REMOVAL OF MANGANESE FROM ACID MINE WATER

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Abstract

Apart from a high concentration of iron, mine water can also contain a higher concentration of manganese. Extraordinarily high concentrations can be found in acid waters from the surroundings of ore deposits, e.g. the water from the sulfitic ore deposits in Smolník contain up to 40 mg.l^{-1} of manganese. The legislation ordains discharge of water into surface water with a maximum concentration of manganese of 1 mg.l^{-1}, and therefore it is vital to reduce the content of manganese in the mine water to a permissible value. Within the research work, a variety of demanganization methods were tested. In conclusion of the paper, so far most optimal method of manganese removal from acid mine water is suggested.

Key words: *Mine water, demanganization.*

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1. Introduction

Manganese usually accompanies iron ores. Among the manganese ores in nature there are for example pyrolusite (MnO_2) and braunite (Mn_2O_3). Manganese transfers into water also from soils and sediments. The anthropogenic sources of manganese can be industrial waste water, e.g. from ore treatment, metallurgical plants and chemical operations where potassium permanganate is used for oxidation.

Manganese can occur in water in its dissolved or undissolved form in oxidation states of II, III, IV and VII.

In *reduction* conditions under the absence of dissolved oxygen and other oxidants, the most stable form of manganese occurrence in water is Mn^{II}.

In *anoxic* conditions the concentration of dissolved manganese in natural waters is limited by the solubility of carbonate, hydroxide or sulphide. The boundary between the coexistence of solid phases of $MnCO_3$ (s), MnS (s) and $Mn(OH)_2$ (s) depends on the concentration ratios of all sulfitic sulphur, carbon dioxide and pH value.

In *oxic* conditions manganese in the oxidation state II is unstable in water. Especially in an alkaline environment it quickly oxidizes and hydrolyzes. Little soluble higher oxides of manganese in the oxidation states of III and IV are released. The product of oxidation is the mixture of $Mn(OH)_2$, Mn_2O_3, Mn_3O_4, MnO(OH) and MnO_2. The surface of manganese oxidation products has sorptive properties. The sorption of own Mn^{2+} ions sometimes explains the nonstoichiometric composition of Mn^{II} oxidation products. In terms of water technology, what is important is the adsorption of NH_4^+ ion, which can be eliminated in the course of water demanganization to a considerable extent due to this process. [1]

2. Occurrence in water

An increased concentration of iron in natural waters is also usually accompanied by an increased concentration of manganese. Frequently, contents below 1 mg.l^{-1} are observed. In ground waters the concentration of manganese is often higher than in surface waters where oxidation processes take place. Neither mineral waters are rich in manganese, e.g. Carlsbad mineral waters contain manganese in the concentrations ranging from 0.07

mg.l^{-1} to 0.3 mg.l^{-1}. Apart from a high concentration of iron, mine waters can also contain a higher concentration of manganese. Extraordinarily high concentrations can be found in acid waters from the surroundings of ore deposits, e.g. the water from the sulfitic ore deposits in Smolník contain up to 40 mg.l^{-1} of manganese.

Manganese is vital for plants and animals. In the concentrations it occurs in natural waters it is unobjectionable. It significantly influences the organoleptic properties of water, even more than iron. In the concentrations higher than 0.3 mg.l^{-1} it can unfavourably affect the taste of water and undissolved higher oxidation forms of manganese can tint materials, which get into contact with such water, brown. Thus, the concentration of manganese is rather strictly limited in drinking and service waters used in the food-processing, textile and paper industries, as well as in laundries and starch factories. Similarly to iron, apart from chemical oxidation of manganese, also its biochemical oxidation by manganese bacteria assert itself in water. An excessive growth of manganese bacteria can cause a fouling process in the water pipes due to biomass, which is another reason for limiting its concentration in water transported by pipes. In all respects, manganese is more harmful than iron and its top permissible concentrations are thus lower than in case of iron.

Drinking water quality requirements state the limit value of 0.1 mg.l^{-1} and the highest limit value is 0.5 mg.l^{-1}. In the water suitable for watering, the concentration of all manganese is up to 3 mg.l^{-1}, in the waterworks courses it is 0.1 mg.l^{-1} and in other course it is 0.5 mg.l^{-1}.[1]
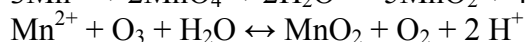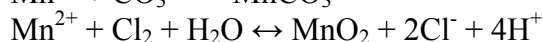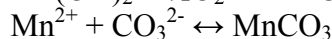
3. Demanganization

A smaller quantity of manganese can be removed by a single-stage treatment, either in a filter medium prepared by higher oxides of manganese or by oxidation and filtration. A larger quantity is removed by liming, sedimentation or in a sludge blanket and filtration. In practice, the following demanganization methods are used:

> ➢ Demanganization by liming (alkalinization)
> ➢ Demanganization by an oxidant
> ➢ Contact demanganization by filtration by a treated sand
> ➢ Demanganization by fining

Fining is selected in cases when manganese is either bound to organic substances present in water or it has a colloid form, or a form of a very fine suspension.

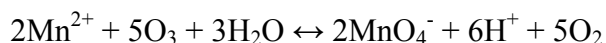In the course of demanganization, the following main reactions take place:

$$Mn^{2+} + 2H_2O \leftrightarrow Mn(OH)_2 + 2H^+$$
$$Mn(OH)_2 + \tfrac{1}{2}O_2 \leftrightarrow MnO_2 + H_2O$$
$$Mn^{2+} + CO_3^{2-} \leftrightarrow MnCO_3$$
$$Mn^{2+} + Cl_2 + H_2O \leftrightarrow MnO_2 + 2Cl^- + 4H^+$$
$$3Mn^{2+} + 2MnO_4^- + 2H_2O \leftrightarrow 5MnO_2 + 4H^+$$
$$Mn^{2+} + O_3 + H_2O \leftrightarrow MnO_2 + O_2 + 2H^+$$
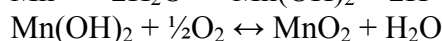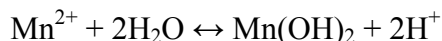
In case of an over-abundance of ozone, the oxidation of Mn^{2+} can turn all the way to permanganate:

$$2Mn^{2+} + 5O_3 + 3H_2O \leftrightarrow 2MnO_4^- + 6H^+ + 5O_2$$

The oxidation of Mn^{2+} by permanganate takes place in a neutral or slightly acid environment, while the oxidation by oxygen occurs rather in an alkaline area. [2]

3.1. Demanganization of the mine water from Jiří Mine – ČS J3

The mine water was sampled in an open pit mine Jiří, from a filling station J3 to be precise. It is characteristic for its high content of iron (approx. 70 mg.l^{-1}), manganese (approx. 8 mg.l^{-1}) and low pH of 2.64. The mine water gets in contact with air, and thus iron occurs here in its trivalent form. The current treatment is neutralization, after which the treated water is pumped into the Panského Pond. The neutralization is, of course, insufficient as the concentration of manganese is high even after treatment.

The following methods of manganese removal were tested:

- Alkalinization by means of $Ca(OH)_2$
- Oxidation by potassium permanganate, hydrogen peroxide and aeration
- Combination of alkalinization ($Ca(OH)_2$) and oxidation ($KMnO_4$, H_2O_2)

- Contact demanganization on silica sand
- Alkalinization and sorption on Slovakite
- Alkalinization and sorption on ettringite

3.1.1. Removal of manganese by alkalinization

Based on the results of the carried out experiments it can be stated that the reduction of the concentration of manganese below 0.5 mg.l^{-1} from the original 8 mg.l^{-1} occurs at pH around 9.5, which was obtained by dosing calcium hydrate (1g to 1 litre of treated mine water) and concurrent stirring in a mixing column at 150 rev.min^{-1} for 20 minutes. When applying such a dose of calcium hydrate, the content of manganese is reduced to a required level but there is a disadvantage of a high pH of the treated water which would have to be decreased before discharge. Therefore, further experiments were focused on the reduction of manganese content at pH required for discharging treated water into surface waters.

Table 1. Results of demanganization by alkalinization

Test No.	Dose of Ca(OH)$_2$, (g.l^{-1})	Stirring time (min.)	pH in the filtrate	c(Mn) in the filtrate, (mg.l^{-1})
1	0,8	10	7,70	5,08
2	0,9	10	8,57	2,66
3	1,0	10	9,36	1,44
4	0,8	20	8,51	1,90
5	0,9	20	8,78	1,89
6	1,0	20	9,48	0,42

3.1.2. Removal of manganese by means of oxidation by oxidants and aeration

Adding an oxidant in an acid environment, the removal of manganese does not occur as oxidation applying an oxidant takes place only in a neutral or alkaline area, and applying atmospheric oxygen as far as in the alkaline area. With regard to the fact that pH of the tested mine water was 2.64 there was no manganese concentration reduction during the tests either due to adding a variety of doses of potassium permanganate or of hydrogen peroxide. On the contrary, using potassium permanganate the concentration of dissolved manganese was logically increased. Thus, the

following experiments concentrated on the removal of the residual manganese by means of oxidants in the mine water, pre-treated (neutralized) to pH around 7 by calcium hydrate.

3.1.3. Removal of manganese combining alkalinization and oxidation

The acid mine water was neutralized by means of $Ca(OH)_2$. A fraction of manganese precipitated in the form of hydroxides and hydrated oxides of manganese, another fraction stayed in a dissolved form. The acquired suspension was supplied with doses of an oxidant, i.e. potassium permanganate and hydrogen peroxide.

a) Application of $KMnO_4$

Calcium hydrate was added into the raw water (a dose of 0.34 $g.l^{-1}$). Based on the measured value of dissolved manganese content post neutralization, a basic dose of potassium permanganate was calculated. The samples of the neutralized water were supplied with multiples of the basic dose and according to the acquired results, an optimal dose was calculated.

In the mine water post neutralization, the content of dissolved manganese is 5.33 $mg.l^{-1}$, the basic dose of $KMnO_4$ is therefore 10.23 ml of 0.1% solution of potassium permanganate to one litre of mine water. The following multiples of the basic dose were tested: 1.0; 1.2; 1.4; 1.,6; 1.8; and 2.0. The results are given in Table 2.

Table 2. Results of demanganization combining alkalinization and oxidation by potassium permanganate

Test No.	Dose of $KMnO_4$ $(ml.l^{-1})$	c(Mn) in the filtrate $(mg.l^{-1})$	pH in the filtrate
1	10,23	2,12	7,02
2	12,28	0,10	6,98
3	14,40	1,15	6,79
4	16,40	1,80	6,61
5	18,40	1,65	6,23
6	20,40	2,45	6,33

What can be considered an optimum result is the result of the experiment No. 2. The pre-treated water was supplied with a 1.2 multiple of the basic dose. This experiment was verified several times and the content of residual manganese in the filtrate was always lower than 0.2 mg.l⁻¹ at pH around 7 (See Table 3).

Table 3. Results of the verification of a selected method

Tests No.	Dose of KMnO₄ (ml.l⁻¹)	c(Mn) in the filtrate (mg.l⁻¹)	pH in the filtrate
1	12,28	0,05	6,83
2	12,28	0,16	6,92
3	12,28	0,15	6,88
4	12,28	0,12	6,91

The concentration of manganese is high after pH adjustment. During the following application of a potassium permanganate oxidant, the content of manganese drops almost to zero, while pH of such treated water complies with the requirements given by law.

b) Application of H_2O_2

Calcium hydrate was added into the raw water (a dose of 0.34 g.l⁻¹). The samples of the neutralized water were supplied with the below mentioned doses of 10% H_2O_2. It is apparent from the results stated in Table 4 that the application of an oxidant - hydrogen peroxide – cannot be recommended for its low effectiveness in dissolved manganese removal.

Table 4. Results of demanganization combining alkalinization and oxidation by hydrogen peroxide

Test No.	Dose of H_2O_2 (ml.l⁻¹)	c(Mn) in the filtrate (mg.l⁻¹)	pH in the filtrate
1	2	5,2	6,98
2	4	5,0	6,92
3	8	4,9	7,02
4	12	4,5	6,98
5	16	4,3	7,01
6	20	4,3	7,04

c) Aeration

Aeration of the acid or neutralized water did not have any effect on the reduction of dissolved manganese. The intensity of aeration was high and the only variable was the aeration time. Even during an intense several-hour aeration there was no significant decrease in the dissolved manganese. At such a high concentration of manganese in the treated water, this demanganization method cannot be recommended.

4. Contact demanganization on silica sand

The principle of this method lies in the adsorption of Mn^{2+} ions onto MnO_2 with a follow-up oxidation of such adsorbed ions. For the experiments we used silica sand of 1 mm grain size, prepared by potassium permanganate and glucose, in a 25-mm-diameter column and feed height of 50 cm.

Even in this case it was necessary to pre-treat the raw water by neutralization. In the raw water the concentration of iron is high. Raw water passing through the column would cause fast clogging of the column by the iron precipitation products. Therefore, post pH adjustment, water is filtered and the filtrate of pH around 7 and of manganese content of approximately 5 $mg.l^{-1}$ is supplied into the column. After flowing through the column, the concentration of dissolved manganese and pH are determined. The flow speed was 1 $m.h^{-1}$, which should be sufficient.

According to the measured results, this method cannot be recommended so far as the concentration of manganese post its passage through the column was almost identical as at its input.

4.1. Demanganization by means of ettringite

Ettringite sludge (pure), which is formed during desulfatation ($3CaO$. Al_2O_3 . $3CaSO_4$. $31H_2O$), was tested as a sorbent of manganous ions. Theoretically, calcium ions can be substituted by divalent ion of Mn^{2+} in the lattice of ettringite.

The mine water was pre-treated to pH 7 and the concentration of manganese was then approximately 5 $mg.l^{-1}$. Mixing the mine water and ettringite, pH gets higher (See Table 6). Thus, for the purpose of

comparison, demanganization was carried out only with Ca(OH)$_2$ (See Table 5) at identical pH as in the mine water treated by means of ettringite. The experiments made use of fresh prepared, non-dried ettringite (humidity around 90 %)

Table 5. Results of demanganization by means of Ca(OH)$_2$

Test No.	Dose of Ca(OH)$_2$ (g.l^{-1})	pH in the filtrate	c(Mn) in the filtrate (mg.l^{-1})
1	0,05	6,98	5,40
2	0,10	7,70	4,88
3	0,15	8,51	2,96
4	0,20	8,98	2,66
5	0,25	9,01	1,97
6	0,30	9,36	1,44
7	0,35	9,48	0,42

Table 6. Results of demanganization by means of ettringite

Test No.	Dose of ettringite (g.l^{-1})	pH in the filtrate	c(Mn) in the filtrate (mg.l^{-1})	c(SO$_4^{2-}$) in the filtrate (mg.l^{-1})
1	2	6,81	4,96	184
2	4	8,92	1,74	232
3	6	9,06	0,81	239
4	10	9,26	0,00	393
5	20	9,39	0,00	558
6	30	9,46	0,00	576

Hence, using ettringite, more effective removal of manganese occurs than when applying only calcium hydrate, which probably means that there is concurrent precipitation and sorption of manganous ions. There is a disadvantage of this process in a reverse liberation of sulphate ions. The question is whether this concentration is permissible or not.

4.2. Demanganization by means of Slovakite (0 – 0.1 mm)

The following doses were tested, which represent 0.1; 0.25; 0.5; 0.75 and 2 multiples of the doses recommended by the manufacturer. The recommended dose is 1 g.l^{-1}. Dosing Slovakite into the mine water with a

high content of manganese, pH increases. The removal of manganese is almost identical as in the case of removal by Ca $(OH)_2$. The input concentration of manganese in the mine water was 8 mg.l^{-1}. With regard to the fact that calcium hydrate is too expensive, Slovakite cannot be recommended for demanganization.

Table 7. Results of demanganization by means of Slovakite

Test No.	Input pH	Dose of Slovakite (g)	pH in the filtrate	c(Mn) in the filtrate (mg.l^{-1})
1	2,64	0,10	3,20	7,50
2	2,64	0,25	4,34	6,97
3	2,64	0,50	7,29	3,50
4	2,64	0,75	7,96	2,90
5	2,64	1,00	8,70	1,72
6	2,64	2,00	9,10	1,50

5. Conclusion

Based on the above mentioned results of several tested methods of demanganization, the most effective can be considered the removal of manganese by neutralization (alkalinization) by calcium hydrate in the combination with oxidation by potassium permanganate adhering to the required pH in the neutral area and respecting the limit values of manganese concentrations for water discharge into surface waters (1 mg.l^{-1}).

6. References

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