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

Module 3

Objective: Proof of precipitation with a test for $Mn^{2+}$and $Mn(OH)_2$((s)

Necessities

List of materials/tools

- **$NaOH$ and H_2O_2**
- **beakers**

In industrial practice, all three cations ($Ni^{2+}, Mn^{2+}, Zn^{2+}$) and chemicals that promote the surface wettability are contained together in the phosphating bath. In order to be able to clearly demonstrate the success of heavy metal hydroxide precipitation in terms of quality, it is necessary, for didactic simplification, to limit it to one cation in the solution. For Mn^{2+} ions, there is a qualitative detection with the reaction in a hydrogen peroxide caustic soda solution, even with very small quantities:

$$Mn^{2+} + H_2O_2 + 2OH^- \rightarrow MnO(OH)_2 \downarrow + H_2O \quad (1)$$

The residual solubility of manganese hydroxide precipitation is 4 × 10^{-4}; therefore, the process is industrially supplemented by post-precipitation with a sulphur-containing precipitant. [1] Of course, if the precipitated substance were unknown, the manganese(IV) oxide hydroxide would of have to be dissolved by boiling in concentrated nitric acid and oxidised with lead(IV) oxide to form the violet permanganate in order to prove that it is manganese ions:

$$2Mn^{2+} + 5PbO_2 + 4H^+ \rightarrow 2MnO_4^- + 5Pb^{2+} + 2H_2O \quad (2)$$

However, since in this experiment in distilled H_2O only $Na^+ + 3OH^- + Ca^{2+}$ are present as accompanying ions in the solution and these cannot be (IV)-valently oxidised, precipitation of these ions is not possible. [2]

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In addition, the solution can be tested with [3] to determine whether the finest $Mn(OH)_2$ particles have passed through the filter [Ø 150mm]:

$$Mn(OH)_2(s) + H_2O_2\,(aq) \rightarrow MnO_2 + H_2O \quad (3)$$

If this were to happen, it would prove that flocculants need to be used in the industry.

Conclusions

The valuable resource of process water is recirculated. Metal ions $Fe^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}$, which are not involved in the growth of the Zn, Ni, Mn phosphate layer through chemical reactions on the surface, end up in the phosphate sludge and rinse water. As heavy metal hydroxide sludge, they have to be deposited underground and, to our knowledge, there is currently no economically viable, industrial process in the world for recovering the individual metals from this sludge. They are irretrievably lost; at AUDI AG this amounted to around 60 tons per year in 2006, which were disposed of underground. [1]

Despite the fundamental need to recycle as much of the raw materials as possible with a growing world population that is also interested in greater material prosperity, the facts do not yet point to a real, fundamental change for the better:

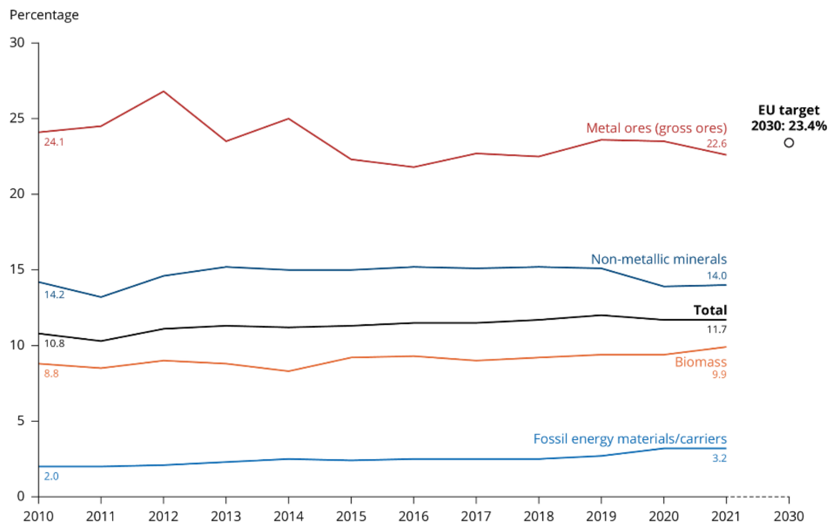

Figure 1 Source: https://www.eea.europa.eu/en/analysis/indicators/circular-material-use-rate-in-europe

It is important to understand the definition of the circular material use rate. [2] It does not mean the percentage of waste that is recycled. Significant progress has been made here. However, as national economies are growing at the same time, meaning that the consumption of raw materials is also increasing in most cases and new products may also require new elements from the periodic table, the proportion of recycled raw materials in the "metabolism" of national economies has remained almost constant over the last 20 years; the graph therefore shows progress that critics say is not sufficient in view of the finite nature of the planet. However, it can only be decided on a case-by-case basis whether an even higher recycling rate would consume so much more energy and chemicals, so that the bonus of lower resource consumption would be more than offset by these negative ecological consequences. And this is where the open field of scientific and social debate begins. As an introduction to an open, perhaps controversial interpretation of this dilemma from 2005, which is often quoted in the academic world,[1] is cited here:

"*It is increasingly recognized that the growing metabolism of society is approaching limitations both with respect to sources for resource inputs and sinks for waste and emission outflows. The circular economy (CE) is a simple, but convincing, strategy, which aims at reducing both input of virgin materials and output of wastes by closing economic and ecological loops of resource flows. This article applies a sociometabolic approach to assess the circularity of global material flows. All societal material flows globally and in the European Union (EU-27) are traced from extraction to disposal and presented for main material groups for 2005. Our estimate shows that while globally roughly 4 gigatons per year (Gt/yr) of waste materials are recycled, this flow is of moderate size compared to 62 Gt/yr of processed materials and outputs of 41 Gt/yr. The low degree of circularity has two main reasons: First, 44% of processed materials are used to provide energy and are thus not available for recycling. Second, socioeconomic stocks are still growing at a high rate with net additions to stocks of 17 Gt/yr. Despite having considerably higher end-of-life recycling rates in the EU, the overall degree of circularity is low for similar reasons. Our results indicate that strategies targeting the output side (end of pipe) are limited given present proportions of flows, whereas a shift to renewable energy, a significant reduction of societal stock growth, and decisive eco-design are required to advance toward a CE.* " [3]

[1] 536 citations in Web of Science, retrieved 19.01.2023.

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As proof of the principle that everyone has a realistic chance of making a difference as an individual, you can discuss this type of initiative with your students by focusing on our main theme in this unit:

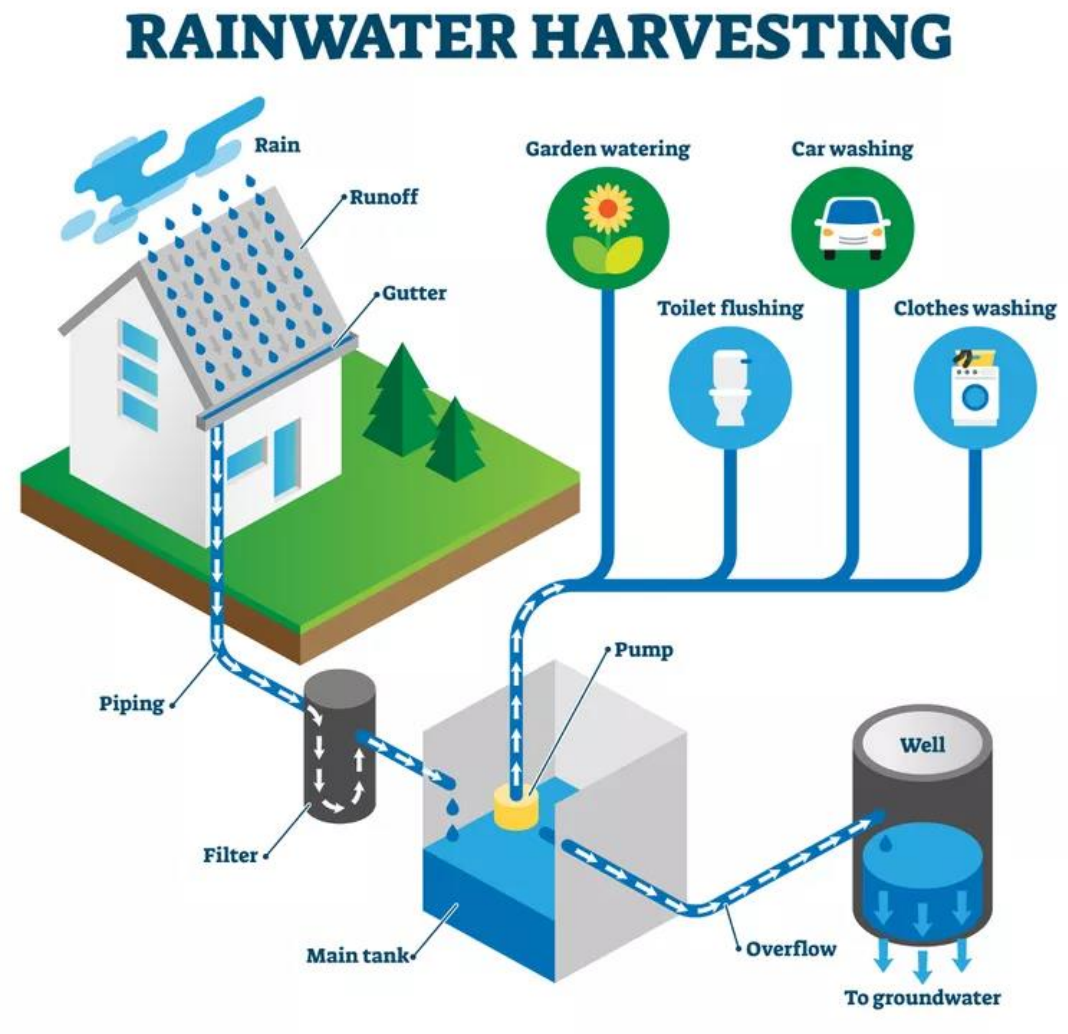

Figure 1 Source: https://www.treehugger.com/beginners-guide-to-rainwater-harvesting-5089884 *and as a case study: [4]*

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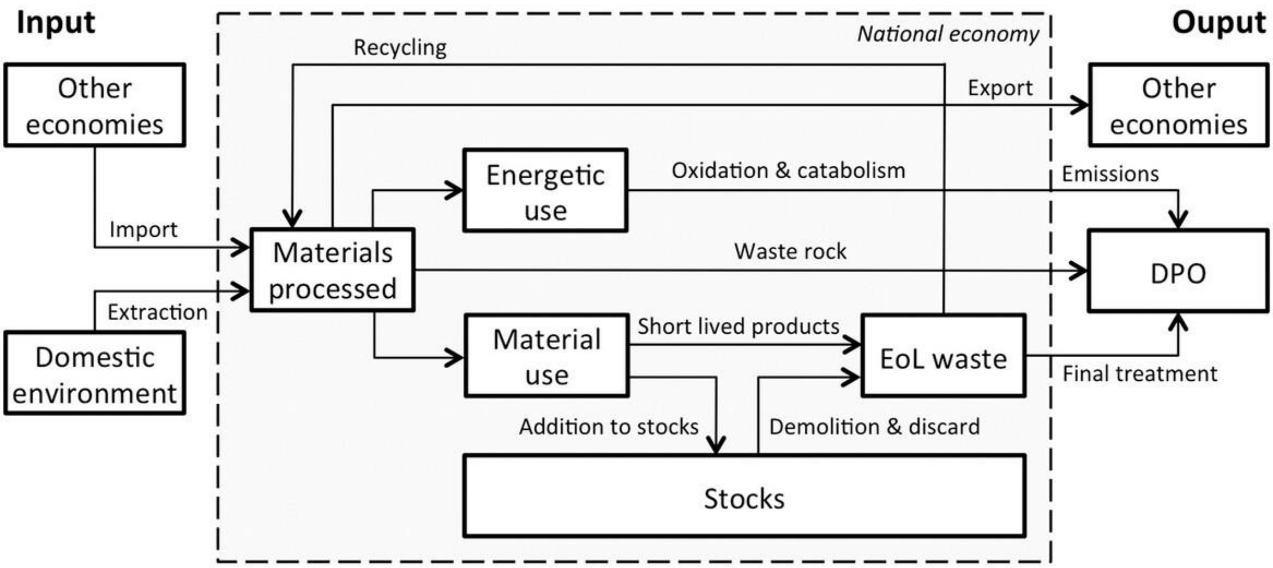

Figure 2. Here is a graphic overview of the authors' argument in the above quote. ***Abbreviations: DPO** = **Domestic produced Output** and **EoL** = **End of Life** Discuss the statements and the proposed solutions Source: [3]*

Literatur

[1] Prof. Dr.-Ing.-habil. E. Gock, Dr.-Ing. Jörg Kähler, Dipl.-Ing. Catherina Eschetshuber. Produktionsintegriertes Recycling von Phosphatierchemikalien bei der Korrosionsschutzbehandlung von Stahl und Aluminium. Abschlussbericht BMBF-Projekt Förderkennzeichen: 01 RW 01 68. Abschlussbericht. Technische Universität Clausthal, Clausthal-Zellerfeld.

[2] SUTIL CORTES Santiago (2018). Circular material use rate. Calculation methode. European Union, Luxembourg.

[3] Haas, W., Krausmann, F., Wiedenhofer, D., Heinz, M. (2015). How Circular is the Global Economy?: An Assessment of Material Flows, Waste Production, and Recycling in the European Union and the World in 2005. J of Industrial Ecology **19**/5, 765–777.

[4] Gleason Espíndola, J. A., Cordova, F., Casiano Flores, C. (2018). The importance of urban rainwater harvesting in circular economy: the case of Guadalajara city. MRR **41**/5, 533–553.