gold mining operations where gold is leached using cyanides.

In this experiment, the principle of metal separation through a sequence of precipitation and leaching steps is illustrated with a mixture of iron and copper salts. Generally iron and copper can be separated by altering the pH-value of an aqueous solution due to the different but in both cases highdependency of the solubility on the pH-value.

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Precipitation and leaching in copper recovery

The hydrometallurgical approach for copper recovery is preferred over pyro-metallurgical processes in the case of low copper content in the feed material or the recovery from composites that can't be broken apart in the common mechanical processing. For leaching of copper from the feed material selectively, ammonium carbonate solution can be used:

$$2\,Cu + O_2 + 4\,NH_3 + 2\,(NH_4)_2CO_3 \rightarrow 2\,[C(NH_3)_4]CO_3 + H_2O$$

In this process, copper is leached together with nickel from ceramics, plastics and iron. The resulting complex can be destroyed on heating. On distillation, the complex dissociates and ammonia can be recovered. Copper precipitates in the form of its hydroxide and oxide. After filtration and drying, this copper-rich precipitate can be combined with other material streams in pyro-metallurgical copper refining.

Ion exchanging

In chemistry there are known different types of bonds between atoms. One of them is an ionic bond which is involved in the formation of salts. As you may remember from the first experiment, dissolved ions can form substances different than the starting materials in chemical reactions. Ion exchangers are organic substances that can do the same thing. They contain an ion that can be exchanged for another one without altering the remaining organic molecule. Here a Cation exchanger, in solid form is used to separate iron from copper.

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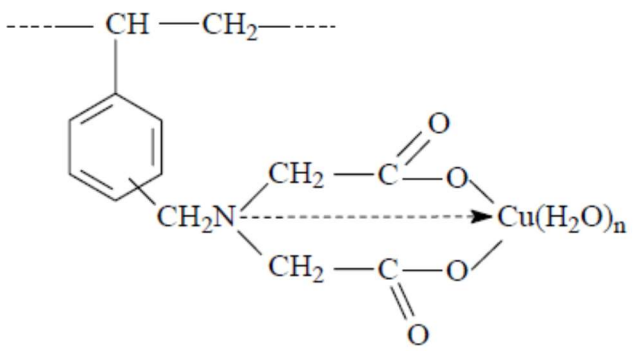
The ion exchanger used in our tests is Lewatit TP 207 with CAS no. 57285-14-0 from Bayer AG. It is a macroporous, weakly acidic ion exchange resin based on a styrene-divinylbenzene copolymer. The active sites consist of iminodiacetic acid groups, which form chelate complexes with divalent metal ions with graded stability, thus allowing selective separation of metal ions. The formation and stability of the complexes correspond to the following order:

Copper > Vanadium > Uranium > Lead > Nickel > Zinc > Cobalt > Cadmium > Iron (II) > Berylium > Manganese > Calcium > Magnesium > Strontium > Barium > Sodium

and the coordination is shown in the figure:



1. What happens when NH_4OH solution is added to the first eluate?

When NH_4 - OH is added, the pH value increases significantly. Iron-II-hydroxide is formed, which precipitates as a white solid or causes turbidity of the previously clear solution. The solid may be yellow to brown in colour due to the presence of trivalent iron in the starting material. As there is no copper in the eluate, there is no blue colouration.

2. $Fe^{2+} + OH^- \longrightarrow Fe(OH)_2$

Lab Procedure

Precipitation and Leaching

Place a sample of the solution A and B in separate test tubes (approx. two cm high). Now add sodium hydroxide solution dropwise with a pipette to both of the test tube. Now filter the contentof the test tubes. Collect the residue on the filter papers in fresh test tubes and add ammonia solution dropwise with a pipette. Now place a sample of solution C in a fresh test tube and repeat the steps mentioned above.

Ion exchanging

Lab Procedure Teachers Card

The preparation of the ion exchanger is preferably carried out by the teacher in advance. The Lewatit TP 207 ion exchanger is first stored overnight in demineralized water in the delivery form. The watered material is then filled into a chromatography column with frit, free of air bubbles. For this purpose, the column is attached to a stand by means of clamps. After attaching a dropping

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funnel, the column is conditioned by exposing it to 0,5 mol $\times L^{-1}$ sulfuric acid, which causes the Na form to change to the H form. The column is then rinsed with demineralized water until the eluate is neutral.

Separation

The feed solution is poured into the dropping funnel attached to the stand above the chromatography column. Then allow the solution to drip slowly into the column, adjusting the outlet so that the liquid level in the column remains constant and the inlet front is parallel to the surface. The eluate is collected in a beaker.

The column is then rinsed with demineralised water.

The ion exchanger is regenerated by rinsing with 1mol $\times \mathrm{L}^{-1}$ sulphuric acid until the ion exchanger shows no colouration, this eluate also being collected in a beaker.

The column is then rinsed with deionized water until pH neutral.

Detection reactions

1. Eluate

Add a few drops of NH_4OH solution to a sample of about 2 ml of the first eluate.

A second sample is mixed with a few crystals of potassium ferricyanide (III).

2. Eluate

Proceed in the same way with samples of the second eluate.

Learning Pathway

Step 1- Time & Activity: 30 minutes - Teachers give a short introduction

Step 2 – Time& Activity*: 120* minutes- Students carry out the experiments

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Evaluation

Module 1 – Precipitation and leaching

What happens on addition of sodium hydroxide? Postulate reaction equations for each sample?

The addition of sodium hydroxide causes the formation of iron(III) hydroxide in the presence of iron (A) and copper hydroxide (B), both insoluble, following these equations:

$$Cu^{2+} + SO_4^{2-} + 2Na^+ + 2OH^- \rightarrow Cu(OH)_2 \downarrow + Na_2SO_4$$

$$Fe^{2+} + SO_4^{2-} + 2Na^+ + 2OH^- \rightarrow Fe(OH)_2 \downarrow + Na_2SO_4$$

What happens on addition of ammonia solution to the filter residues?

The addition of ammonia has no effect on the precipitated iron salt. In the presence of copper, a dark blue, readily soluble complex, Tetraamminecopper(II) hydroxide is formed, following this equation:

$$Cu(OH)_2 + 4\,NH_3 \rightarrow [Cu(NH_3)_4](OH)_2$$

The complex cation differs in its chemical and physical properties from the bare copper-ion. This is easily observed due to the colour changing.

Can you think of an easier procedure to get to the same results for solution C?

The addition of sodium hydroxide causes both elements to form precipitates as mentioned above. Therefore this step is not very selective if not performed very carefully. So this step might be skippedand the addition of ammonia solution is used to form the soluble copper complex and the insoluble iron(III) hydroxide in one step. Separation would be achieved by filtration and washing of the residue.

Module 2 – Ion exchange

Why is a macroporous structure important for ion exchange?

The macroporous structure offers a large internal reaction surface. The liquid flowing past can diffuse into the pores and release the copper ions at the reactive groups to the ion exchanger, which in turn releases H^+ ions.

What happens in the exchanger column, where does the blue colour come from?

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As described, copper ions are bound to the ion exchanger. Copper ions are coloured pale blue in aqueous solution (aqua complex). At the ion exchanger the complexation state changes, because chelate complexes are formed with the reactive groups of the ion exchanger. This makes the colour more intense because the ligand is stronger.

Description of Student's Cards

Student's Card 1 – Precipitation and leaching

Student's Card 2 – Ion Exchange

Sources

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