

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

Modules 1




Objective: Preparation of the solution and Hydroxide precipitation

Necessities



List of materials/tools

- Laboratory balance
- pH meter
- 3 beakers
- Spatula
- Burette
- Stir plate
- Quantitative filter paper, diameter 150 mm

Reagents	Formula		Quantity (g) or Concentration (M)
Manganese dichloride tetrahydrate	$MnCl_2(H_2O)_4$		variable, less than 0.1 g
Sodium hydroxide	NaOH		2 ml, 1 mol/L

Preparation and execution of experiments

- A solution containing manganese should be prepared in 100 ml distilled H_2O . As this experiment is only concerned with a qualitative understanding of the precipitation process, the concentration can be set arbitrarily.
- Criterion: Use as few manganese as possible, but at the same time enough to show a clear plateau between the pH value increase to compensate for the acid and the end of precipitation (see Fig. 3)

Calculation of the mass to be weighed in with $MnCl_2(H_2O)_4$ (manganese dichloride tetrahydrate)

- Molar mass = 54.938043 g/mol.
- Molar mass $MnCl_2(H_2O)_4 = 197,91$ g/mol

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

In the experiment documented here, 0.0575 g $MnCl_2(H_2O)_4$ fell on the weighing boat. From this follows: $\frac{m}{M} = n$.

$$\frac{0,0575g \text{ } MnCl_2(H_2O)_4}{197,91 \frac{g}{Mol}} = n$$

$$= 2,90536 \times 10^{-4} Mol \text{ } Mn. \quad (1)$$

In other words, we use a solution that works with:

$n \times M$: 0,015961g Manganese in 100 mL dist. H_2O .

According to (3), this addition of manganese corresponds to an input of $2,90536 \times 10^{-4} H^+ - Ionen$ which would correspond to a pH value of ~ 4.6 if fully complexed. In this specific case, 5.7 was measured, meaning that only around 11 % of the manganese ions were complexed. Manganese precipitation starts at pH 8.7 and is completed at around pH 10.5.

Calculations

At this point, it makes sense to introduce a deeper chemical fact by observation. After preparation of the model wastewater solution with manganese chloride, the previously neutral pH value (dist. H_2O) drops significantly. An elementary phenomenological introduction to the concept of complex chemistry and Lewis acids and bases can explain this observation. ¹



Figure 1 "Metal ions that contain partially filled d subshell usually form coloured complex ions; ions with empty d subshell ($d0$) or with filled d subshells ($d10$) usually form colourless complexes. This figure shows, from left to right, solutions containing $[M(H_2O)_6]^{n+}$ ions with $M = Sc^{3+}(d0)$, $Cr^{3+}(d3)$, $Co^{2+}(d7)$, $Ni^{2+}(d8)$, $Cu^{2+}(d9)$, and $Zn^{2+}(d10)$. (credit: Sahar Atwa) ". Source, direct quote from: [1]

¹ Further information:

[https://chem.libretexts.org/Bookshelves/General_Chemistry/Chemistry_1e_\(OpenSTAX\)/19%3A_Transition_Metals_and_Coordination_Chemistry/19.2%3A_Coordination_Chemistry_of_Transition_Metals](https://chem.libretexts.org/Bookshelves/General_Chemistry/Chemistry_1e_(OpenSTAX)/19%3A_Transition_Metals_and_Coordination_Chemistry/19.2%3A_Coordination_Chemistry_of_Transition_Metals)

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

Some transition metal ions (or atoms), including Mn^{2+} are electron pair acceptors (Lewis acids) and the ligands, in our case 6 H_2O are electron donors (Lewis bases). Together they form a coordinate covalent bond. The peculiarity of this bond is that it lowers the pH value, although no Brønsted acid is present that could release H^+ -ions.



The reaction (3) is subject to an equilibrium constant.

- The proportion of manganese hexa-aqua-complexes is proportional to the real measured pH value reduction.
- If all Mn^{2+} -ions were complexed, the total amount of added Mn^{2+} -ions added would have to be mathematically proportional to the pH value reduction.

$$\alpha = \frac{c(Mn(H_2O)_5OH^+)}{c(Mn)} \quad (5)$$

$$\alpha \times c(Mn) \sim c(H_3O^+) \quad (6)$$

Mn^{2+} – Ionen $\left[2,90536 \times 10^{-4} \frac{M}{L} Mn\right]$ See Fig. 5 for a calculated pH value of 3.54. However, the measured value was 5.7; the actual deprotonation induced by the complexation is therefore: $\alpha = \frac{10^{-5,7}}{10^{-3,54}} = 0,69 \%$. The remaining Mn^{2+} -ions are not complexed. This very low degree of complexation is due to the fact that in our experiment dist. H_2O is used in our experiment. The complexed proportion increases with the $NaOH$ - content. [2]. The metal complexes absorb in one area of the wavelength spectrum and reflect in another. This determines the specific colour of the respective metal complex. In the case of the $MnCl_2(H_2O)_4$ the crystal is pale pink and the manganese aqua complex should also take on this colour. At the low concentration, the colouring is not perceptible to the eye.

The second chemical process is the precipitation of the heavy metals as hydroxides with the addition of $NaOH$.² On the one hand, this is optically visible due to the initially slightly yellowish and then brownish black turbidity and floc formation. However, it does not necessarily follow from this that

² The addition of $Ca(OH)_2$ is only necessary for the amphoteric zinc salts because calcium hydroxide forms sparingly soluble basic salts. The above sentence therefore refers to the general procedure commonly used in industrial practice. In the case of our model experiment with manganese, caustic soda is sufficient for precipitation.

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

the manganese ions must precipitate as hydroxide. In the minds of the learners, they may be "just some grains that suddenly appear". The following experiment can help them to understand this.

As long as *only H^+ -ions recombine with OH^- -ions* recombine to form water, the pH value rises steeply with the addition of *NaOH* rises steeply up to precipitation point A. From this point onwards, *additional OH^- ions* are "consumed" to form the heavy metal hydroxide ions and the increase in pH value requires larger quantities of *NaOH*. Thus, if the precipitation process is observed by titration, the optically visible onset of precipitation can also be observed in parallel in the delayed increase in pH value.



Figure 2 Precipitation of manganese(II) hydroxide becomes visible from pH 7.5 and reaches a maximum between pH 8 - 9. $T = 20\text{ }^{\circ}\text{C}$. Photo: TU Clausthal

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

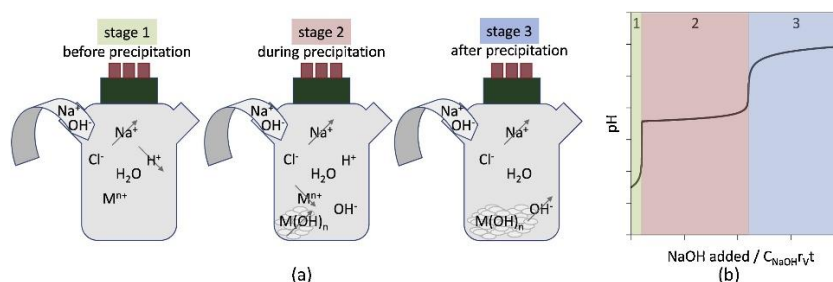
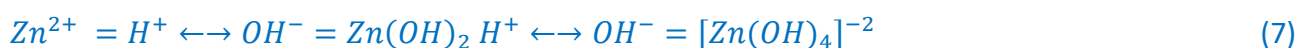


Figure 3 Sodium and hydrogen ions do not take part in the reaction. The metal ion concentration decreases, while the metal hydroxide concentration increases during precipitation. After the pH-dependent and metal-specific end of precipitation, the OH^- concentration increases again steeply. The idealized form here (before, during and after precipitation) is in principle also recognisable in Fig. 3 from our experiment. The curve of the titration measured experimentally in individual cases depends on many influencing variables. [2]

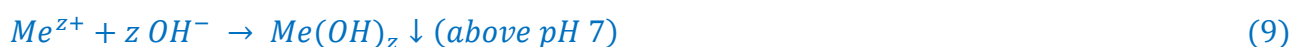
In the case of manganese, precipitation begins at pH 8.7 and is completed at pH 10.5.³ In the case of Zn^{2+} –ions, the first precipitation begins at NaOH begins at pH 7.6. Zinc has the particularity of



The addition of milk of lime ($\text{Ca}(\text{OH})_2$) the soluble tetrahydroxozincate is converted into a sparingly soluble calcium zincate:



Precipitation of the milk of lime itself only takes place from pH 12.4 - 13.9 according to the general formulae:



The heavy metal hydroxides precipitating as finely dispersed solids ($\text{Ni}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$, $\text{Ca}[\text{Zn}(\text{OH})_4]$) precipitate between pH 7.6 - 11.5. [3]

³ The information alone is contradictory at: [3] These values, which were used for the following calculations, can be found on page 134. The same author's data on the overview page; p.140 are different (pH 10.5- pH 11.5). Accompanying conditions also play a major role.

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

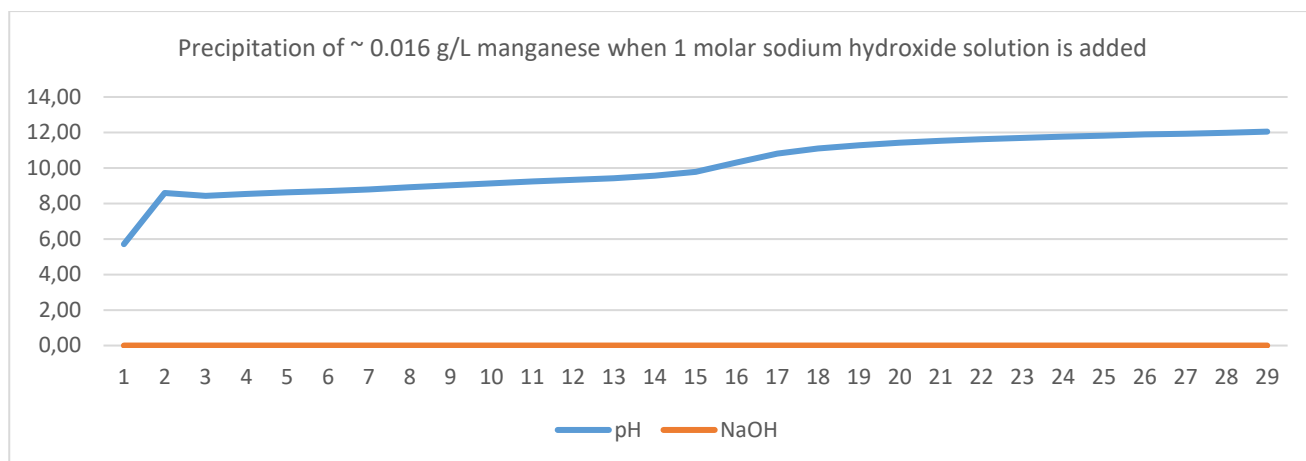


Figure 4 Conditions: $T = 20\text{ }^{\circ}\text{C}$, 100 mL dest. H_2O , magnetic stirrer, $700\frac{\text{V}}{\text{min}}$, time interval between two drops: ~ 54 sec. $1,25\text{ ml } 1\frac{\text{M}}{\text{L}} \text{ NaOH}$

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



Figure 5 For the conversion of $0.016 \frac{g}{L} Mn$, equal to $2.90536 \times 10^{-4} \frac{M}{L} Mn$ are calculated for $Mn(OH)_2$ $5,81072 \times 10^{-4} \frac{M}{L} NaOH$ is required. In 29 steps, 1.25 ml of one-molar NaOH is added as free-falling drops from the burette. Photo: TU Clausthal

Conclusions

Now ask your students to match the experimental result, which is a model for the industrial process of heavy metal hydroxide precipitation in the automotive industry, with the process flow diagram from their PowerPoint presentation. In the real industrial case, what happens to the solid particles deposited at the bottom of the beaker?

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

Verfahrenschema der chemisch/physikalischen Abwasserbehandlungsanlage

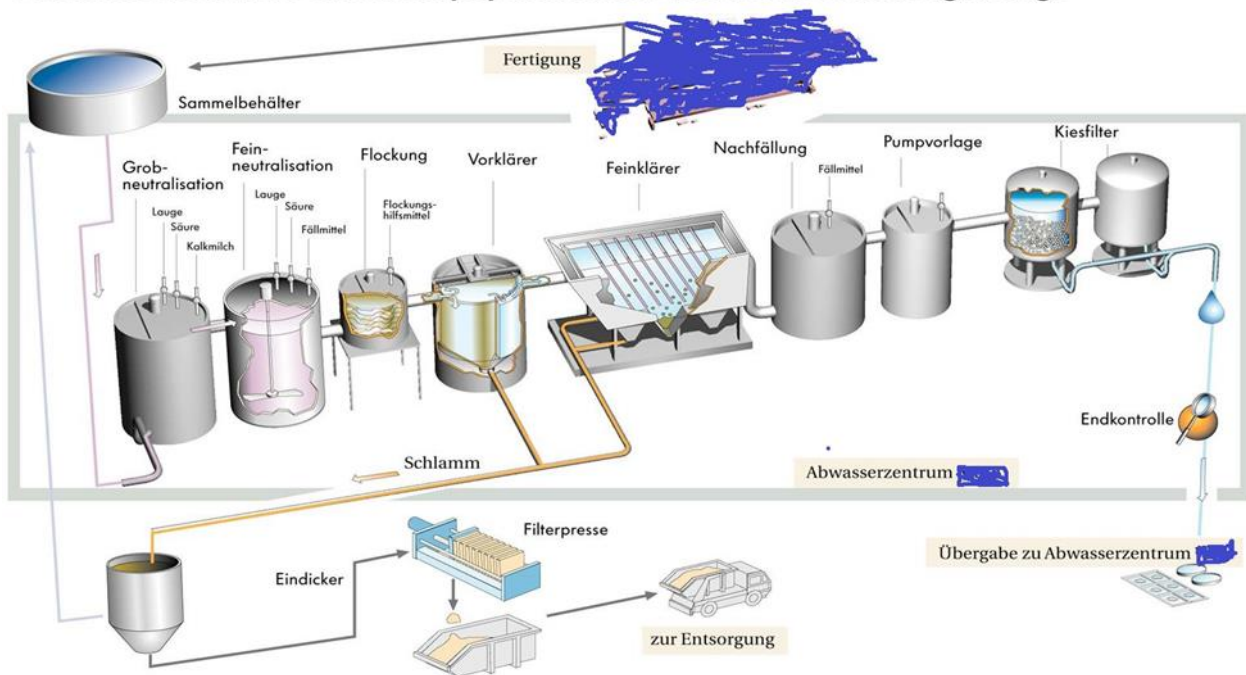


Figure 6 Wastewater treatment at the Volkswagen AG plant in Wolfsburg. Image courtesy of VW AG. The exact name of the site has been obscured at the request of VW AG. The German names are explained in the text below.

Explanation of the processes in Figure 6

The wastewater 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, the acidic wastewater containing metal ions is treated with NaOH and $\text{Ca}(\text{OH})_2$ to initiate an initial neutralisation. These flocs settle in the *primary clarifier* (**Vorklärer**) (solids sink), where a large proportion of the sludge (**Schlamm**) is removed from the top of the tank funnel and conveyed for sludge treatment. This is followed by the *fine clarifier* (**Feinklärer**) (lamella clarifier) and *secondary precipitation*, in which organosulphides are used if necessary. It can 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 treated wastewater is conveyed to the biological treatment plant, where it is further treated. After dewatering using a *thickener* (**Eindicker**) and *chamber press*,

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

(Kammerpresse) the heavy metal hydroxide sludge is transported to an (underground) landfill .⁴
[3]

The correct answers are:

- Our filtration symbolises the solution leaving the *fine clarifier*, while the particles deposited in the filter correspond to the sludge deposited in the *primary clarifier* and the *fine clarifier*.
- The difference with the industrial case is that our model experiment does not include a second "police" precipitation with sulphur-containing precipitants.

Literatur

- [1] LibreTexts. 19.2 _Coordination_Chemistry_of_Transition_Metals.
<https://chem.libretexts.org/@go/page/38322> (letzter Zugriff am 23-01.2024).
- [2] Eggermont, S. G., Prato, R., Dominguez-Benetton, X., Fransaeer, J. (2020). Metal removal from aqueous solutions: insights from modeling precipitation titration curves. *Journal of Environmental Chemical Engineering* **8**/1, 103596.
- [3] Hartinger, L., Lerch, A. (2017). *Hartinger Handbuch Abwasser- und Recyclingtechnik. Komplett in Farbe*, 3. Aufl. Hanser, München.
- [4] 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.

⁴ It would be technically possible to recycle the metals, but more expensive to obtain them from "fresh", mined raw materials. At AUDI AG in Neckarsulm, the usable proportion of phosphating chemicals in 2002 amounted to Zn^{2+} (74%), Mn^{2+} (54,2 %), Ni^{2+} (15,5%). The remainder ends up in the phosphating sludge and in the rinsing water. The usable proportion of nickel is low because nickel primarily acts as a catalyst for layer formation. [4] Explanation of the process sequence in Fig. 6 using part of the email from Florian Lehnert, VW Kraftwerk GmbH to J. Brinkmann, 06/06/2023.