

# Development of fly ash granules for the heavy metal removal from mine waters

Theofanis Zoumis, Wolfgang Calmano

*Dept. of Environmental Science and Technology, Technical University of Hamburg-Harburg, Eissendorfer Str.40, D-21073 Hamburg, Germany*

*Phone: +49/40/42878-3319, Fax: +49/40/42878-2315, e-mail: theofanis@tu-harburg.de*

**Abstract:** The common way to treat acidic, heavy metal contaminated waters is the remediation in huge treatment facilities with high capital and running costs. Our approach is the passive treatment of mine waters with reactive materials, i.e. the introduction of the selected material underground into the water flow ("permeable reactive barrier") to demobilize heavy metals from solution by sorption and precipitation. Earlier research showed good heavy metal removal with different industrial by-products like brown coal fly ash and red mud from aluminum industry (Zoumis et al., 2000). The problem of these materials is the small particle size distribution which leads to a bad permeability for a barrier. The solution for that problem is the granulation of the materials with different binding agents. The most important point is to keep good capacitative factors (sorption and acid neutralization capacity). First results showed relatively good values for a possible use of fly ash as main component in a low-cost granule.

## 1 INTRODUCTION

The *Elbe* river, with a length of approximately 1100 km and a catchment area of 148.000 km<sup>2</sup>, is one of the largest and most highly polluted river systems in Europe. The main cause for the heavy metal contamination is the flooding of ore mines in several mining areas like the *Freiberger Revier* in the *Erzgebirge, Germany*. Because of the pyrite weathering in veins, acidic, sulfate-rich waters are developed, which contain great amounts of dissolved heavy metals. High heavy metal loads leave the mine area on the waterway and lead to toxic concentrations in several environmental compartments up to the mouth of the river *Elbe*. Mine flooding can be divided into two phases (Figure 1). The „first phase“ led to a very high contamination of the river *Triebisch*. Year by year, the heavy metal content decreased, and reached a relatively high „equilibrium level“ today („second phase“), e.g. the Zn load was 2000 t/a in 1971 and 34 t/a in 1997. Parallel, the acid production decreased and the pH increased from 3.8 to 6.2. The objective of this study is above all to reduce the long-term heavy metal discharges from the pits („second phase“) to the adjacent surface waters with economical in-situ measures. In the case of the *Freiberger* pit a method has been developed, which ensures the removal of heavy metals from mine water in the day level and in the shaft, respectively. Since an engineered system has, except of high capital costs, also high running costs, materials are tested, which can be filled into shafts and can remediate mine waters by sorbing or precipitating heavy metals and bind them on a long-term basis ("reactive geochemical barriers").

Earlier results (Zoumis et al., 2000) showed very good capacitative properties, i.e. sorption and acid neutralization capacity, for red mud and fly ash. But a problem of both materials is the small particle size which prevents permeability for high water streams. To solve the problem, particle size can be increased by means of granulation with different binding agents.

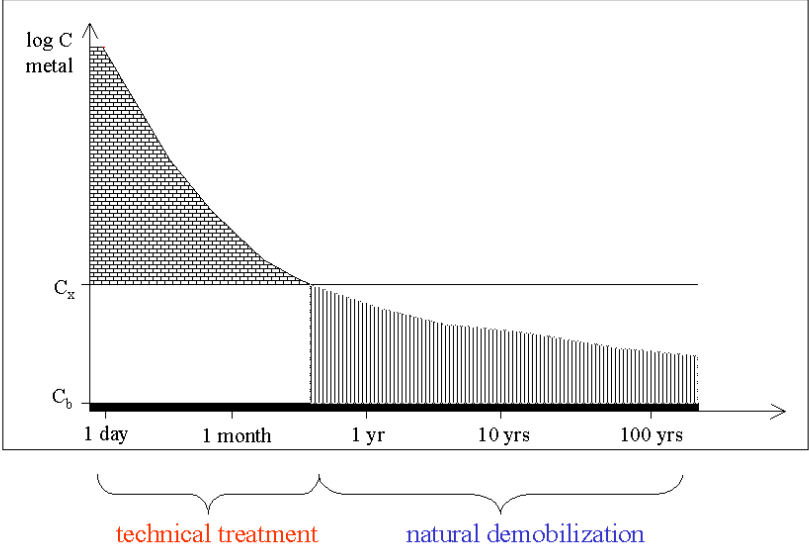
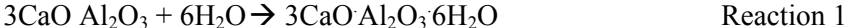


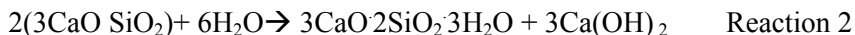
Figure 1 Two phases of ore mine flooding ( $c_b$ : harmless heavy metal concentrations - the water needs no treatment,  $c_x$  – heavy metal concentrations which determine the end of the first phase).

**2 MATERIALS AND METHODS**

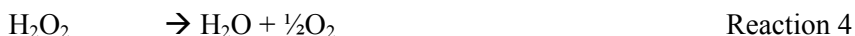
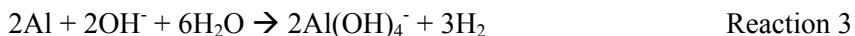
Granules of fly ash were developed with the addition of portland cement as a binding agent. Portland cement is made by firing limestone with clays at about 1450°C, causing partial fusion and the formation of a clinker, which is then powdered. Its typical chemical composition is: 67% CaO, 22% SiO<sub>2</sub>, 5% Al<sub>2</sub>O<sub>3</sub>, 3% Fe<sub>2</sub>O<sub>3</sub>, and small amounts of MgO and SO<sub>3</sub>. The mineralogical composition is: 45% 3CaOSiO<sub>2</sub>, 27% 2CaO SiO<sub>2</sub>, 11% 3CaO Al<sub>2</sub>O<sub>3</sub>, 8% 4CaO Al<sub>2</sub>O<sub>3</sub> Fe<sub>2</sub>O<sub>3</sub>, 0.5% Free-CaO, 3.1% CaSO<sub>4</sub>.

The anhydrous phases of portland cement react exothermically with water at different rates by complicated mechanisms to form ultimately a hard mass of hydrated compounds. Two of all the simultaneous reactions can be mentioned as they are the ones which play the most important role in the setting of portland cement (Mohamed and Antia, 1998):





To enhance the specific surface area of the material some auxiliary components can be added to increase porosity. For the experimental setup of this work, two auxiliary materials were used: aluminum powder and hydrogen peroxide. In both cases, the porosity of the agglomerates was increased due to chemical reactions in which gaseous phases were produced. The reactions lead to a production of hydrogen (Reaction 3) and oxygen (Reaction 4).



Twelve different granules were prepared and comparatively characterized. The amounts of all components were varied to determine the optimum composition (Table 1). The fly ash content varied between 80 and 95% and portland cement between 5 and 20%. Additionally, hydrogen peroxide, aluminum powder or just distilled water was added.

Table 1 Agglomerates prepared during the experimental work

Code	Fly ash, g	Cement, g	H <sub>2</sub> O <sub>2</sub> , drops	Al, mg	distilled water, mL
FAG 6	95	5	-	-	30...40
FAG 7	95	5	~ 15	-	"
FAG 8	95	5	-	50	"
FAG 9	90	10	-	-	"
FAG 10	90	10	~ 15	-	"
FAG 11	90	10	-	50	"
FAG 12	85	15	-	-	"
FAG 13	85	15	~ 15	-	"
FAG 14	85	15	-	50	"
FAG 15	80	20	-	-	"
FAG 16	80	20	~ 15	-	"
FAG 17	80	20	-	50	"

The solid materials were mixed in a bowl until homogeneity was achieved. Then, the water was added until the mixture looked like a homogeneous mud. All

samples were dried in an oven at 100°C for 48 hours. To samples FAG 7, FAG 10, FAG 13 and FAG 16 hydrogen peroxide was added before drying.

After the drying time, the blocks of each sample were crashed carefully with a hammer and the agglomerates were obtained. Granules with a size between 4 and 5 mm were collected and used for the experiments.

The specific surface area and density were determined with a BET Surface Area Analyzer (NOVA-1200, Quantachrome Cooperation). The acid neutralization capacity (ANC) was determined by titration with  $c_{\text{HNO}_3}=1 \text{ mol L}^{-1}$  to a pH of 4. The compressive strength was measured after guidelines of the DIN EN 196.

To identify the removal efficiency of the materials for zinc, manganese, cadmium, and nickel, batch experiments with model water were conducted. The model water used was very similar to the *Reiche Zeche* shaft water from the *Freiberger* pit in Germany (Zoumis et al., 2000). Table 2 shows the composition of the used model water. To describe sorption kinetics, 50 mL of model water were shaken with different concentrations of agglomerates (2 g/L, 6 g/L, 10 g/L). After certain periods of time (1 min, 3 min, 5 min, 10 min, 20 min, 60 min) water samples were taken and analyzed by AAS. To describe sorption equilibrium, the model water was shaken with six different solid/solution ratios (1 g/L, 2 g/L, 4 g/L, 6 g/L, 8 g/L, 10 g/L) for 24 hours. The pH value was measured in all samples.

Table 2 Model water composition

Cations	ppb	ppm
<b>Zn</b>		<b>111.0</b>
<b>Cd</b>	<b>100.0</b>	
<b>Ni</b>	<b>89.3</b>	
Co	40.0	
B	309.92	
<b>Mn</b>		<b>15.0</b>
Mg		42.9
Cu	45.1	
Ca		335.8
Sr	610.0	
Na		439.3
K		13.2
As	80.1	
Anions	ppb	ppm
Cl		220.0
NO <sub>3</sub>		790.9
SO <sub>4</sub>		881.6
CO <sub>3</sub>		191.0
Final pH	5.9	

### 3 RESULTS AND DISCUSSION

#### Specific Surface Area

The results for the measurement of the specific surface area and the average pore radius for the agglomerates are shown in the following figures.

Figure 2 illustrates the behavior of the agglomerates with increasing cement content, and Figure 3 shows the influence of the addition of hydrogen peroxide and aluminum on the specific surface area of the agglomerates.

As it can be seen in Figure2, specific surface area increases with increasing cement concentration. With regard to the pore radius (Figure3), it can be concluded that there is not much difference between all samples. The specific surface area of the samples with same amount of cement is always higher for the samples containing hydrogen peroxide than the sample with no additives. The lower value is for the sample with aluminum.

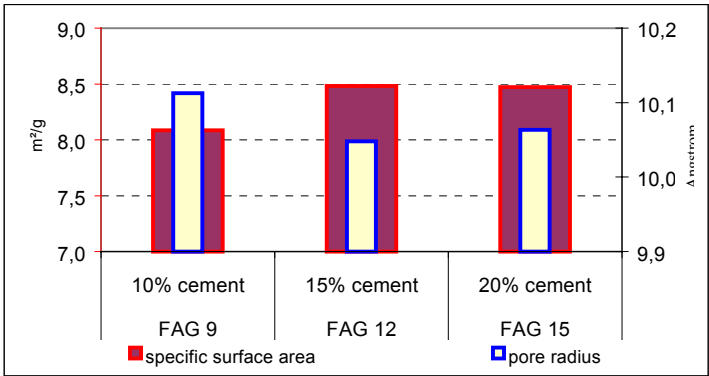


Figure 2 Specific surface area (m<sup>2</sup>/g) and pore radius (Angstrom: 1 Angstrom = 0.1 nm) for samples of fly ash with only cement

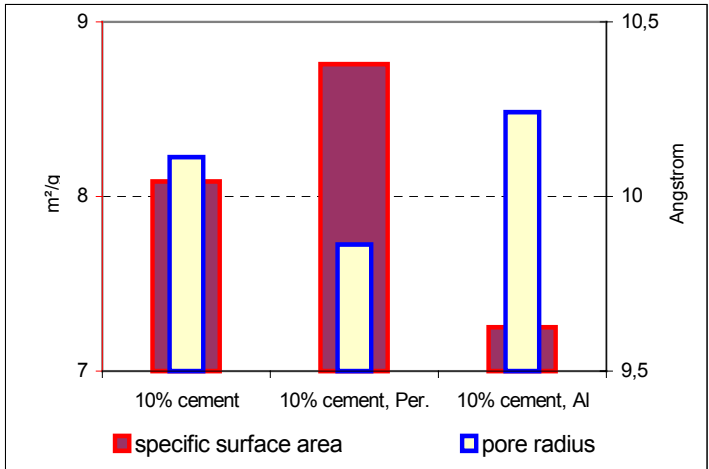


Figure 3 Specific surface area (m<sup>2</sup>/g) and pore radius (Angstrom) for samples with 10% cement only, 10% cement + H<sub>2</sub>O<sub>2</sub> (Per.) and 10% cement + Al

With this it can be concluded that for these agglomerates, the aluminum does not play an important role in increasing the porosity, but the hydrogen peroxide does it very well (Reactions 3 and 4 respectively).

**Acid Neutralization Capacity (ANC)**

The ANC formation and reaction can be explained by two complementary mechanisms:

- 1.  $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{heat}$  Reaction 5
- $\text{Ca(OH)}_2 \leftrightarrow \text{Ca}^{2+} + 2\text{OH}^-$  Reaction 6
- ↳  $\text{Ca(OH)}_2 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O}$  Reaction 7
- 2.  $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_{3(s)} + \text{H}_2\text{O}$  Reaction 8
- $\text{CaCO}_{3(s)} \leftrightarrow \text{Ca}^{2+}_{(aq)} + \text{CO}_3^{2-}_{(aq)}$  Reaction 9
- $\text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{OH}^-$  Reaction 10
- ↳  $\text{CaCO}_3 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$  Reaction 11

Figure 4 presents the ANC-behavior of the agglomerates with increasing cement content, and Figure 5 illustrates the influence of the addition of pore formation agents to the ANC value.

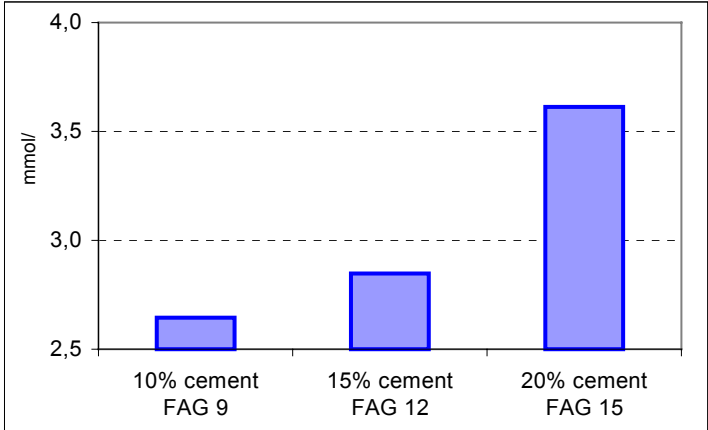


Figure 4 Acid neutralization capacity (mmol/g) for samples of fly ash with only cement

Similar results as obtained for the specific surface area are observed for the ANC behavior. An increase of cement content yields also an increase in ANC. This can be explained by the increased amount of CaO present, and with this the amount of hydroxide (Reactions 5 and 6). The agglomerates with hydrogen peroxide presented the higher values for the acid neutralization capacity, followed by the ones containing aluminum. This decrease due to aluminum can be explained with Reaction 3, assuming that a certain amount of Al did not react during agglomeration.

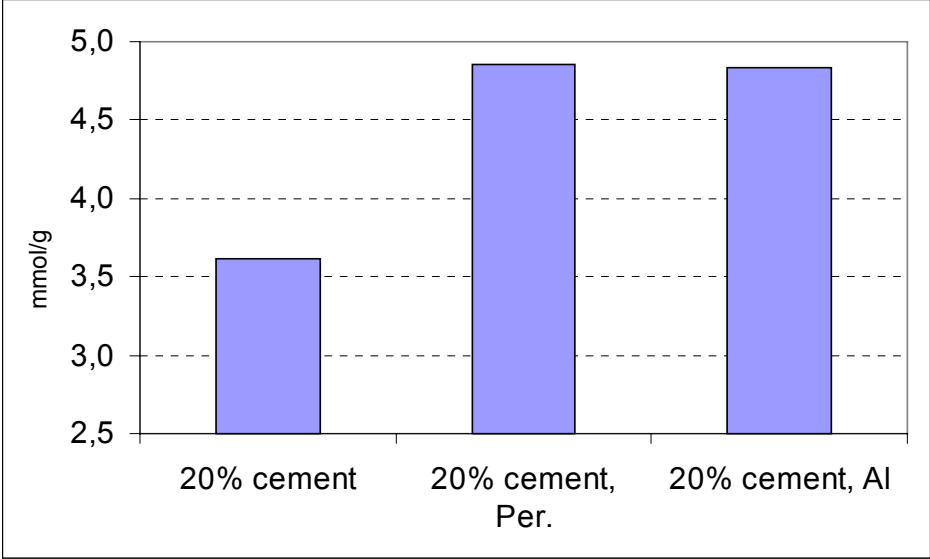


Figure 5 Acid neutralization capacity (mmol/g) for samples of fly ash with 20% cement only, 20% cement + H<sub>2</sub>O<sub>2</sub> (Per.) and 20% cement + Al

**Compressive strength**

Figure 6 shows the results of the compressive strength tests. The value of the agglomerate with 15% cement content is higher than the 10% -value, what conforms with the theory. However, the 20%-value is lower. It has to be remarked, that during the experimental part (handling and sieving of the agglomerates), the samples with 20% of cement were the most stable ones, what indicates a possible mistake during the compressive strength tests. The samples with 5% of cement were almost completely converted to dust after sieving and therefore not tested further on.

Figure 7 compares granules with the same cement content of 15%, with and without pore formation agents. The decrease of compressive strength for the agglomerates with a higher porosity is relatively clear and easy to understand.

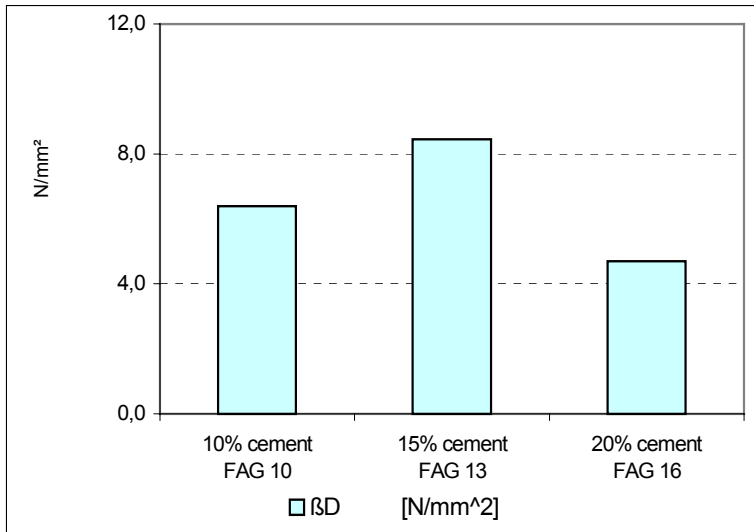


Figure 6 Compressive strength  $\beta_D$  (N/mm<sup>2</sup>) for samples with H<sub>2</sub>O<sub>2</sub> (Per.) and different amounts of cement (10%, 15%, 20%)

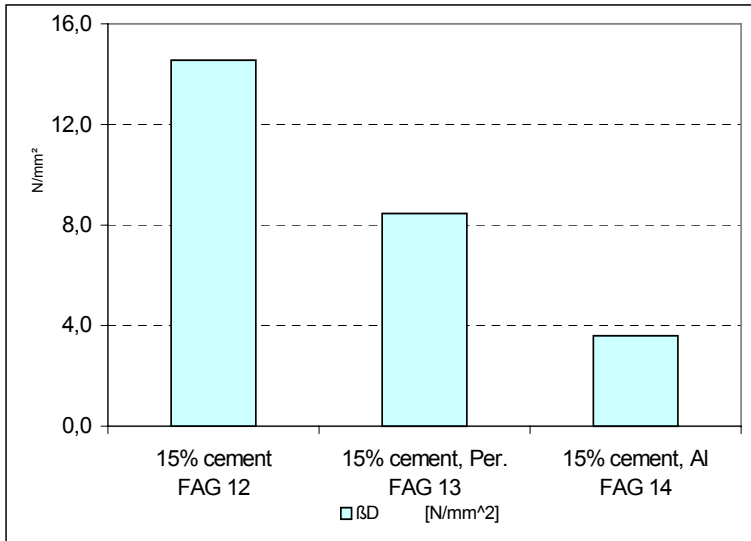


Figure 7 Compressive strength  $\beta_D$  (N/mm<sup>2</sup>) for samples with 15% cement only, 15% cement + H<sub>2</sub>O<sub>2</sub> (Per.) and 15% cement + Al

### Comparison of agglomerates

A comparison based on specific surface area, acid neutralization capacity and compressive strength is made to make a selection of the best agglomerate suitable



for the removal of heavy metals in reactive barriers. It was observed that acid neutralization capacity increased with the cement content (Figure 8). The results of compressive strength tests were not well interpretable. FAG 16 showed the best characteristics of all agglomerates. Therefore, it was decided to continue tests on heavy metal removal from model water with this sample.

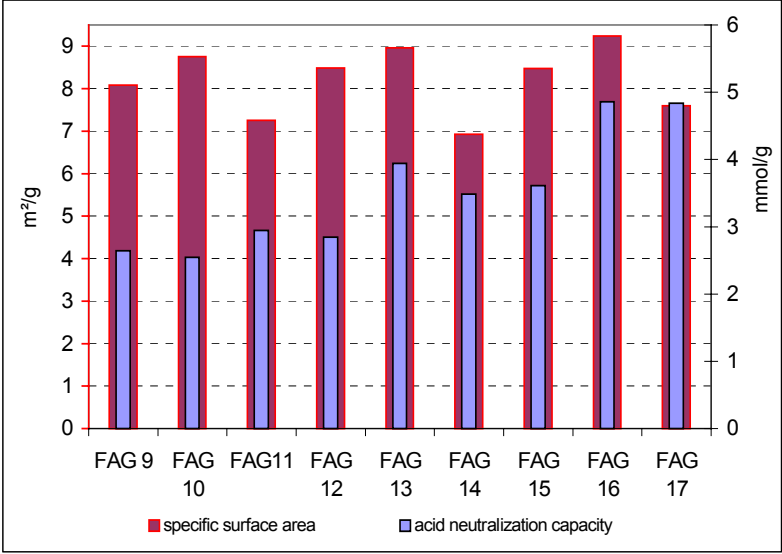


Figure 8 Specific surface area (m<sup>2</sup>/g) and acid neutralization capacity (mmol/g) for all samples

### Sorption Kinetics

Experiments of sorption kinetics were carried out for FAG16. Figures 9 and 10 show the pH values measured during the sorption experiments for different solid/solution ratios and different time intervals. As expected the pH value increased very fast and reached a high level after 10 minutes of reaction time. After 24 hours it reached, dependant on the solid/solution ratio, a value between 10 and 12. The increase took place due to the alkalinity of fly ash and portland cement. This process enhances metal precipitation and avoids desorption of heavy metals adsorbed on agglomerates back to the solution.

Figures 11 and 12 illustrate the removal of Zn, Cd, Ni, and Mn with different concentrations of FAG16 within one hour. With 10 g/L FAG 16 all heavy metals were removed during the first hour of the batch experiment (Figure 11), not been the same case for 2 g/L (Figure 12), e.g. for Cd total removal is achieved with 10 g/L after one hour. On the other hand, with 2 g/L FAG16, only 15% of Cd was removed.

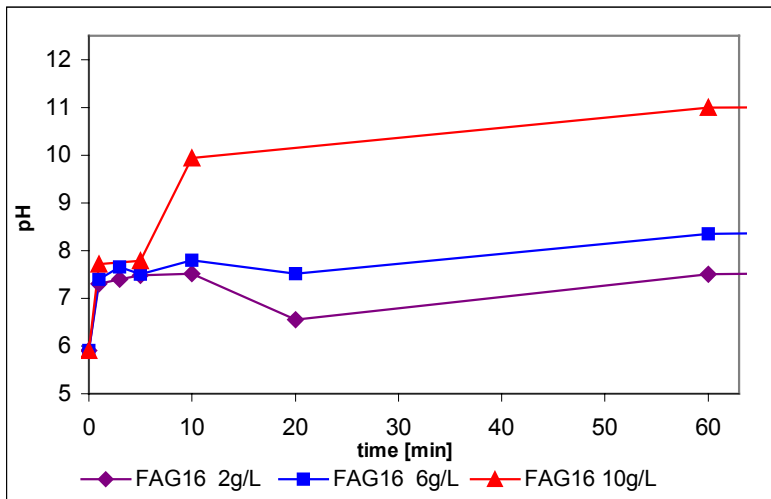


Figure 9 pH course within one hour for the batch experiment with granule FAG16 (80% fly ash, 20% cement and 15 drops H<sub>2</sub>O<sub>2</sub>)

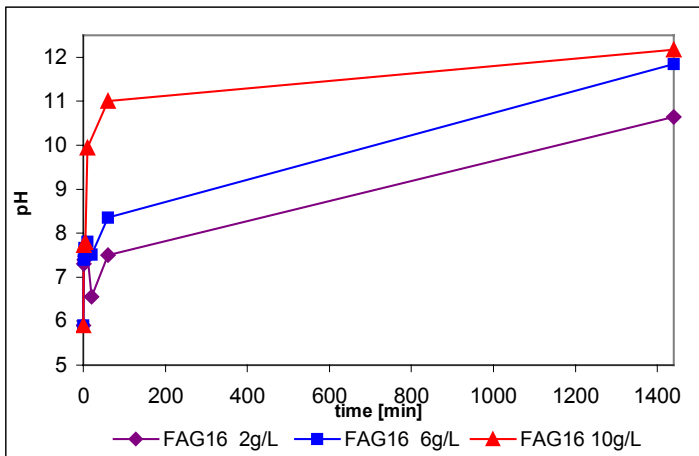


Figure 10 pH course within 24 hours for the batch experiment with granule FAG16 (80% fly ash, 20% cement and 15 drops H<sub>2</sub>O<sub>2</sub>)

The mechanism of removal seems to be sorption during the first minutes of the experiment. Following that part, it is observed that pH is increased and the removal of heavy metals is still increased, showing here precipitation of the heavy metals. Finally it was observed that no re-dissolution of the heavy metals occurred in the experiment with 10 g/L FAG 16 at pH 12.

The rate of removal depends, of course, on the amount of agglomerate and its removal capacity. The maximum load of the granule FAG16 was found to be 69.5 mg/g for Zn, 44.5 µg/g for Ni, 50 µg/g for Cd, and 7.5 mg/g for Mn.

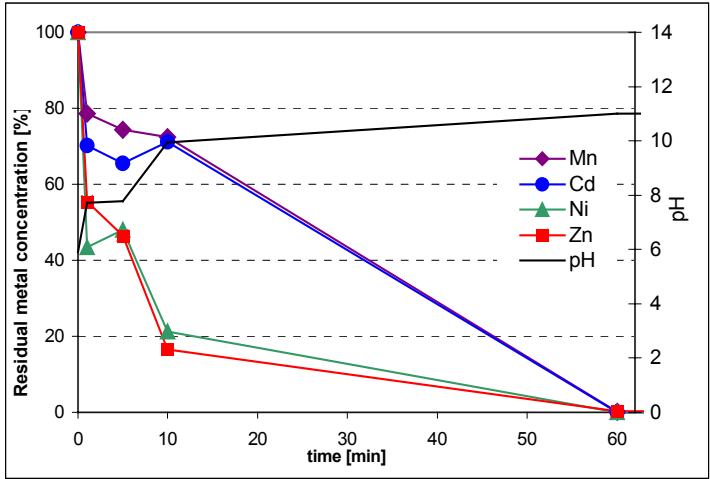


Figure 11 Removal of Zn, Cd, Ni, and Mn from model water with 10 g/L FAG16 (80% fly ash, 20% cement and 15 drops H<sub>2</sub>O<sub>2</sub>) - sorption kinetics

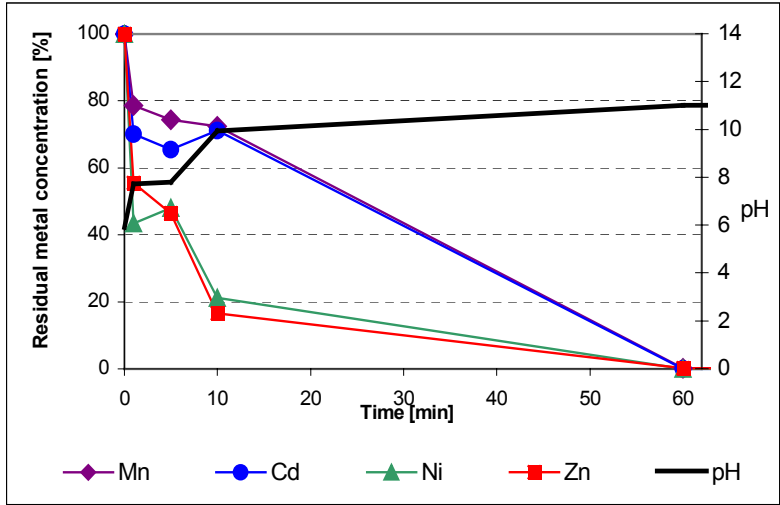


Figure 12 Removal of Zn, Cd, Ni, and Mn from model water with 2 g/L FAG16 (80% fly ash, 20% cement and 15 drops H<sub>2</sub>O<sub>2</sub>) - sorption kinetics

**Sorption Equilibrium**

The results for the sorption equilibrium reached at 24 hours are presented in Figure 13. All metals were removed after 24 hours with a minimum solid/liquid ratio of 2g/L FAG16. This reveals a great removal capacity for the four heavy metals when the contact time is sufficient, and that good treatment of the contaminated water can be obtained with this type of agglomerate.

It is important to remark again that even though high pH values are reached for higher concentrations of agglomerates, no re-dissolution of anionic metal hydroxo complexes was measured.

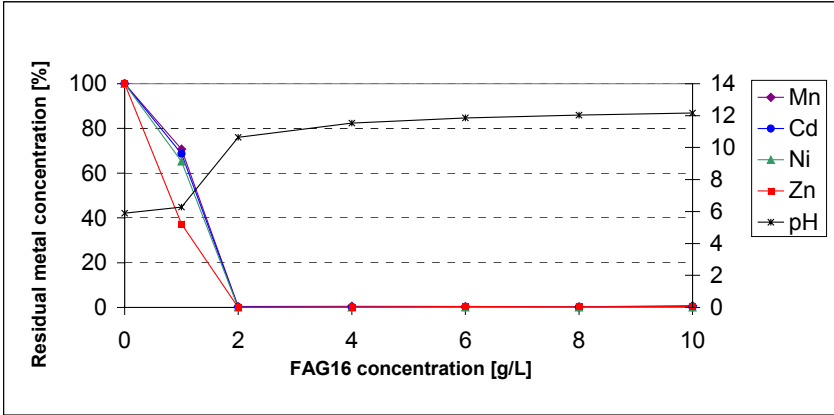


Figure 13 Removal of Zn, Cd, Ni, and Mn from model water with FAG16 (80% fly ash, 20% cement and 15 drops H<sub>2</sub>O<sub>2</sub>) - sorption equilibrium (24 hours)

Table 3 Results from compressive strength tests ( $\beta D$ ) for all samples

Name		$\beta D$ , N/mm <sup>2</sup>
FAG 9	10% cement only	6.6
FAG 10	10% cement + H <sub>2</sub> O <sub>2</sub>	6.40
FAG 11	10% cement + Al	n.m*
FAG 12	15% cement only	14.55
FAG 13	15% cement + H <sub>2</sub> O <sub>2</sub>	8.45
FAG 14	15% cement + Al	3.60
FAG 15	20% cement only	4.10
FAG 16	20% cement + H <sub>2</sub> O <sub>2</sub>	4.70
FAG 17	20% cement + Al	4.85

#### 4 CONCLUSIONS

Analyzing the capacitative factors of the developed granules, FAG16 was found to be the one with the best performance. It was chosen because it had the best values for acid neutralization capacity and specific surface area. To obtain agglomerates with the necessary compressive strength, it is recommended to use at least 10% cement, lower content was not enough to maintain the structure of the agglomerates. The higher the cement content, the better is the hardness.

The results obtained with the batch experiments corroborate the possible use of FAG 16 as a material for reactive barriers. As it was observed, the removal of heavy metals is a result of a combination of two mechanisms. A first stage of sorption is followed by an increase in pH that promotes also precipitation. Both mechanisms are influenced by the concentration of the agglomerates, more surface area for sorption is available as well as more reactive alkalinity is present.

The kinetics of the heavy metal removal is as follows: zinc is the one removed first, followed usually by nickel, then cadmium and finally manganese. This could be attributed to the solubilities of the hydroxides, since zinc hydroxide has the lowest solubility and is the first to precipitate, followed by the others in the same order.

It should be mentioned that during this work, the long-term stability of the agglomerates has not been analyzed.

## REFERENCES

- Mohamed A.M.O & Antia H.E. 1998. Geoenvironmental Engineering, Elsevier, The Netherlands, 707 pp.
- Zoumis T., Calmano W. & Förstner U. 2000. Demobilization of heavy metals from mine waters, *Acta Hydrochimica et Hydrobiologica* (in press)

### **Wytwarzanie ziaren pyłu lotnego do usuwania metali ciężkich z wód kopalnianych**

Theofanis Zoumis, Wolfgang Calmano

**Streszczenie:** Popularnym sposobem oczyszczania kwaśnych wód zanieczyszczonych metalami ciężkimi jest ich obróbka w dużych oczyszczalniach, co związane jest z wysokimi kosztami inwestycyjnymi i eksploatacyjnymi. Nasze rozwiązanie proponuje bierne oczyszczanie wód kopalnianych materiałami reaktywnymi, tzn. umiejscowienie wybranego materiału pod powierzchnią, w strumieniu wody („przepuszczalna bariera reaktywna”), aby zapobiec rozpuszczaniu metali ciężkich poprzez ich sorpcję i wytrącanie. Wcześniejsze badania wykazały, że metale ciężkie dobrze się usuwa za pomocą różnych przemysłowych produktów ubocznych takich jak popiół węgla brunatnego i czerwony szlam z przemysłu aluminiowego (Zoumis i in., 2000). Problemem jest dystrybucja cząstek małego rozmiaru, która prowadzi do złej przepuszczalności bariery. Rozwiązaniem tego problemu jest granulacja materiału za pomocą różnych czynników wiążących. Najważniejsze jest zachowanie dobrych właściwości pojemnościowych (sorpcja i zdolność neutralizowania kwasów). Pierwsze wyniki były względnie dobre dla zastosowania lotnego pyłu jako głównego składnika taniego ziarna.