

# Treating Mine Water contaminated with Iron, Manganese and high solid Carbon Loads under Tropical Conditions<sup>1</sup>

Stefan Kurtz<sup>2</sup>, Felix Bilek<sup>3</sup>, Jörg Schlenstedt<sup>4</sup> and Hans-Jürgen Kochan<sup>5</sup>

<sup>2</sup> Groundwater Research Center Dresden, 01217 Dresden, Germany, skurtz@gfi-dresden.de

<sup>3</sup> Groundwater Research Center Dresden, 01217 Dresden, Germany, fbilek@gfi-dresden.de

<sup>4</sup> LMBV-International, Knappenstr. 1, 01968 Senftenberg, Germany, J.Schlenstedt@lmbvinternational.de

<sup>5</sup> eta-AG, Dissenchener Str. 50, 03042 Cottbus, Germany, hjkochan@eta-ag.com

## ABSTRACT

Surface and underground coal mines in the North-Vietnamese coal mining district are characterized by acidic iron and manganese enriched mine waters. A group of German companies is planning and constructing a mine water treatment plant in the Vang Danh coal mines together with the Vietnamese mining industry. The discharged mine waters show very different qualities, changing fluxes and transport high amounts of suspended coaldust. Laboratory and bench scale tests proved, that a separation of the solids together with precipitated hydroxides is possible. The resulting sludge density is much higher than pure hydroxide sludge and its structure and sedimentation is strongly dependant on the ferrous iron concentration in the water. No sludge recycling (HDS-technique) is necessary, because the sludge density proved to be sufficient for effective dewatering. Manganese removal is only partially performable during oxidation and neutralisation in a reaction basin, even if values up to pH 9 are used. To remove surplus manganese, a final demanganisation step is necessary. Investigations of oxidizing and catalyzing techniques to remove manganese in fixed bed reactors in long term laboratory and bench scale tests were performed to support outline planning.

Additional Key Words: treatment plant, coal sludge, catalytic demanganisation

## INTRODUCTION

In the province Quang Ninh in the north-east of Vietnam anthracite coal is extracted from underground mines near the small town Vang Danh (Figure 1). The local state-owned mining company planes to treat the mine waters, which are currently released into the river and eventually into the Halong-Bay, which is classified as world natural heritage by the UNESCO. A group of German companies is planning and constructing a mine water treatment plant together with the Vietnamese partners for the mine site Vang Danh.

---

<sup>1</sup> Paper presented at Securing the Future and 8th ICARD, June 23-26, 2009, Skellefteå, Sweden.



Figure 1. Vietnam, the province Quang Ninh and the mining area in Vang Danh.

The acidic mine waters which are discharged from 4 adits are characterized by elevated concentrations of Fe(II) and Mn(II) and show high BOD<sub>5</sub>- and COD-values as well as high amounts of suspended solids, which mainly consist out of coaldust and already precipitated hydroxides. The water qualities and water fluxes show high fluctuations. An elaborated local monitoring program and laboratory investigations proved that the high BOD<sub>5</sub>- and COD-values resulted from coaldust in the water samples, which is the dominant part of the suspended solids.

Table 1 shows the water qualities of the occurring mine waters and their variance. Also the design values for the treatment plant, which are used as planning criteria, and the Vietnamese standards for industrial wastewaters are given.

Table 1. Mean composition of the occurring mine waters, the design values for the treatment plant and Vietnamese standards for industrial wastewaters.

Main parameters (concentrations in mg/l)	Compositions of the mine waters from the adits					Design values for averaged inflow of the mine water treatment plant	Vietnamese standards for industrial wastewaters (TCVN 5945-B)
	+120	+122 dong	+122 tay	+130	+135		
pH	6.86 ± 0.72	6.26 ± 1.03	6.69 ± 0.41	7.86 ± 0.23	5.94 ± 0.74	5.8	5.5 - 9
Fe <sub>total</sub>	2.16 ± 3.21	15.6 ± 13.9	6.09 ± 4.43	0.68 ± 0.88	49.4 ± 49.2	50.0	5
Mn	1.25 ± 1.47	6.23 ± 1.97	3.58 ± 2.51	0.29 ± 0.19	15.5 ± 9.5	11.4	1
Al	0.34 ± 0.42	6.44 ± 11.12	0.99 ± 2.56	0.17 ± 0.30	2.07 ± 3.46	13.9	-
Ca	64.6 ± 15.8	93.2 ± 29.7	109 ± 37	65.9 ± 12.9	154 ± 31	108.5	-
Mg	25.2 ± 9.9	80.5 ± 28.7	96.9 ± 39.7	21.8 ± 5.4	123 ± 50	91.2	-
Sulfate	189 ± 125	528 ± 153	322 ± 241	113 ± 76	674 ± 383	723.8	-
TS <sup>*1</sup>	539 ± 374	612 ± 345	1616 ± 326	838 ± 813	1391 ± 1082	1000	-
TSS <sup>*2 *3</sup>	13.7 ± 8.2	121 ± 207	53.3 ± 35.1	80.8 ± 59.6	141 ± 181	180.3	100
COD <sup>*3</sup>	19.2 ± 17.5	78.1 ± 86.0	69.7 ± 83.4	50.3 ± 18.5	103 ± 145	110.0	80
BOD <sub>5</sub> <sup>*3</sup>	7.50 ± 7.61	27.5 ± 30.1	24.3 ± 34.6	18.5 ± 7.4	38.8 ± 62.5	42.9	50
DOC	1.39 ± 0.62	2.19 ± 1.29	1.61 ± 1.21	1.8 ± 1.3	2.92 ± 1.61	1.8	-
Hg	< 0.0002	0.0003 ± 0.0001	0.0002 ± 0.0001	< 0.0002	0.0004 ± 0.0002	0.00032	0.005
other heavy metals	traces	traces	traces	traces	traces	-	-

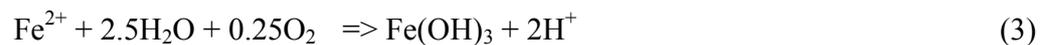
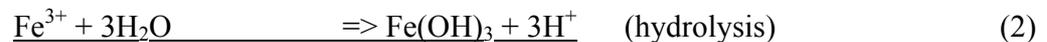
<sup>\*1</sup> total solids <sup>\*2</sup> total suspended solids <sup>\*3</sup> measured after a defined period of settlement of the solids according to a Vietnamese method for analysing surface waters

Local conditions are characterized by high temperatures and high humidity in summer and seasonal high rain falls in the hilly areas of the mine site. The rainfalls can lead to a rise of the local branches of the Vang Danh River of several meters right in the mine site. The production area is prone to be flooded occasionally. These conditions require a robust type of construction and process technology. Strict separation of mine water and surface runoff is necessary to exclude uncontaminated surface runoff from entering the plant. High temperatures reduce oxygen dissolution and thus make enlarged aeration devices necessary. All parts of the plant need to operate under a wide range of volume fluxes and inflow water qualities.

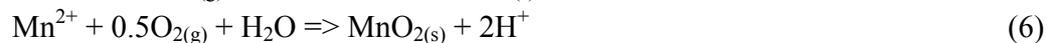
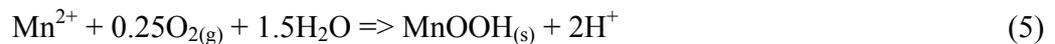
Laboratory and bench scale tests have been performed to identify the crucial parameters for the designing process. For this purpose a bench scale treatment plant, which also is used for the capacity building of Vietnamese engineers, was built in Germany. The major process steps of the required mine water treatment have been evaluated and tested to verify the treatment plant design.

### OXIDATION OF IRON AND MANGANESE

*Metal precipitation* as hydroxide was planned to be the key process of treatment. It is a two step process comprising of oxidation (equation 1) and hydrolysis (equation 2). Ongoing polymerisation and water release of the freshly formed hydroxides eventually leads to the creation of solids which can be precipitated. The overall rate limiting step (equation 3) is oxidation, which depends on pH, Fe(II)- and O<sub>2</sub>-concentration (equation 4; various papers cited in Sung & Morgan, 1980). According to Tamura et al. (1976), Sung & Morgan (1980) and others the total rate of iron oxidation is controlled by the sum of the homogeneous (in solution) and the heterogeneous (sorption of the reduced metal species to surfaces before oxidation) rate.



$$-\frac{d[\text{Fe(II)}]}{dt} = k[\text{OH}^-]^2 \cdot [\text{Fe}^{2+}] \cdot [\text{O}_2] \quad (4)$$



*Manganese oxidation* follows the same laws, whereas under natural conditions Mn(III)-phases like β-MnOOH are formed (equation 5), which recrystallise and disproportionate in the long run to form Mn(IV)-oxides like MnO<sub>2</sub> (equation 6; various possible pathways are discussed by Tebo et al., 2004). Energy gain by Mn-oxidation under atmospherical conditions is much lower compared to iron oxidation and thus Mn-oxidation represents a major technological challenge. Figure 2 compares the changes in Eh- and pH-conditions, which have to be performed to enable oxidation under purely homogeneous and abiotic conditions. To minimize the efforts for Mn-oxidation the activation energy, which is necessary to initialize the reaction, has to be reduced by microbial catalysis (Bohm, 1992; Tebo et al., 2004) or by providing catalyzing surfaces (Tamura et al., 1976; Wehrli, 1990). Both techniques enable the technological performance of the desired

reactions even if pH- and redox-conditions in the bulk solution exist, which are not sufficient for acceptable homogeneous rates (Sharma, 2001) under purely chemical conditions.

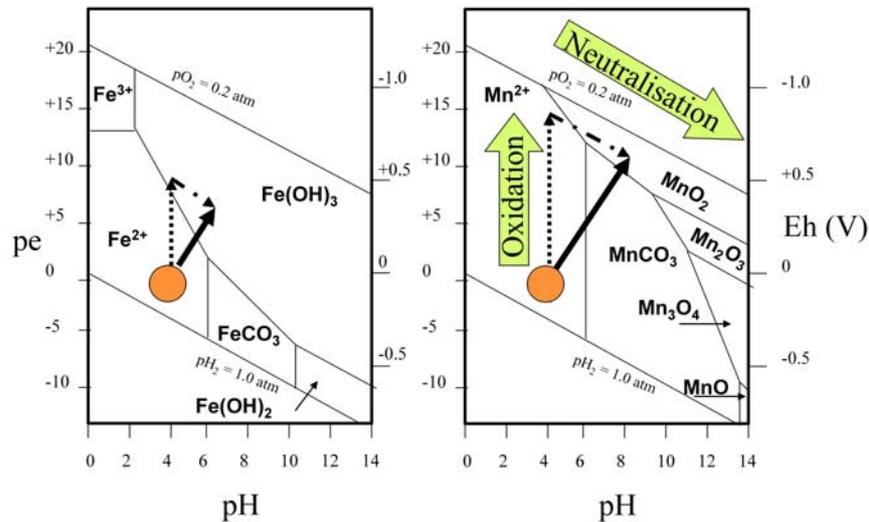


Figure 2. Comparison of the combined oxidation and neutralisation step in a pH/Eh-diagram for iron and manganese.

By *sorption to surfaces* the metal ions lose parts of their hydrated shell and thus electron transfer is facilitated (Junta & Hochella, 1994). Catalysis of the oxidation process can occur at foreign surfaces (surfaces of different mineralogical structure compared to the precipitating mineral; heterogeneous catalysis) or at already existing surfaces of a solid Mn-phase which is currently precipitating (homogeneous catalysis). The rates of the heterogeneous process are determined by the structure of the solids (Junta & Hochella, 1994).

*Chemoorganotroph microbes catalyze Mn-oxidation* by sorbing them to their cell membranes and by creating oxidation promoting chemical conditions in the biofilm. In this case manganese oxidation is not so much controlled by thermodynamic but by biological conditions. These include the availability of nutrients, oxygen, a carbon source, the absence of toxic substances, the absence of competing microbes and ambient temperatures. Due to the low amount of releasable energy during Mn-oxidation, Fe-oxidizing bacteria outcompete Mn-oxidizers if more than 0.5-2 mg/L iron are present (Canfield et al., 1993).

An alternative to oxidation is the Mn-removal merely by *sorption to Fe(III)-hydroxides* (Sung & Morgan, 1981) if enough surfaces can be provided.

Initially five options for manganese removal were considered:

1. Raising the oxidation-level by adding ozone. Tests with ozone showed that manganese removal was successful but high investment and energy costs of the ozone generation were expected. Also it was expected that remaining organics from the coaldust would use up high amounts of ozone and thus increase the ozone demand
2. Biological treatment was considered to be rather risky because of the high fluctuations of the water quality (Table 1) and the danger of mine water contamination with biotoxic substances caused by mining activities

3. Sorption of Mn(II) to freshly formed Fe(III)-hydroxides or to coaldust particles (without oxidation).
4. Rising of the pH to perform Mn-hydroxide precipitation along with Fe-precipitation.
5. Catalytic demanganization by heterogeneous oxidation using Mn-(hydr)oxide-surfaces.

Tests were performed to evaluate the last three possibilities. The results are presented below.

### DESIGN OF THE BENCH SCALE TREATMENT PLANT

The preliminary process design of the bench scale treatment plant, which corresponds to the design of the full scale mine water treatment plant in Vang Danh, is shown in Figure 3. Iron and coaldust will be removed by aeration and neutralisation in a reaction basin and by separation of the precipitated hydroxides and the coaldust in a subsequent sedimentation basin. The demanganisation is intended to be performed in subsequent fixed bed filters.

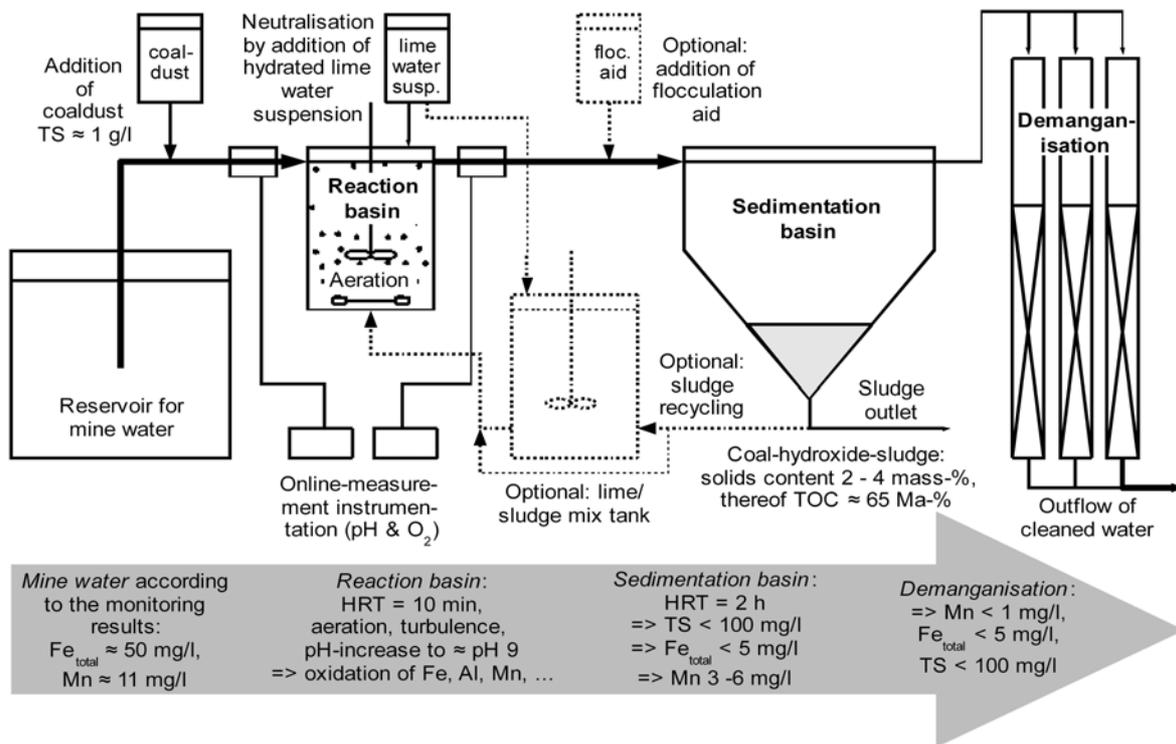


Figure 3. The process design of the bench scale treatment plant at the GFI in Dresden.

The full scale mine water treatment plant will have three stages of extension, each of them able to treat 800 m<sup>3</sup>/h. To perform tests in the bench scale plant (Figure 4), basin volumes, and fluxes of the full scale treatment plant were downscaled by a factor of 5000. The same hydraulic residence times (HRT) in the reaction basin (10 min) and in the sedimentation basin (2 h) as intended in the full scale plant were used.

For most of the laboratory and bench scale tests it was necessary, to create artificial mine waters (according to column 7 in Table 1), because it was not possible to transport sufficient amounts of original water from Vietnam to Germany. It was shown, that the suspended coaldust-solids influence the treatment procedure and due to their high amounts compared to the metal load, the produced sludges are dominated by coaldust. Thus a creation procedure for artificial mine waters with coaldust was developed to ensure comparable properties to the original water samples from Vang Danh, which were only obtainable in small amounts. Therefore field water samples were analyzed and characterized in terms of their dissolved and solids content, the particle size distribution of the solids and their sedimentation behavior. The physicochemical behavior of the artificial mine water was then adjusted to the field samples by varying the coaldust sources, the grinding procedure and the technology of adding the coaldust into the mine water. An addition of coaldust slurry into the turbulent waste water flux just before entering the bench scale treatment plant was proved to be the most realistic and successful technique.

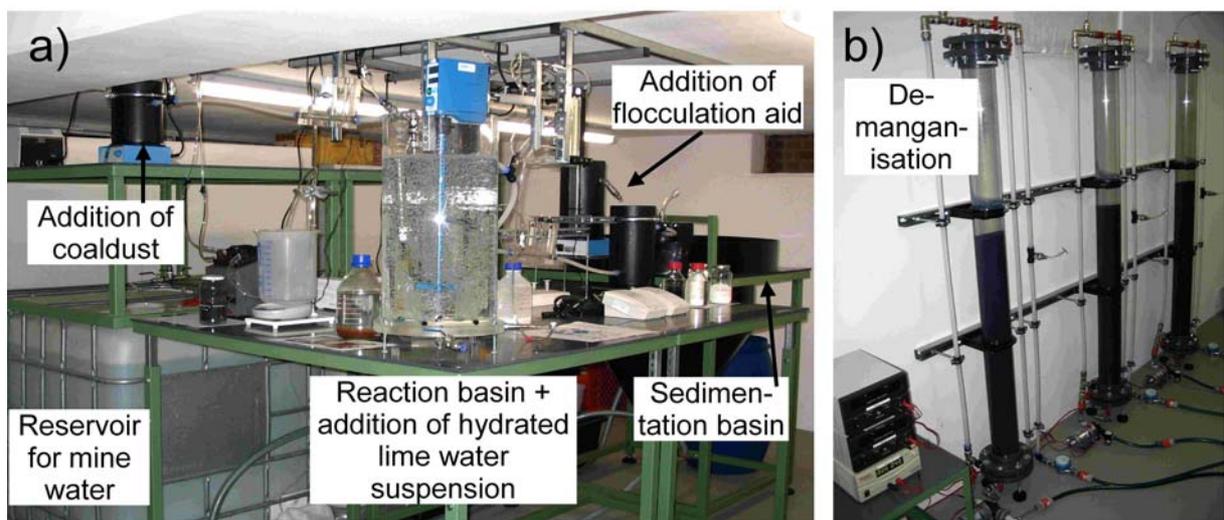


Figure 4. a) The bench scale treatment plant and b) the demanganisation step at GFI Dresden.

## RESULTS

### Removal of Iron and suspended solids

To evaluate the oxidation process of iron in the reaction basin together with the coaldust and the sedimentation of solids, two-step sedimentation batch tests were performed. In the first step the artificial mine water was neutralized and oxidized with hydrated lime water suspension (of 50 g/l CaO) and in the second step sedimentation was allowed. Concentrations of ferrous iron, solids loads and pH-values (pH 7 - pH 9) were varied. In some tests flocculation aid was added.

The tests showed, that separation of the organic solids together with the freshly forming hydroxides works well. The formation of the hydroxides supports the sedimentation process of the solids and forms a coal-hydroxide-sludge by creating discrete coal particle-hydroxide flocs. The resulting sludge solids contents of (2-32 mass-%) are much higher than pure hydroxide

sludge (experimental result for a water with 50 mg/l Fe(II) = 0.3 mass-%). Its structure and sedimentation process is strongly dependant on the initial ferrous iron concentration in the mine water (Figure 5). If the iron concentrations are below 10 mg/l, no particle-hydroxide flocs are forming and the coaldust (TS=1 g/l, Table 1) predominantly stays dispersed as single particles in the water column, which settle according to their grain size and density and create a very dense sludge (20-40 mass-%). In this case a complete sedimentation was not achieved after 2 hours.

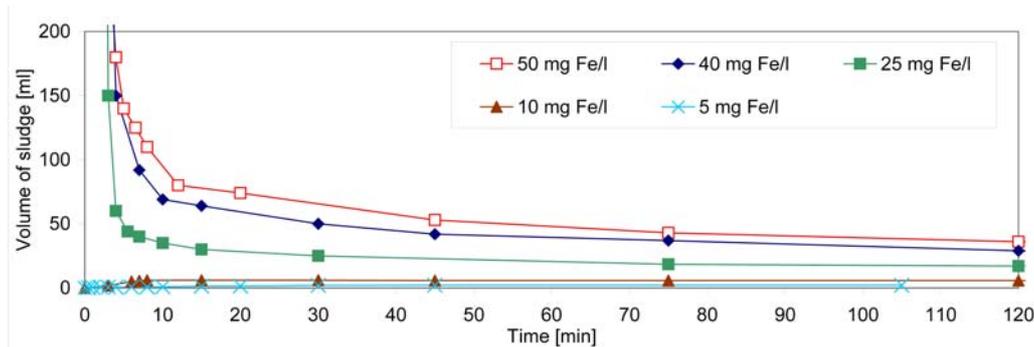


Figure 5. Development of the sludge volume created out of one litre of mine water within a sedimentation time of two hours for a test series with 1 g/l of coaldust, pH 8 and no addition of flocculation aid.

The density and solids content of coal-hydroxide-sludge is also dependant on the pH-value in the reaction basin and on the addition of flocculation aid. It was found, that the tested flocculation aid supports the sedimentation process by creating larger flocs (faster settlement), but also that its application is not necessary at Fe(II)-concentrations > 10 mg/l, because the settling process is effective enough within the HRT of two hours in the sedimentation basin. The detected solid loads of the runoff were far below the required Vietnamese standard for the TSS of 100 mg/l (Table 1). No sludge recycling with or without an additional lime/sludge mix tank (HDS-technique; e.g. Aubé, 2004) proved to be necessary, because the solids content of the sludge of 2 to 4 mass-%, which is expected for a Fe(II)-concentration of 50 mg/l and a TS of 1 g/l proved to be sufficient for effective dewatering.

### Demanganisation techniques

For the choice of an adequate demanganisation technique for the mine water treatment plant in Vang Danh, several techniques of manganese removal were tested in laboratory and bench scale tests at the GFI in Dresden.

#### *Oxidation and sorption of manganese in the reaction basin*

By increasing the pH-value in the reaction basin, parts of the Mn can be sorbed to suspended solids or are precipitated as hydroxides. To explore the relation between pH-value and Mn-removal, several titration tests were conducted, using original samples and artificial material. Furthermore the influence of the amount of suspended Fe(III)-hydroxides and coaldust on the Mn-removal was investigated.

The tests showed, that an increase of the pH-value up to 9 leads to a Mn-removal of more than 50 % with a comparatively small amount of additional hydrated lime (factor  $\approx 1.4$  compared to pH 7, Figure 6b). At a pH-value of 10 complete Mn-removal would be possible, but because of the required high amounts of hydrated lime (factor  $> 2$  compared to pH 7; Figure 6b), the resulting high running costs and an overstepping of the effluent pH-values, this technique is not reasonable. To remove surplus manganese a final demanganisation step is necessary.

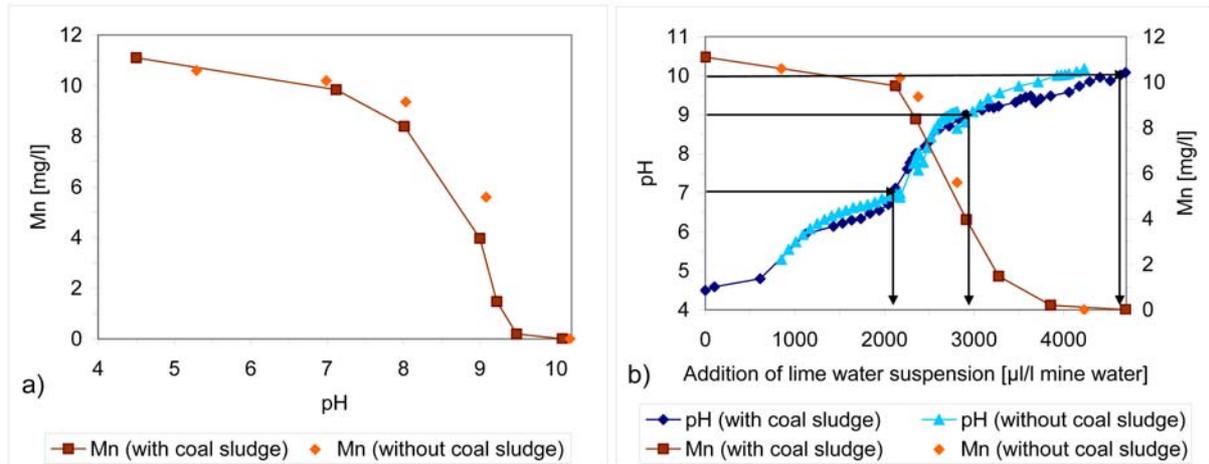


Figure 6. Mn-removal and consumption of lime water suspension during a Mn-precipitation-test with and without an addition of artificial coal sludge and 50 mg/l of Fe(II).

The manganese-precipitation-tests also showed, that higher amounts of Fe-hydroxides support Mn-removal, while increased amounts of coaldust have a rather small effect (Kurtz, 2008). Mn-concentrations declined during the HRT of 10 minutes in the reaction basin, but no additional Mn-removal was observed during the HRT of 2 hours in the sedimentation basin. Thus an equilibrium between dissolved Mn and Mn sorbed to the hydroxide coaldust flocs was assumed after a reaction time of 10 minutes. This ruled out sludge recycling as remediation process, because the recycled sludge would be saturated with Mn, too. Besides, increased amounts of sludge in the reaction basin caused a significantly higher consumption of hydrated lime to adjust the pH-value (Figure 6b).

The pH-values declined during the residence time of the water in the sedimentation basin by about 0.2 units. An increase of the pH in the reaction basin by this amount might be possible to increase the Mn-removal, which is highly sensitive to the pH-value in this range (Figure 6a). The pH-decline is due to atmospheric CO<sub>2</sub>-take up and depends on the geometry and hydraulics of the sedimentation basin. Thus it can not adequately be tested in the laboratory.

A drop of the Mn-concentration below the critical value of 1 mg/l is not possible by solely increasing the pH-value in the reaction basin. Thus a subsequent catalytically enhanced Mn-oxidation is necessary. A reduction of the Mn-load before the catalytic demanganisation will minimize the costs for filter materials and chemicals and increase the intervals of backwashing.

### Catalytic oxidation of manganese

In preparation of tests with the backwashable fixed bed bench scale filters (Figure 4b), smaller column experiments (length 50 cm) were performed to pre-evaluate the following three catalytic Mn-(hydr)oxide-materials: 1) Mg/Ca-Oxides with Mn-oxide coating, 2) silicate sand with Mn-oxide coating and 3) natural Mn-ore. All three filter materials do not require additional oxidizing chemicals. The inflowing mine water had a mean Mn-concentration of 6 mg/l (Figure 7, due to the elevated pH-value about 50 % of the design value in Table 1), an average O<sub>2</sub>-concentration of 10 mg/L and pH-values between 8.7 and 9, representing the runoff of the sedimentation basin. No backwashing of the test columns was possible and thus eventual breakthrough was expected.

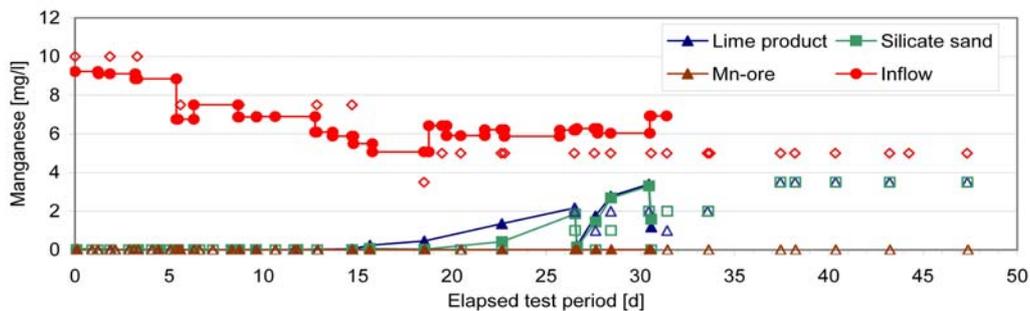


Figure 7. Manganese removal by catalytic oxidation during a column experiment with three different filter media. The data points marked with open symbols represent measurements with a semi-quantitative method.

Figure 7 also shows, that the manganese ore worked properly over the whole test period. In case of the other two products, a breakthrough started after 15 days. The O<sub>2</sub>-consumption was depending on the filter material between 0.1 and 0.3 mg/l, which is not sufficient to oxidize the complete Mn-load (equation 5). Thus the solids are assumed to be the major electron acceptors. Further tests with the bench scale filters will focus on the regeneration of the Mn-hydroxide surface by backwashing and the mass balances of Mn, O<sub>2</sub> and the electrons.

## CONCLUSIONS

The results of the laboratory and bench scale experiments led to a specification of the process design for the mine water treatment plant in Vang Danh (Figure 3).

The experiments showed, that an *addition of flocculation aid* is not necessary, because the created *coal-hydroxide-sludge* is settling sufficiently within the hydraulic residence time of two hours in the sedimentation basin. Anyhow this element was decided to remain in the process design as option to react on considerable changings of the mine water composition.

Furthermore it was found, that a *sludge recycling* is not necessary, because the detected sludge densities and solids contents proved to be sufficient for effective dewatering and because the recycling process will not support the manganese removal in the reaction basin as much as necessary to legitimate the rising operating costs for the much higher consumption of hydrated lime water suspension.

The *demanganisation* shall take part in two steps: firstly a removal of more than 50 % of the manganese concentration in the reaction basin will be performed and secondly *catalytic demanganisation* will be done using Mn-oxide coated products or natural Mn-ore as filter material.

#### **ACKNOWLEDGEMENTS**

We would like to thank the German Ministry of Education and Research (BMBF) for the funding of the research project "Water Management and Water Treatment" within the RAME-project (Research Association Mining and Environment in Vietnam). The authors are indebted to the employees of VINACOMIN, VITE and IET in Hanoi and Vang Danh for their kind support and hospitality.

#### **REFERENCES**

- Aubé, P. 2004. The science of treating acid mine drainage and smelter effluents. Downloaded at 16.03.2007 under <http://www.infomine.com/publications/docs/Aube.pdf>.
- Bohm, L. 1992. Optimierung der chemielosen Entmanganungsfiltration. PhD-Thesis at the Technical University of Dresden.
- Canfield, D.E., B. Thamdrup and J.W. Hansen. 1993. The anaerobic degradation of organic matter in Danish coastal sediments: Iron reduction, manganese reduction, and sulfate reduction. *Geochim. Cosmochim. Acta.* 57, p. 3867-3883.
- Junta, J.L. and M.F. Hochella. 1994. Manganese (II) oxidation at mineral surfaces: A microscopic and spectroscopic study. *Geochim. Cosmochim. Acta.* 58(22), p. 4985-4999.
- Kurtz, S. 2008. Exemplarische Behandlung von Bergbauwässern in Labor- und Technikumsmaßstab am Beispiel eines Bergbaustandortes in Vietnam (Vang Danh). 4th research-report of the GFI Dresden to the BMBF.
- Sharma, S.K. 2001. Adsorptive iron removal from groundwater. PhD-Thesis at the Wageningen University at the international Institute for Infrastructural, Hydraulic and Environmental Engineering
- Sung, W. and J.J. Morgan. 1980. Kinetics and product of ferrous iron oxygenation in aqueous systems. *Environ. Sci. Technol.* 14(5), p. 561-568.
- Sung, W. and J.J. Morgan. 1981. Oxidative removal of Mn(II) from solution catalysed by the  $\gamma$ -FeOOH (lepidocrocite) surface. *Geochim. Cosmochim. Acta.* 45, p. 2377 - 2383.
- Tamura, H., K. Goto and M. Nagayama. 1976. The effect of ferric hydroxide on the oxygenation of ferrous ions in neutral solutions. *Corros. Sci.* 16, p. 197-207.
- Tebo, B.M., J.R. Bargar, B.G. Clement, G.J. Dick, K.J. Murray, D. Parker, R. Verity and S.M. Webb. 2004. Biogenic manganese oxides: Properties and mechanisms of formation. *Annu. Rev. Earth Planet. Sci.* 32, p. 287-328.
- Wehrli, B. 1990. Redox reactions of metal ions at mineral surfaces. In: W. Stumm (ed.) *Aquatic chemical kinetics: Reaction rate processes in natural waters.* p. 311-336, New York: Wiley.