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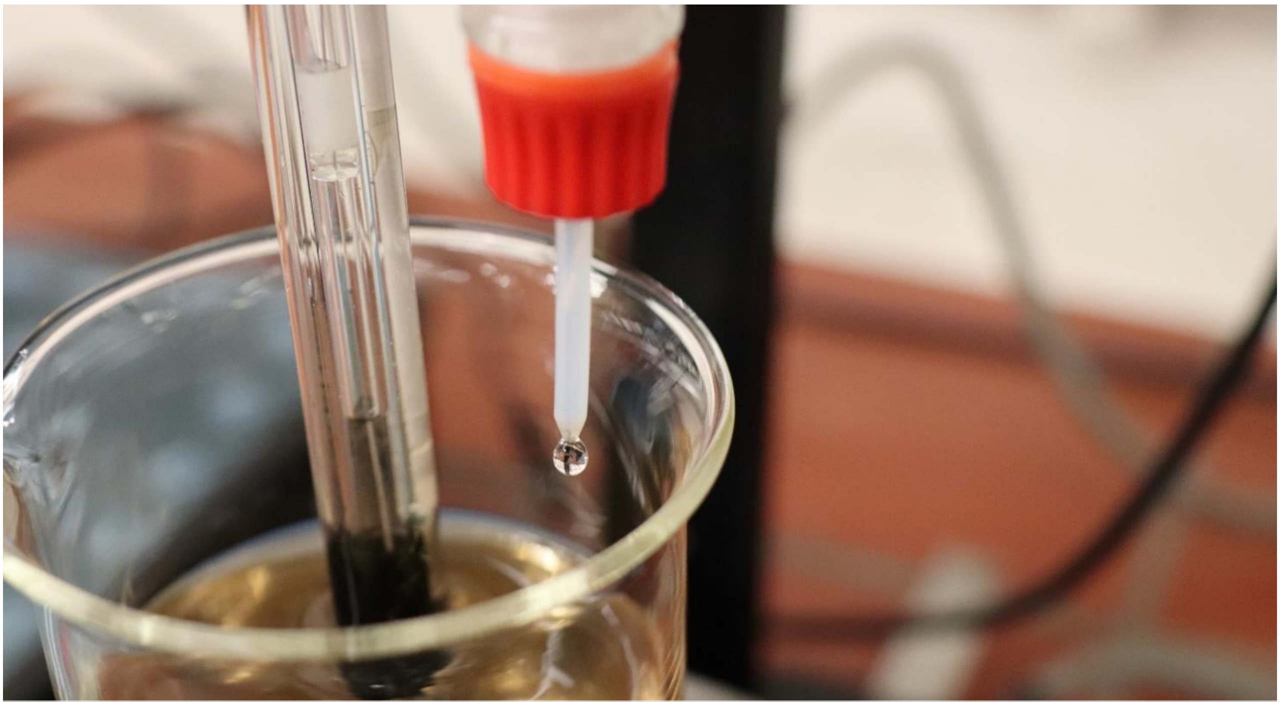

Removal of heavy metals from wastewater, e.g. chemical precipitation in the automotive industry

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General Introduction

Without water, there would be no life and no food. Fresh water is a scarce resource in many countries. Consumption has risen sharply and is reaching its limits, exacerbated by climate change and population growth. [1]

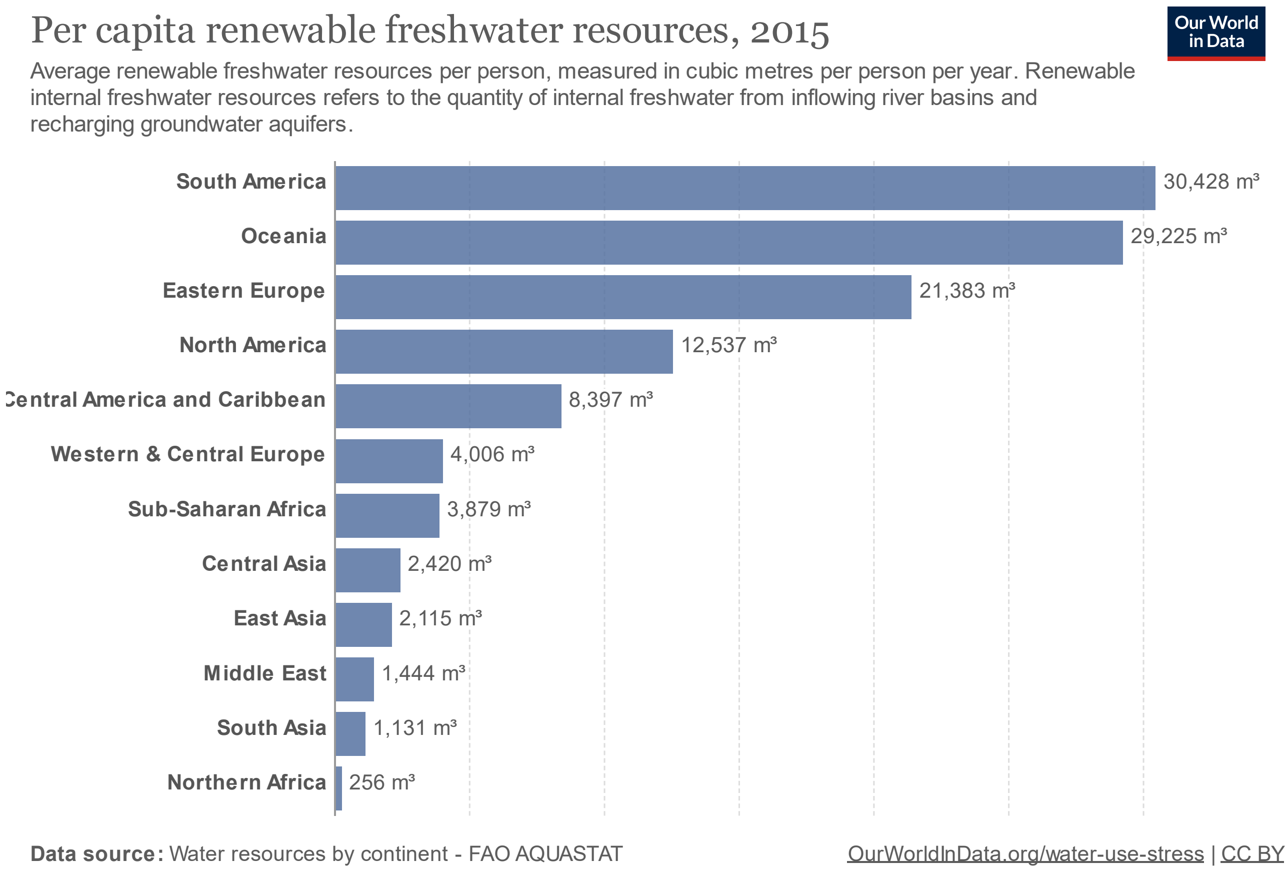

Figure 1 Clean water technologies will be urgently needed to increase production for growing populations in many countries.

[1] https://ourworldindata.org/water-use-stress ; https://www.imperial.ac.uk/news/249415/climate-change-blame-devastating-drought-syria/

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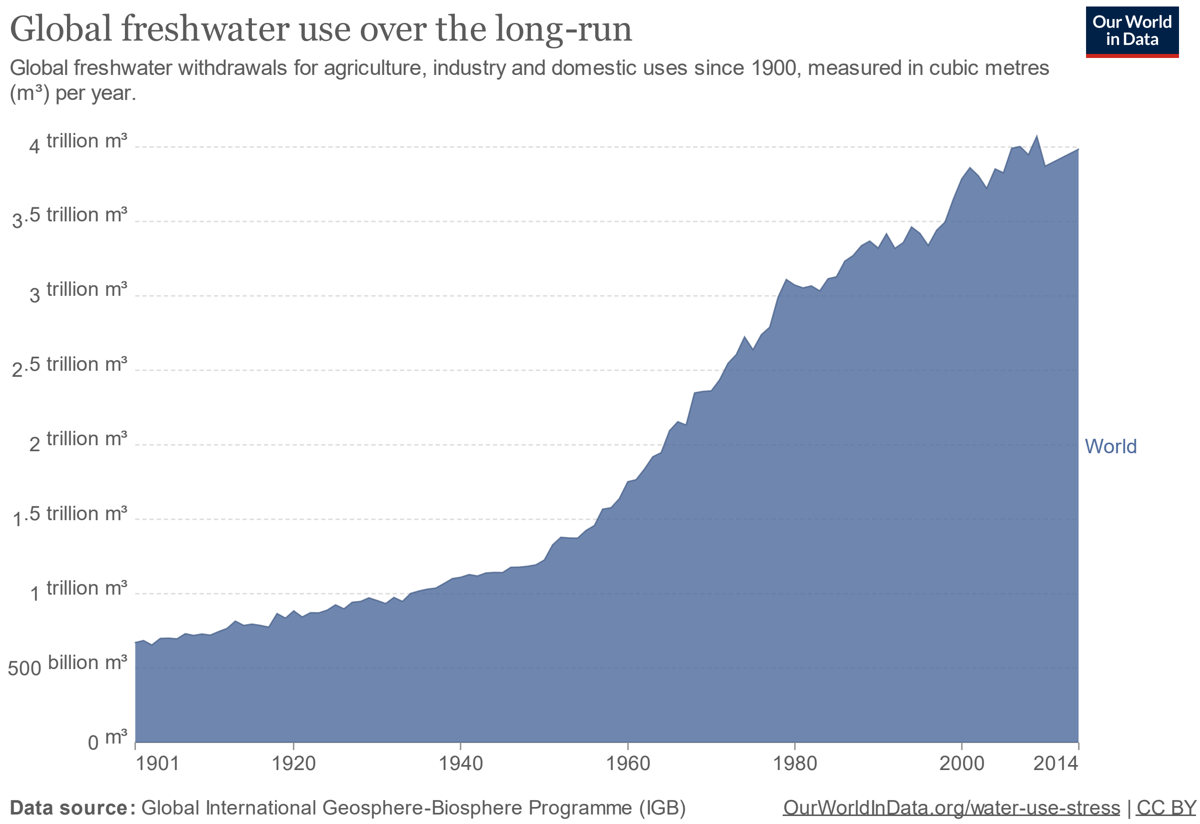

Figure 2 Even as the world's population grows, the amount of fresh water available seems to be reaching a ceiling. This is most likely not due to increased efficiency, but to scarcity.

This course deals with a partial aspect of wastewater treatment in the automotive industry and carries out the heavy metal hydroxide precipitation in a model experiment on manganese and, after filtering the Mn(II) hydroxide, shows a qualitative negative proof of the precipitation success in the filtered "wastewater". In the specific practical example presented here, the heavy metal hydroxides produced as solids are not recycled. A valuable resource, process water, can be recycled. The metal ion load (Fe, Ni, Mn, Zn) of the rinsing and spent active baths must be precipitated, extracted, thickened and disposed of, in the specific practical example (VOLKSWAGEN AG, Wolfsburg, Germany) in an underground landfill.

Keywords:

Corrosion protection, metal ions as Lewis acid, hydroxide precipitation, (current) limits of wastewater recycling in a special field

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Extended background information

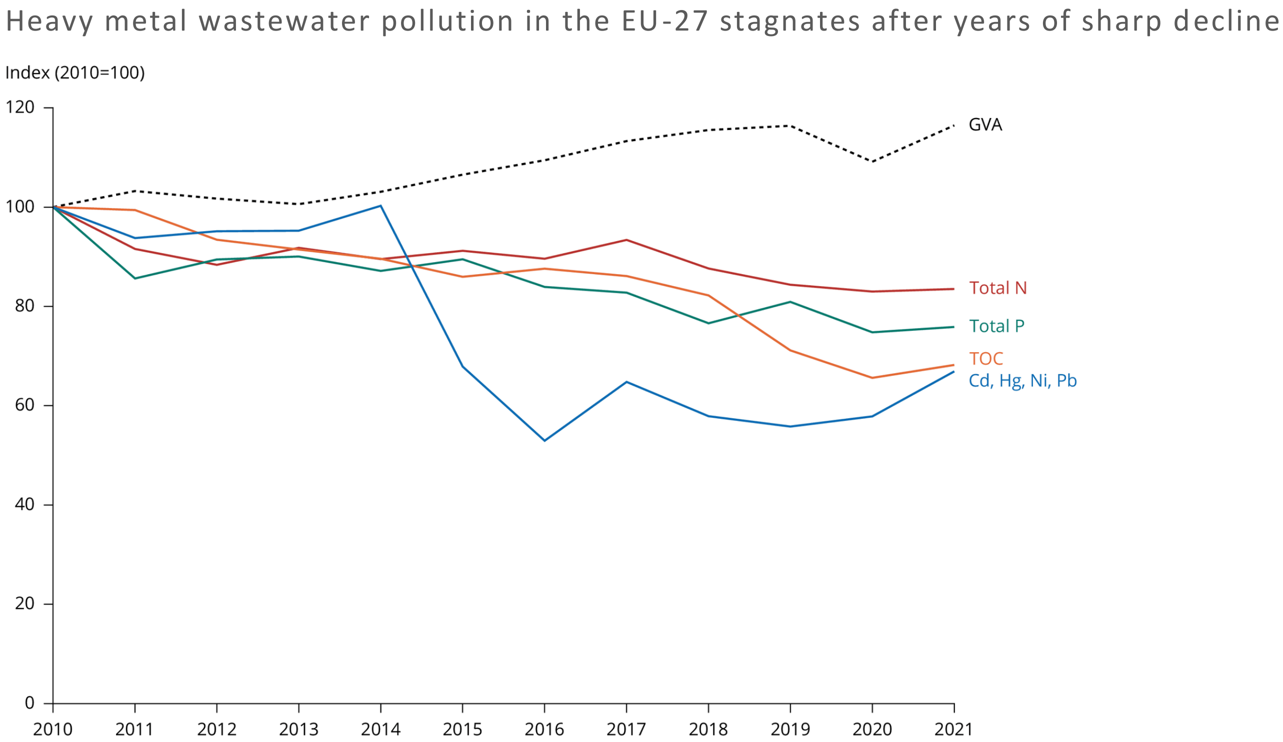

Figure 3: Heavy metal pollution from industrial processes in the EU-27, source European Environment Protection Agency, April 2023

A reduction of 40 %, especially of the particularly hazardous heavy metal loads in wastewater, with a simultaneous increase in gross national product of 16 % in the same period (GVA line in Fig. 1) is pleasing, as it shows that progress is possible. Further efforts are needed, as only 40 % of water bodies in Europe are in good ecological condition and only 35 % are in good chemical condition. The valuable resource of water is also under pressure in Europe, as the European Environment Agency has recognized.

54 % of water abstraction in Europe is for industrial activities. Using the automotive industry in Germany as an example, the following section explains why heavy metals end up in wastewater and how they are removed. As the removal of heavy metals from wastewater by means of precipitation as hydroxide has a success rate of more than 99.9%, it is immediately understandable why heavy metal pollution from industrial wastewater has fallen over the last decade and a half. This learning unit provides the chemical background to this success story.

75 % of heavy metal pollution in water bodies in Germany no longer comes from industrial direct dischargers, but from diffuse sources in urban areas and is carried into rivers by rainwater. [1,2] At this point, students can research the development of heavy metal emissions for their city or region from reputable internet sources under the guidance of their teachers, provided there is time for this project, for example as part of a project week including an excursion to a wastewater

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treatment plant. We recommend this source: https://industry.eea.europa.eu/explore/explore-by-pollutant/

Main insight here, here as an example related to Germany:

Shift of the main emitters from industry to diffuse sources with simultaneous massive reduction of both dust and gaseous heavy metal emissions as well as heavy metal emissions in wastewater. [3]

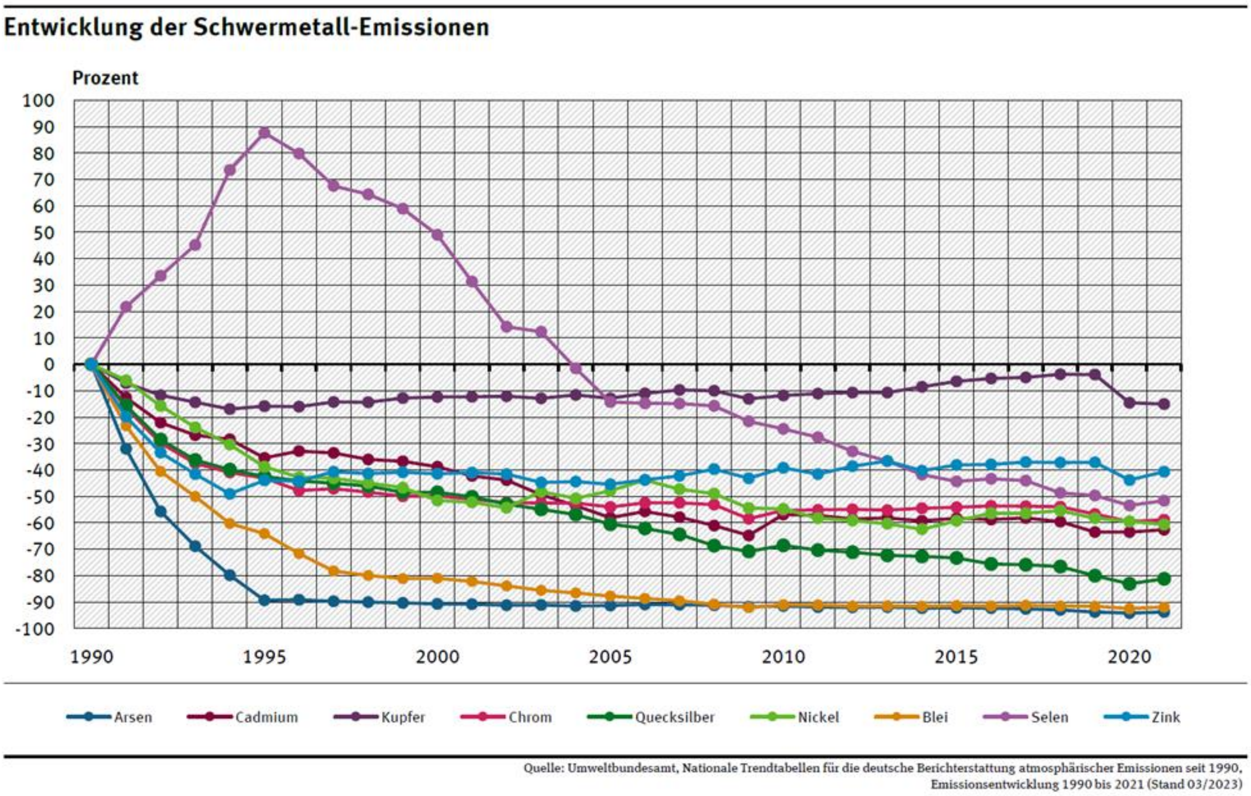

Figure 4 After years of a significant decline in emissions (1990-2005), heavy metal emissions in Germany are stagnating. The disproportionately strong decline in lead, mercury and cadmium emissions is due to legislative initiatives; the stagnation in copper, zinc and nickel is partly due to an increase in traffic (including brake and tyre abrasion). [2]

[2] https://www.umweltbundesamt.de/themen/luft/luftschadstoffe-im-ueberblick/metalle-im-feinstaub/nickel-im-feinstaub#emittenten und https://www.umweltbundesamt.de/daten/luft/luftschadstoff-emissionen-in-deutschland/schwermetall-emissionen#entwicklung-seit-1990

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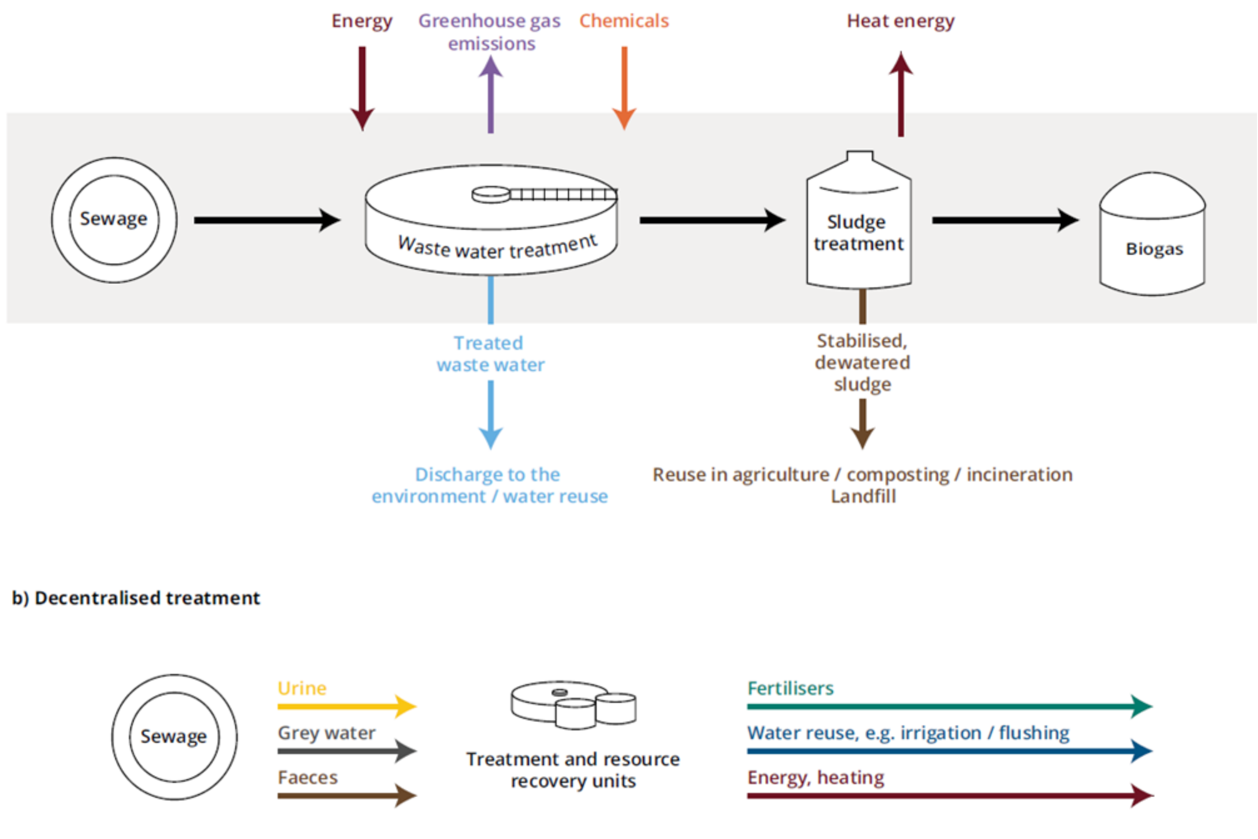

Figure 5 Sewage treatment plants require energy and chemicals. In addition to the high quality of the treated water, it is also desirable to use the nutrients in sewage sludge as fertiliser. Due to concerns about pollutants, including heavy metals, in sewage sludge, its use is being restricted in several European countries. The report from which these images are taken looks at possible solutions.[1]

How do heavy metal ions get into process wastewater from the automotive industry?

In the automotive industry, the bodyshells are immersed in a phosphating bath containing a mixture of iron, zinc, nickel and manganese ions in particular. The first step is pickling. The acid attack breaks down adhering oxide layers and, in the case of steel bodies, dissolves iron ions to form hydrogen:

$$Fe + 2H^{+} \rightarrow Fe^{2+} + H_2 \uparrow \qquad (1)$$

The iron ions now form iron phosphates with the anions of the phosphoric acid. Hydrogen ions are consumed, the pH value rises in the immediate vicinity of the surface and the concentration of phosphate ions also increases. If the solubility product of the primary phosphate is exceeded, it precipitates on the surface. Phosphoric acid can dissociate in three stages. Accordingly, three iron(II) phosphates are possible:

- Primary iron phosphate: $Fe(H_2PO_2)_2$
- Secondary iron phosphate: $FeHPO_4$ und
- Tertiary iron phosphate: $Fe_3(PO_4)_2$

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The layer-forming tertiary phosphate forms on the nuclei of the surface. When a certain layer thickness is reached, the access of free acid to the metal surface is no longer possible and the pickling reaction is complete. If the solutions also contain zinc, manganese and nickel salts, corresponding phosphate layers are deposited. [3] In combination with other bath parameters, this creates a corrosion-resistant, dense and low-friction protective layer. [6-8] The exact composition of the bath is usually a trade secret.

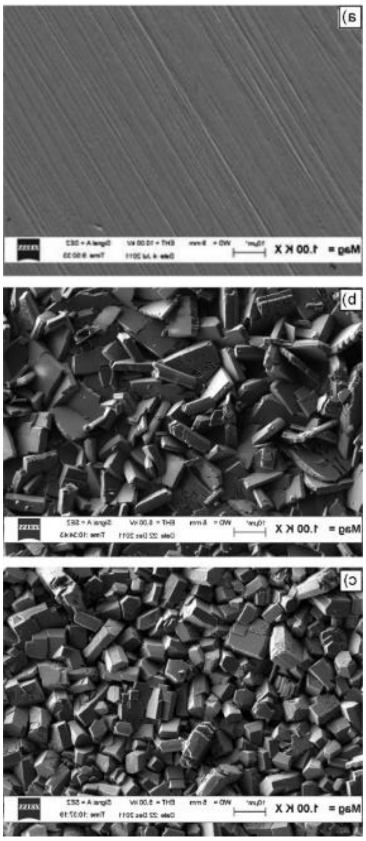

Figure 6 An example: steel surface before phosphating, (b) after phosphating without nickel addition, (c) with nickel as a catalyser - the surface coating is denser and has finer crystals. Source: [2]

Wastewater comes from two sources. Firstly, the active baths are contaminated by impurities and accompanying reactions (e.g. sludge formation). Then, according to the feed and bleed principle, fresh solution is added and old solution is removed; the latter becomes effluent. Secondly, the car bodies are rinsed before and after treatment. Both wastewater streams are fed into the plant's own wastewater treatment system before being mixed with fresh water to reduce the neutral salt concentration and returned to the process water cycle or discharged into a receiving watercourse. [3]

[3] *"Since the phosphate layers are deposited from a liquid film that is in constant exchange with the entire bath volume, the phosphating bath must be chemically composed in such a way that it is in or at least close to the heterogeneous solution equilibrium of the layer-forming substance."* (translated, originally German) [5] An understanding of heterogeneous solution equilibria is not necessary for the objective of this learning unit - wastewater treatment by heavy metal hydroxide precipitation - and is therefore excluded here.

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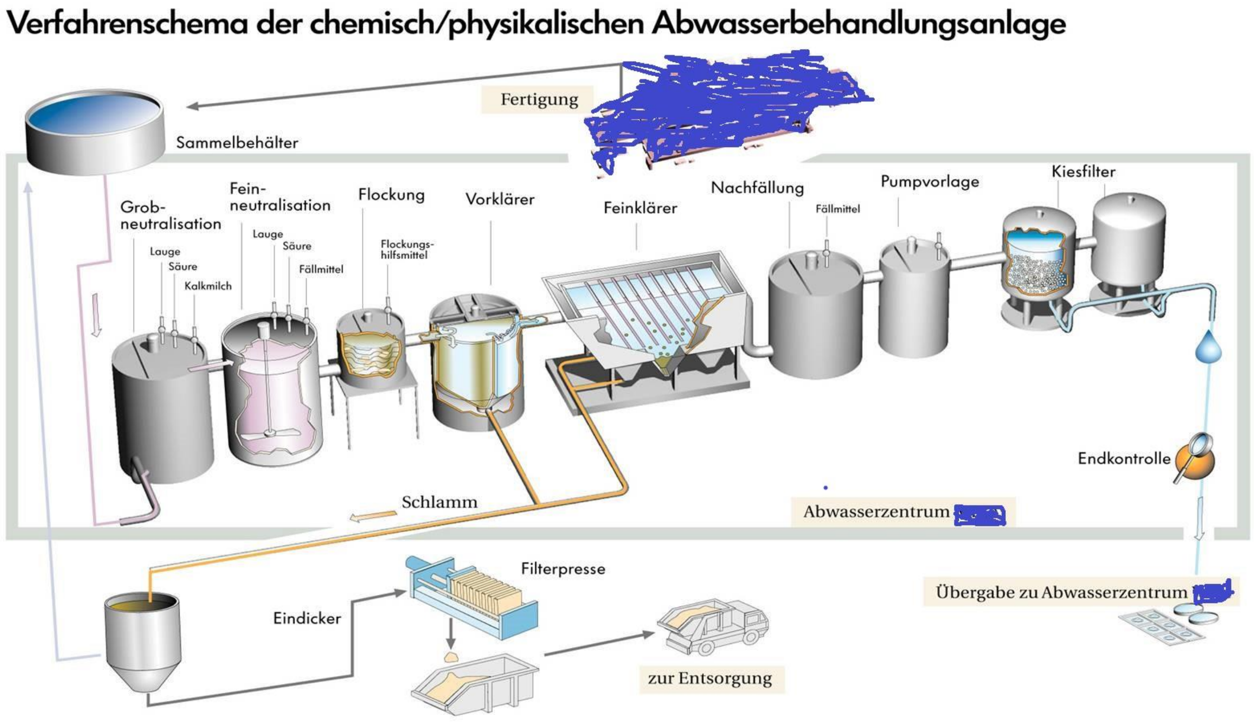

Figure 7 Wastewater treatment at the Volkswagen AG plant in Wolfsburg. Image courtesy of VW AG. Exact location name made unrecognisable at the request of VW AG. The German designations are explained in the following text.

Explanation of process steps in figure 7

The waste water from the pre-treatment of the carcasses before painting is channelled from production into a collection tank. From there, it enters an initial coarse neutralisation process ***(“Grobneutralisation”***). Here, $NaOH$ and $Ca(OH)_2$ are added to the acidic wastewater containing metal ions to initiate initial neutralisation. These flocs settle in the primary clarifier ***(“Vorklärer”)*** (solids sink) ***(“Feststoffsenke”)***, where a large proportion of the sludge is removed from the top of the hopper and conveyed for sludge treatment. This is followed by the fine clarifier ***(“Feinklärer”)*** (lamella clarifier) (***“Lamellenklärer”)*** and secondary precipitation, in which organosulphide is used if necessary. This is to be regarded as a kind of "police precipitation" if nickel is still measured above the desired effluent concentration. A gravel filter (***“Kiesfilter***”) is installed before the final inspection (also monitored online for Ni). The purified wastewater is conveyed to the biological treatment plant, where it is treated further. After dewatering using a thickener ***(“Eindicker”)*** and chamber press (**“Kammerpresse”),** the heavy metal hydroxide sludge (***“Schlamm”)*** is transported to an (underground) landfill. In principle, "sulphur-containing precipitants such as sodium sulphide, organosulphides, polysulphides or mixtures of different precipitants are used as precipitants [for this field of wastewater treatment]." [3]

Because heavy metal ions above a certain level are harmful to health and/or to flora and fauna, Germany has set limit values for them in wastewater; for nickel this is 0.5 mg/L, for zinc 0.2 mg/L and for manganese a limit value of 0.08 mg/L is recommended, especially for infant nutrition.[4]

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In this unit, the removal of manganese ions from wastewater is investigated experimentally. The aim of the experiment is to show qualitatively that heavy metal ions can be almost completely removed from wastewater by precipitation as hydroxide; the concentration of the neutral salt load can only be reduced by adding fresh water. A high proportion of process water can therefore be recirculated.[4]

When solutions containing nickel sulphate are precipitated with NaOH, milk of lime or soda, precipitation starts uniformly at pH values just below 8. Precipitation up to 0.5 mg/l is only possible at pH values above 9.9; if only nickel is present in the solution, pH values well above 10 must be reached to achieve precipitation up to 0.5 mg/l. [3]

The precipitation of all three conductive elements, zinc, nickel and manganese, is successful with rates above 99.9%. We chose manganese for the experiment because the qualitative success of the precipitation reaction can be demonstrated with a simple detection reaction.[5]

Glossary *(if necessary)*

Waste water treatment in the automotive industry – exemplary heavy metal hydroxide precipitation.

Learning Outcomes

At the end of the lesson the students will be able to:

- Explain the need for phosphating baths in the automotive industry
- Give an example of the chemical formula of heavy metal hydroxide precipitation
- Recognize that one circular economy process – clean water technology – is combined with one solid toxic waste stream – the precipitated heavy metal hydroxides
- Recognize the progress made in the field of water quality protection

Key Competence European Framework

Literacy competence

[4] The heavy metal hydroxides that precipitate together accumulate at Volkswagen AG in Wolfsburg, Germany as hazardous waste that must be disposed of. Lecture for the student group of the chemistry course, Gymnasium Fallersleben on 27 June 2023 Dipl.-Ing. Florian Lehnert and Dr. Frederike Drawert, Volkswagen AG.

[5] Zinc ions could be detected as zinc salts with a Co (II) compound at high temperature in a characteristically green product as "Rinmann's green", an experiment which is not suitable for school experiments due to the toxicity of Co. The detection with potassium hexacyanoferrate is only possible in hydrochloric acid solution buffered with acetate, but the precipitation of the heavy metal hydroxide takes place with the addition of $NaOH$ and $Ca(OH)_2$ in the pH range 8.5 - 11. Me^{2+}cations would have to be quantitatively separated beforehand, which means that this method cannot be used due to Ca^{2+}ions from the added milk of lime.

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S3. Ability to interpret the world and relate to others.
Multilingual competence
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.
S2. Understanding of mathematical term and concept and know how to apply it.
S5. Capacity for quantitative thinking.
S6. Ability to extract qualitative information from quantitative data
S7. Ability to formulate problems mathematically and in symbolic form so as to facilitate their analysis and solution.
S8. Ability to design experimental and observational studies and analyse data resulting from them.
S9. Ability to formulate complex problems of optimisation and decision making and to interpret the solutions in the original contexts of the problems

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

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✓	Energy – the golden thread	✓	Sustainable use of terrestrial ecosystems
	Safety of workers and economic growth		Promote peaceful and inclusive societies
✓	Resilient infrastructure and sustainable industrialization		Better access to technology and innovation

Contents – Theoretical principles

The model wastewater solution must be prepared (molecular mass). The (first!) change in pH (Lewis acid and Lewis base, metal-water complex) should be understood, as well as the precipitation of heavy metal hydroxides by the addition of $NaOH$ and, in the case of amphoteric zinc, by the additional addition of $Ca(OH)_2$The qualitative, in our case negative, proof that "this solution no longer contains (?) Mn^{2+}-ions requires an understanding of redox reactions. The (?) represents a brief reflection on the specific example: I don't see any precipitated solid, does this mean that none has precipitated in the solution? The limits of qualitative testing are the limits of observability.

Lab Procedure/Activity

In the automotive industry, body shells are immersed in phosphating baths to protect them from corrosion. In aqueous solutions, the main components of which are $Zn^{(2+)}$ Mn (2+) and Ni(2+) and phosphate, chemical reactions create a thin layer that significantly slows down corrosion and at the same time makes painting easier. However, before the car bodies enter the paint shop, they have to be rinsed off, which carries heavy metals into the rinsing water. Content: The course carries out the heavy metal hydroxide precipitation in a model experiment on manganese and, after filtering off the Mn(II) hydroxide, a qualitative negative detection. The background information puts this example in a broader context.

Module 1 - Preparation of the solution and Hydroxide precipitation

Module 2 - Analysis of precipitated result

Module 3 – Test of remaining Mn^{2+}-Ions after precipitation and filtration

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Learning Pathway

Step 1- Time & Activity: 45 minutes - The teacher gives a introductory lecture using the prepared PowerPoint presentation.

Step 2 – Time& Activity*:* 45 minutes - Students are divided into groups (preferably the number of students in one group is 3-4). Each group prepares of solution of the model process water, containing Mn^{2+}**-**Ions and performs the precipitation via titration of 1 molar $NaOH$ and filtration.

Step 3 – Time& Activity: 45 minutes - *After drying the filter, the weight is measured and the amount of substance precipitated is calculated. In addition, the amount of substance is also estimated from the amount of NaOH used for precipitation.*

Step 4 – Time& Activity: ***45 minutes -*** How well did the precipitation process work? And more generally, what has been achieved in terms of the concept of circularity in Europe? A broader perspective on the relevant issues of population growth and resources, open for questions and discussion, concludes the toolkit.

Evaluation

In each module at the end suggestions for a test of understanding are given.

Description of Student's Cards

Student's Card 1 - Preparation of the solution and Hydroxide precipitation

Student's Card 2 - Analysis of the precipitated result

Student's Card 3 – Detection test of Mn^{2+}-Ions and $Mn(OH)_2$(s)

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Acknowledgement

This unit included an excursion to the Wolfsburg plant of Volkswagen AG with the chemistry class of Mrs Karin Grunewald, Gymnasium Fallersleben, Wolfsburg, on 27 June 2023. Dr. Frederike Drawert and Dipl.-Ing. Florian Lehnert, Volkswagen AG, led the tour through the wastewater centre of Volkswagen AG. The experiments were carried out by Jochen Brinkmann, Ronny Wenske and Chancy Kenmoe Kenmoe in the chemical laboratory of the Institute of Mineral Processing, Recycling and Waste Management Systems with the active support of the laboratory manager, Mrs Petra Sommer. Phillip Benedikt Moog proofread the manuscript and was my colleague in discussing all chemical issues and is therefore co-author of the learning unit. First results were presented at the SCIENCE FAIR WETSUS (26-29 September 2023). The structure and approach have been improved for the written version.

Sources

[1] Whalley, E. Beyond water quality: sewage treatment in a circular economy.

[2] Abdalla, K., Rahmat, A., Azizan, A. (2014). Influence of activation treatment with nickel acetate on the zinc phosphate coating formation and corrosion resistance. Materials & Corrosion **65**/10, 977–981.

[3] Hartinger, L., Lerch, A. (2017). Hartinger Handbuch Abwasser- und Recyclingtechnik. Komplett in Farbe, 3. Aufl. Hanser, München.

[4] Umweltbundesamt (2019). Leitfaden zur umweltfreundlichen öffentlichen Beschaffung: Bettwaren und Bettwäsche. Leitfaden zur umweltfreundlichen öffentlichen Beschaffung, Dessau-Roßlau.