

Student's Card 1

Heavy metal hydroxide precipitation in wastewater treatment in the automotive industry

Modules 1

Purpose of phosphating baths in the automotive industry - Preparation of a Mn(II) solution

Introduction




In the automotive industry, bodysells are immersed in phosphating baths containing a mixture of primarily iron, zinc, nickel and manganese ions. The resulting zinc phosphates protect the body from corrosion, nickel phosphates improve paint adhesion and manganese phosphates have a friction-reducing effect. The bodies are rinsed before painting. Waste water comes from used active baths (*feed and bleed*) and from the rinsing baths. In a simplification, instead of a tri-cation solution (Zn, Ni, Mn,) plus Fe, we use a model solution containing only Mn^{2+} ions.

Necessities



List of materials/tools

- 4 beakers
- Stir plate
- pH meter
- Burette
- Filter 150 mm ø
- Laboratory balance

Reagents	Formula		Quantity (g) or Concentration (M)
Manganese(II) chloride-tetrahydrate	$MnCl_2(H_2O)_4$	 Use lab protection: gloves, coat, glasses	$2,9 \times 10^{-4} \frac{M}{L}$ Mn Prepare a solution for 100 mL
Sodium hydroxide solution	$NaOH$		1 molar concentration, amount 2 ml

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

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



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: $Fe(H_2PO_4)_2$
- Secondary iron phosphate: $FeHPO_4$
- Tertiary iron phosphate: $Fe_3(PO_4)_2$

The tertiary layer-forming phosphate is formed on nuclei on the surface. When a certain layer thickness is reached, the access of free acid to the metal surface is prevented and the pickling reaction is complete. If the solutions contain additional zinc, manganese and nickel salts, corresponding phosphate layers are deposited.¹ In combination with other bath parameters, this creates a corrosion-resistant, dense and friction-reduced protective layer. [2,3] The exact composition of the bath is usually a company secret.

¹ "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." [1] 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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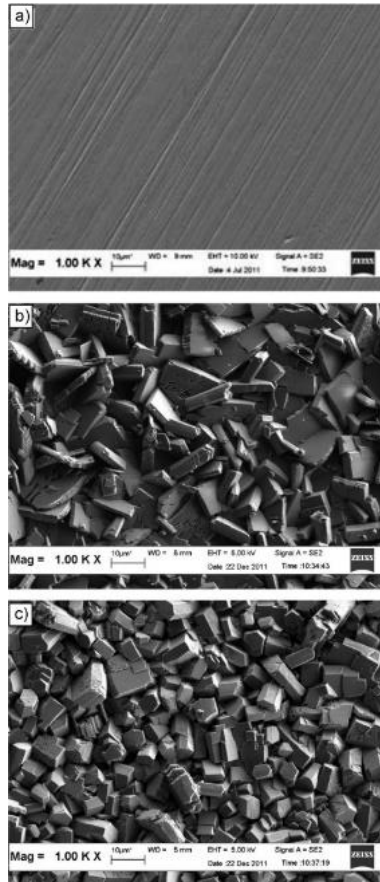


Figure 1 Example. Steel surface before phosphating, (b) after phosphating without the addition of nickel, (c) with nickel as a catalyst - the surface coating is denser and has finer crystals. Source: [4]

Wastewater is produced from two sources. Firstly, active baths are contaminated by introduced impurities and accompanying reactions (including sludge formation). Then, according to the *feed and bleed* principle, fresh solution is added and old solution is removed; the latter becomes waste water. Secondly, the bodies are rinsed before and after the treatments. 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 fed back into the process water cycle or discharged into a receiving watercourse. [5]

Lab Procedure

- Preparation of Manganese (II) solution in 100 mL distilled water
- Calibration of pH-meter with buffer solutions
- Measurement of initial pH value
- Adjust the hot plate with magnetic stirrer approximately to 100 rpm

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- After each NaOH-drop from the burette the solution needs to adjust, first compensation of free acid, with the beginning of the hydroxide precipitation "all new" OH^- and Mn^{2+} ions have to collide and precipitate. Then the pH value reaches a steady state. Due to our experience, in a 100 mL solution, containing ~ 0.05 g of Mn(II)-chloride tetrahydrate, if each drop needs roundabout a minute to form and fall, you will reach this chemical "rhythm". Note the new pH value after each drop, transfer to an excel graph. You will see, ideal reaction times presumed, a pattern similar to Figure 1 (b):

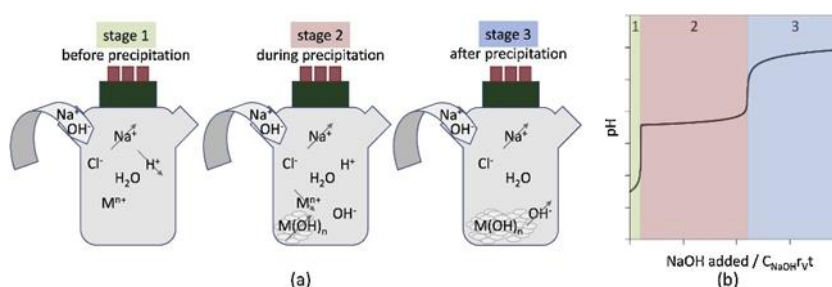


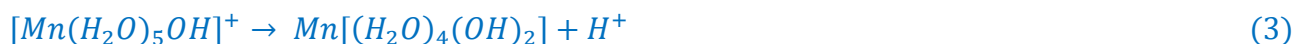
Figure 2 Source: [6]

- Make a note of the total NaOH amount you need for the titration until the end of the experiment.
- The steep rise at the beginning records the amount of NaOH. The flat curve from the second inflection point onwards shows the increase in the pH value per drop NaOH in the solution. Why does the curve have a flat slope in between?

Consider the general formula for heavy metal hydroxide precipitation:



For the small proportion that is present in the solution as a metal complex, this transformation is to be expected with the addition of NaOH this conversion can be expected:



Consider what effect this transformation has on the resulting pH.

The above processes are derived slightly differently, with the same result:
[https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental Modules and Web sites \(Inorganic Chemistry\)/Coordination Chemistry/Complex Ion Chemistry/Reactions of the Hexaaqua Ions with Hydroxide Ions](https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Web_sites_(Inorganic_Chemistry)/Coordination_Chemistry/Complex_Ion_Chemistry/Reactions_of_the_Hexaaqua_Ions_with_Hydroxide_Ions)

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Analyse the statement in the following figure for your experiment:

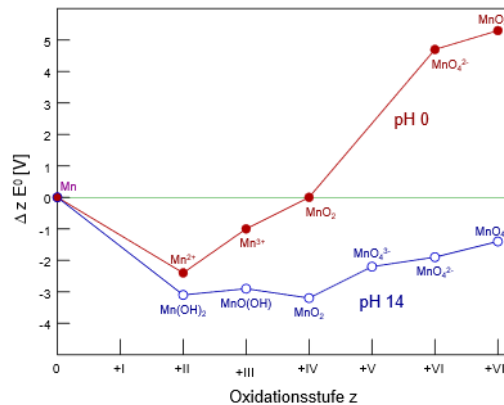


Figure 3 Manganese can exist in a basic environment under electrochemically similar conditions as Mn(II) hydroxide, Mn(III) oxide hydroxide or as manganese dioxide, Mn(+IV) oxide. Source: University of Freiburg, Lecture Chemistry of Metals, Frost diagram of manganese. Online: http://ruby.chemie.uni-freiburg.de/Vorlesung/metalle_mn_gruppe.html

To do this, read which colours the different manganese oxides take on and observe the colour progression during precipitation.

You can now approach an approximate quantitative determination of the precipitation products in the following way:

1. Calculate from the weighed quantity of $MnCl_2 \cdot (H_2O)_4$ calculate the potential quantity of Mn required for a precipitation as $Mn(OH)_2$, $MnO(OH)$ and MnO_2 is available. Divide the total amount of $NaOH$ in mL by the number of your individual titration steps and multiply this quantity by the number of steps that lie between the first and second inflection points of your titration curve. Converted into moles, this should roughly correspond to the amount of OH^- ions that were "consumed" for the conversion. From this, you can determine a possible maximum weight of your precipitation products. And you can calculate the initial amount of Mn into the stoichiometric ratio to OH^- .
2. Weigh a filter with a pore size of 150 mm on an ultra-fine balance and carefully pour your solution with the well-suspended precipitation products over the filter. Then dry the filter and weigh it again with the precipitation products. The difference before and after should correspond to the weight of the precipitation products. Due to the several possible reaction products described above, the actual weight may vary depending on their unknown mixing ratios.

Other possible sources of quantitative uncertainty could be

- adsorbed water molecules from the ambient air,
- sodium atoms adhering to the filter, which dried out in the filter and,
- because hydroxide precipitation is only the first step in wastewater treatment, in our case after precipitation we still detected a residual concentration of

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$0,15 \text{ m} \frac{\text{mg}}{\text{L}}$ Mn is detected after precipitation, surface loading of the filter with Mn^{2+} -ions is also possible.

And a further uncertainty resulting from two simplifications must be addressed. No flocculant was used. Finely dispersed solid particles, be they $\text{Mn}(\text{OH})_2$ oder MnO_2 could pass through the filter and "reappear" as manganese in the ICP analysis.² However, the value found in this way does not necessarily reflect the residual solubility, but is due to the modified procedure. In short: The experiment here describes an approximation of the real conditions and the closer the quantitative values are "looked at", the more the deviations from industrial practice become apparent under this "microscope".

The pore size of the filter is 150 mm, solid particles below this size, which did not agglomerate - no flocculant was used - were removed. For filtration, choose a funnel with a long tube.

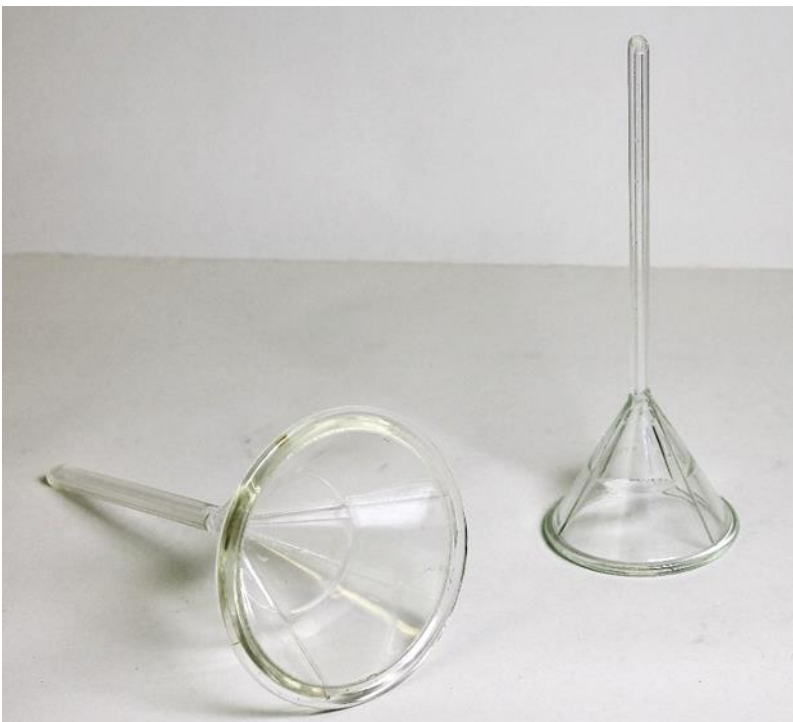


Figure 1 Long Flow Tube. Photo: Georg-August-Universität Göttingen

This will create a slight vacuum as the droplets fall, due to the displaced air mass, and the solution will flow more quickly from the funnel into the beaker.

²A possible device for trace elements: https://en.wikipedia.org/wiki/Inductively_coupled_plasma_mass_spectrometry

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Figure 1 Precipitation of manganese (II) hydroxide becomes visible from pH 7.5 and reaches a maximum between pH 8 - 9. $T = 20\text{ }^{\circ}\text{C}$. F Photo: TU Clausthal



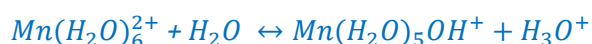
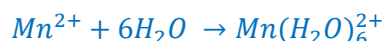
Figure 2 Filtering with quantitative filter paper, diameter 150 mm (Albert Lab Science). Photo: TU Clausthal.

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Calculations *(if necessary)*

Manganese ions act as a Lewis acid. Calculate the maximum pH shift due to:



and compare it, in percentage to the real shift.



Questions/Quiz

What is the purpose of phosphating baths in the automotive industry?

Write the chemical formula of Mn^{2+} hydroxide precipitation?

Literature

- [1] Rausch, W. (2005). The phosphatisation of metals. ... 104 Tab, 3rd ed. Leuze, Bad Saulgau.
- [2] Hofmann, H., Spindler, J. (2020). Processes in coating and surface technology, 4th ed. Hanser, Munich.
- [3] Duszczuk, J., Siuzdak, K., Klimczuk, T., Strychalska-Nowak, J., Zaleska-Medynska, A. (2018). Manganese Phosphatising Coatings: The Effects of Preparation Conditions on Surface Properties. Materials (Basel, Switzerland) **11/12**.
- [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.
- [5] Hartinger, L., Lerch, A. (2017). Hartinger Handbook of Wastewater and Recycling Technology. Complete in colour, 3rd ed. Hanser, Munich.
- [6] Eggermont, S. G., Prato, R., Dominguez-Benetton, X., Franssaer, J. (2020). Metal removal from aqueous solutions: insights from modelling precipitation titration curves. Journal of Environmental Chemical Engineering **8/1**, 103596.