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

Module 2

Objective: Analysis of the result of the precipitation

Necessities

List of materials/tools

- Filter paper,150 mm Ø
- Laboratory Balance
- Funnel with long flow tube
- Beakers
- Screw-on plastic container for the clear solution
- Tweezers for gripping the filter
- Lab Gloves

Procedure

- Wear laboratory gloves to protect yourself when pouring off the solution, as it is highly alkaline, and when handling the filter paper; the latter to avoid leaving grease marks on the filter between measurements, which could falsify the result.
- Weigh your filter on a support on the laboratory balance and record the result. For an accurate result, ensure that the laboratory balance is not exposed to vibration or wind before and during the measurement; close the doors, do not place anything next to the balance or write on it.
- Fold the filter paper to fit your funnel and moisten it so that it lies flat against the wall.
- Shake the solution containing the precipitated solids well. Pour the solution into the funnel to the level of the fill line.

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Store the clear solution in a plastic container with a screw cap for the following qualitative determination of any residual manganese ion content

- Dry the filter overnight and weigh it again the following day. The difference between the filter without and with the deposited solid particles should correspond to the corresponding mass of the manganese substance originally prepared, now as precipitated solid compound(s).
- The students are faced with two questions:
- How do I adjust the burette so that a drop falls at regular intervals?
- And what is the correct time to read the pH value after the conversion(s)?
- You will see that the pH rises sharply after the drop has fallen and then rises again when the concentration of the freshly added caustic soda solution has equalised. You will also be able to observe that, at the very first precipitations, above pH 7.5, the solution becomes slightly yellowish and, as the solid particles continue to precipitate, it becomes brownish to black.

Calculations

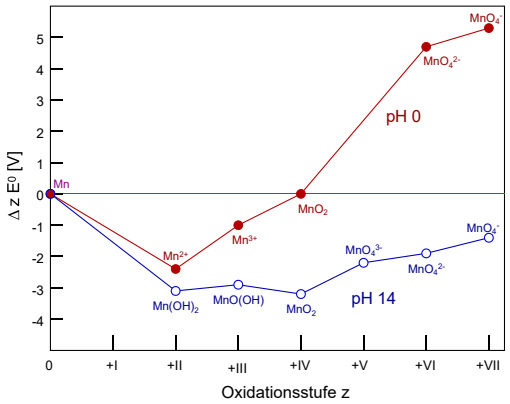

Figure 1 Manganese can exist in a basic environment under electrochemically similar conditions as Mn(II) hydroxide, Mn(III) oxide hydroxide or as manganese dioxide, Mn(+IV) oxide. Source: University of Freiburg, Lecture Chemistry of Metals, Frost diagram of manganese. Online: http://ruby.chemie.uni-freiburg.de/Vorlesung/metalle_mn_gruppe.html

The addition of $NaOH$ initially causes the Mn^{2+}-ions to precipitate as hydroxides, which are then oxidised by dissolved oxygen on the surface of the solid particles to form the compounds mentioned. This process in turn leads to slight shifts in the pH value with the result that when the Mn^{2+}solution is precipitated with $NaOH$, it can sometimes be difficult to find a "temporal" end point at which the pH value becomes stable, as there are - unknown - equilibrium positions for all the conversions.

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For the small fraction present as a complex, the following paths are possible:

$$[Mn(H_2O)_5OH]^{2+} \rightarrow [Mn(H_2O)_4OH]^{+} + H^{+} \quad (2)$$

$$[Mn(H_2O)_4OH]^{+} \rightarrow Mn[H_2O)_4(OH)_2] + H^{+} \quad (3)$$

$$Mn[H_2O)_4(OH)_2] + {}^{1}/_{2}\, O_2 \rightarrow MnO_2 \downarrow + 5\, H_2O \quad (4)$$

To estimate the range required for hydroxide precipitation (Figure 2), we chose the range from the 2nd to the 17th point (pH: 8.59 - 10.82), as this corresponds to the end point of free acid compensation and, at the second reversal point, approximately the pH at the end of precipitation. In between, $NaOH$ solution was required for precipitation.

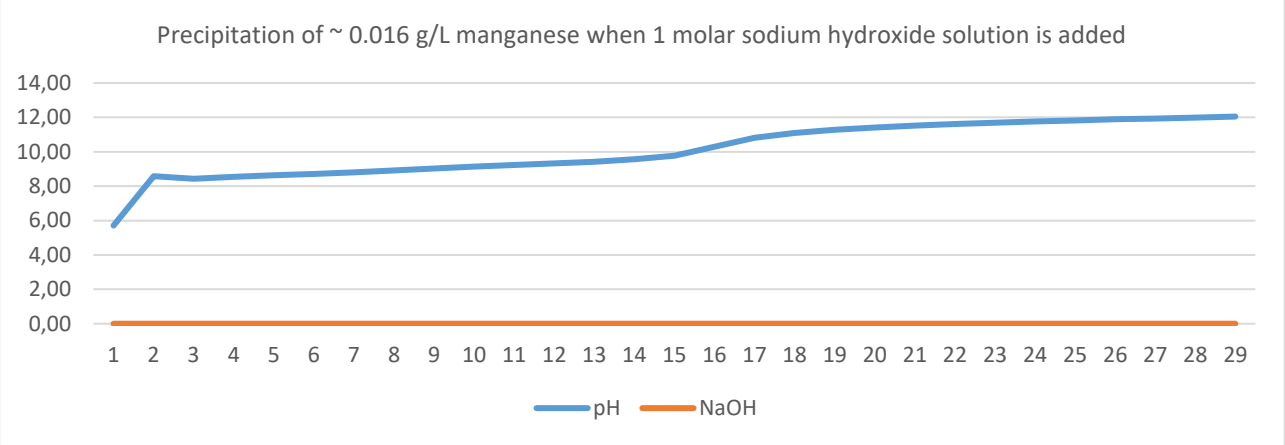

Figure 2 *T =20 °C,100 mL dist. H_2O, Magnetic stirrer,700 rpm, drop falling speed ~ 54 sec.1.25 ml 1 M/L NaOH*

We calculate:

$1{,}25 \times 10^{-3} L \; x \; \frac{M}{L}$ NaOH: 29 (drops) x 15 (drops) = $6{,}46552 \times 10^{-4}\, M$ (12)

The excess over stoichiometry is therefore only about 11 percent. The initial increase in the pH corresponds to the OH^- ions required to compensate for the H^+ions generated by the complexation of the Mn^{2+}-ions. When the precipitated manganese solution is poured onto a fine-pore filter paper, the difference in weight between the filter paper before and after - dried - measurement should correspond to the amount of $Mn(OH)_2 \downarrow$.

The uncertainties in this calculation are an (unknown) fraction of manganese dioxide (MnO_2) and an equal fraction calculated according to:

$$[Mn(H_2O)_6]^{+2} + 2\, OH^- \rightarrow [Mn(H_2O)_4(OH)_2] + 2\, H_2O \quad (13)$$

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Which precipitates as a neutral complex. Therefore, only a gravimetric determination could give the exact amount of precipitated manganese. The filter used for the separation of the precipitated manganese weighed 1.5094 g net and 1.5482 g dried in air after the solution with the precipitation

$2{,}90536\,x\,10^{-4}\,\frac{M}{L}\;x\;54{,}938043 = 0{,}015961\;g\;(Mn) + 0{,}009296\;g\;(O) + 0{,}00058\;g\;(H)$ = **0,025837 g $Mn(OH)_2$**.[1]

The possible alternatives in Figure 3 $MnO(OH), MnO_2, Mn(OH)_2$ are electrochemically close to each other in a basic environment:

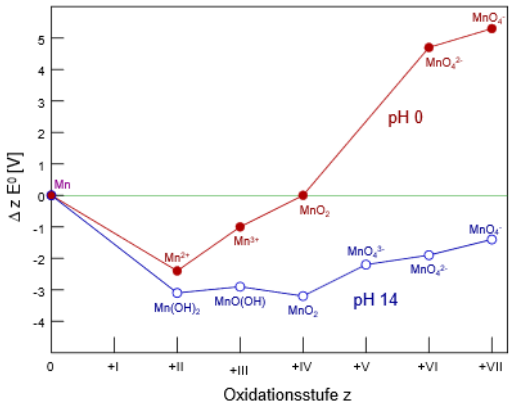

Figure 3 Manganese can be present in a basic environment under electrochemically similar conditions as Mn(II) hydroxide, Mn(III) oxide hydroxide or as manganese dioxide, Mn(+IV) oxide. Source: University of Freiburg, Lecture Chemistry of Metals, Frost diagram of manganese. Online: http://ruby.chemie.uni-freiburg.de/Vorlesung/metalle_mn_gruppe.html

This opens a "window" of possible weighing results in a range between:

1.53462 g with MnO_2

1.53498 g with $MnO(OH)$

1.53523 g with $Mn(OH)_2$

The filter therefore weighed 0.01297 g - 0.01358 g more than it "should" have weighed. At the end of the experiment, the solution had a pH of 12.05 (Figure 2). This means that about 1.9 g of sodium was poured over the filter. Could ~ 0.007 % of this concentration have dried into the cellulose from the wet state? Another possible explanation for the deviation could be drying in air and not in the drying cabinet. Therefore, a certain amount of residual moisture always remains in the filter paper when exchanging with the ambient air.

[1] Weighed in was 0,0575 $g\;MnCl_2(H_2O)_4$. This would correspond to 0.025837 g of manganese (II) hydroxide, assuming complete precipitation without taking into account any unknown residual solubility.

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Figure 4 Filtering with quantitative filter paper, ash-free, diameter 150 mm (Albert Lab Science). Photo: TU Clausthal

Conclusions

A valuable resource, process water, is recycled. Metal ions that have not chemically reacted to form the coating layer (Fe, P, Ni, Mn, Zn) are disposed of as phosphate sludge and dewatered heavy metal hydroxide sludge in an underground landfill, unless they form the coating of the car body. In this case, no metal recycling takes place.

- *How has the recycling rate of different material groups developed over time in Europe as a whole?*
- *And how does your country compare with this trend?*

You can find information on how to answer the first question at
https://www.eea.europa.eu/en/analysis/indicators/circular-material-use-rate-in-europe

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