

Utilization of iron ochre – making auxiliary water treatment materials from mine water treatment waste

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Abstract

In the Lusatian lignite mining area huge amounts of iron and sulphate enter the receiving water bodies caused by groundwater rise after closure of many opencast lignite mines in the 1990th. Water treatment actions mainly for iron removal prepared and accomplished by the mining rehabilitation company LMBV and ochre sedimentation in still unprotected water bodies result in huge iron sludge accumulations, which have to be removed/ disposed. This paper presents a novel approach on significantly decreasing the iron sludge amount through utilization. It involves mechanical and thermal dewatering/drying and subsequent production of auxiliary water treatment chemicals. The produced chemicals had comparable treatment properties as commercial products. The proposed utilization will lead to a significant decrease of the ecological and economical foot print.

Keywords: lignite mine closure, iron ochre, iron hydroxide sludge, groundwater rise, auxiliary water treatment chemicals

Introduction

In the Lusatian lignite mining area the regional water balance is heavily changed by the past and present mining industry. Caused by the groundwater rise significant amounts of iron and sulphate enter the receiving water bodies. The mining rehabilitation company LMBV (Lausitzer und Mitteldeutsche Bergbau-Verwaltungsgesellschaft mbH) prepared and accomplished various water treatment actions in particular for the removal of the iron load. Both the LMBV water treatment measures and the ochre sedimentation in water bodies not protected so far lead to a large amount of iron sludge.

About 70.000 t iron ochre is accumulated every year which has to be removed and disposed. The LMBV classified 5 different types of iron sludge with regard to their origin:

1. Sludge from water site clearance (dredgings)
2. Sludge from pristine or nearly-naturally designed sedimentation ponds
3. Sludge from river water treatment

4. Sludge from ground water treatment
5. Sludge from in lake treatment measures

These types vary greatly in terms of their dry mass, iron content and impurities. Therefore it is clear, that utilization of the total sludge amount is almost impossible. Considering its sludge strategy “prevention before utilization before flushing before landfilling” the mining rehabilitation company LMVB has identified two main options for dealing with the huge sludge amounts: a) liquefying by mixing with water and flushing in a specifically prepared pit lake and b) deposit in an industrial mono-landfill. But both of these options are extremely expensive and every ton which does not have to be dumped or flushed will save costs.

Many attempts for the utilization of iron ochre from abandoned mines have already been undertaken, e.g. application as pigments (Hedin, 2002), production of sorbents (Simon, 2016; Kießig, 2004) and bricks, application for phosphor removal from wastewaters.



Recently, a new idea arose being worth enough to start further investigations. It involved the utilization of iron ochre for the production of auxiliary water treatment chemicals such as solutions of FeCl_3 , Fe_2SO_4 or FeClSO_4 which are widely used as flocculants.

Project idea and scope of work

Flocculants based on iron salts are usually produced from pickling solutions from the steel industry as raw material with the disadvantage of a difficult and expansive oxidation step from ferrous to ferric iron. Excavated iron ochre from drainage ditches and iron hydroxide sludge from water treatment plants contains the iron already in the trivalent status. Therefore oxidation is not needed and a simple dissolution of the iron ochre in acid (HCl , H_2SO_4) should be appropriate to produce flocculant solutions being utilizable as auxiliary water treatment reagents.

The main project idea is the production of auxiliary water treatment chemicals (FeCl_3 , Fe_2SO_4 or FeClSO_4) from the iron ochre sludge, using the iron ochre sludge as cheap raw material.

Cost saving can be expected in the areas of raw material, energy, auxiliary materials and finally lower disposal costs due to mass reduction of iron ochre sludge for flushing or landfilling.

To check the feasibility of this idea a two stage project was established funded by LMBV. The first stage was carried out on lab scale and had the aims a) to identify suitable sludge qualities, b) to prove the basic technical feasibility and c) to evaluate the quality of the produced flocculants. In the second stage which is now in preparation a pilot test on industrial scale is planned to prove economic feasibility.

Types of sludge

For the first stage the following sludge types were selected and tested for conversion after sampling

- Lime rich iron ochre sludge (water treatment plant Borna-West)
- Iron ochre sludge with a pH around neutral (“Eichower Fließ”)
- Acidic iron ochre sludge with a fraction of Schwertmannite (“Meuroer Graben”)

Before carrying out the experimental work on dewatering/drying and chemical conversion all sludges were chemically analysed and soil parameters were determined as shown in **Table 1**.

The chemical conversion was accomplished with hydrochloric or sulphuric acid according to the following main reactions:



Because of minor components in the iron ochre sludge several side reactions are possible, for example

- $\text{CaCO}_3 + 2 \text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$
- $\text{CaMg}(\text{CO}_3)_2 + 4 \text{HCl} \rightarrow \text{CaCl}_2 + \text{MgCl}_2 + 2 \text{CO}_2 + 2 \text{H}_2\text{O}$
- $\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{CO}_2 + \text{H}_2\text{O}$
- $\text{CaMg}(\text{CO}_3)_2 + 2 \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{MgSO}_4 + 2 \text{CO}_2 + 2 \text{H}_2\text{O}$

Preliminary considerations included the acid amount and concentration as well as the iron content in the raw material required for the conversion.

Commercially available Iron(III)-chloride solutions contain 40% FeCl_3 (13.8% iron as active substance), marketable Iron(III)-sulphate solutions contain 12.5% iron as active substance.

Table 1 Characterization of test sludges

Sludge	Clay	Silt	Sand	Gravel	DMC	Iron	Sulphate	Calcium	TOC
Borna	*	95%	5%	0%	41%	12%	2.5%	14.8%	1.3%
Eichow	18%	23%	56%	3%	54%	22%	0.8%	1.0%	7.4%
Meuro	39%	41%	20%	0%	38%	14%	3.3%	0.3%	10%

*analytical problems due to high lime content

DMC= dry mass content

elemental and TOC contents are given in percent by weight in dry mass



To achieve comparable iron contents the following aspects had to be considered:

- Iron content in the raw material
- Dry mass content in the raw material
- Concentration of the used acid

The iron content in the raw material is dependent on the dry mass content. Lower concentrated acids used for chemical conversion and sludges with a lower dry mass content introduce more water into the product solution. Both aspects lead to a diluted product solution.

To raise the iron content in the raw material an energy efficient dewatering and drying procedure is necessary.

Dewatering/Drying experiments

Lab tests were performed to determine energetic key figures for the technical design of a dryer as well as characteristics of the bulk material (incrustation, caking, dust formation) in the dryer.

One priority of the experiments was the development of suitable drying/conveyor belts.

These belts were a decisive control parameter to influence the drying result for different raw materials (grain size, dry mass content).

The combination of materials (special woven plastics), perforation and operation mode was identified as crucial parameter for the drying result. However, the influence of the sludge's chemical composition was found to be not very significant.

The tested pilot drying system had a capacity of 2.8 kg sludge per minute and achieved a mechanical dewatering grade up to 49% DMC. It can be predicted to achieve a DMC of 55% at a larger scale with solely mechanical dewatering.

Thermal drying would enable a DMC of up to 100%. However, the targeted DMC is dependent from the subsequent chemical conversion and the needed dry mass content there.

The use of mechanical dewatering as much as possible before thermal drying is very important because the effort for mechanical dewatering is only 50% in comparison to thermal drying for each percent of dry mass content.

Therefore the combination of mechanical dewatering and thermal drying is the most appropriate solution concerning both technological and energetic efficiency.

Chemical Conversion

The basic principle of the intended chemical conversion is the dissolution or leaching of the sludge with hydrochloric acid or sulphuric acid.

Different parameter fields were tested:

- Dry mass content of the raw material
- Acid concentration
- Reaction temperature (room temperature, reflux)
- Pressure

The performed tests allowed the following statements:

- Using raw material with a higher DMC and using higher acid solutions lead to higher iron concentrations in the product solution
- Very high DMC and acid solution require the addition of water to provide a homogeneous and stirrable solution
- Product solutions include a proportion of Fe(II). The concentration of Fe(II) raises with a conversion at higher temperatures
- Some product solutions tend to gel at prolonged standing time
- Active iron concentration in the product solution varies between 40 and 80 g/kg product solution
- Amount of residuals varies between 7% and 76% referring to DMC of the raw material

Challenges of the chemical conversion

Some product solutions tend to gel at prolonged standing time. This gelation effect is likely the result of a condensation reaction of silica. Further experiments are currently in progress to solve this challenge. First results are promising and investigations will be continued in the second project phase.

In addition a large scale test of technical solar drying is in preparation in that phase.

Chemical conversions applying higher temperatures or increased pressure led to likewise increased Fe(II) contents in the



product solutions. Different tests were performed concerning the removal of organic components from the raw material by washing. It can be clearly stated that most of the Fe(II) in the product solution is a result of Fe(III) reduction by organic material in the iron ochre, preferably at higher temperatures or pressures.

The product solutions have to be compared with standard market solutions for which the product has to meet specific quality criteria. One quality criterion is the heavy metal concentration in the product solution.

The guideline values for the different heavy metals are specified in the leaflet DWA-A 202 of the DWA (German Association for Water, Wastewater and Waste) and are given as relation of heavy metal concentration to active substance (iron) in mg/mol.

A theoretical calculation was conducted, assuming that all iron and all heavy metals dissolve and can subsequently be detected in the product solution.

The theoretically calculated values exceeded the guideline values only in single cases (Cr at “Meuro”, Ni/Zn at “Borna”) and were confirmed at the test stage.

In conclusion, it is possible to identify and exclude non usable sludges with excessive heavy metal levels or to find compositions of different sludge types to avoid an exceeding.

Application tests

The produced solutions of $\text{Fe}(\text{Cl})_3$ and $\text{Fe}_2(\text{SO}_4)_3$ were tested and compared with regular market products on a broad base:

- Testing effectiveness of the products by using synthetic waters
- Transfer of the results to original waters
- Evaluation of the achieved water qualities
- Comparison with regular market products
- Evaluation of the resulting sludges (sedimentation properties)

An example of an application test is given in Table 2. The test was accomplished with water from a sewage treatment plant after the mechanical treatment step which had the following parameters:

- | | |
|-----------------------------------|------|
| • pH | 7.02 |
| • turbidity (TE/F) | 100 |
| • total P [mg/L] | 2.63 |
| • total PO_4^{3-} [mg/L] | 8.05 |
| • COD [mg/L] | 166 |

The results clearly show that the produced treatment chemicals had a comparable product quality regarding phosphor elimination and COD reduction although the amount of active substance in the product solution was lower.

Table 2: Application test results

Product	Product solution			After treatment		
	DMC	Acid	Fe [g/kg]	Total P [mg/L]	Total PO_4^{3-} [mg/L]	COD [mg/L]
Fe ₂ (SO ₄) ₃ standard product			138	< 0.5	< 1.5	66.1
Westrandgraben	20.4 %	55% H ₂ SO ₄	62.08	< 0.5	< 1.5	47.5
Westrandgraben	100%	55% H ₂ SO ₄	72.52	< 0.5	< 1.5	64.2
Westrandgraben	70.8 %	55% H ₂ SO ₄	64.07	< 0.5	< 1.5	49.6
Eichow	47 %	55% H ₂ SO ₄	76.43	< 0.5	< 1.5	63.1
FeCl ₃ standard product			125	< 0.5	< 1.5	63.0
Westrandgraben	20.4 %	31% HCl	45.64	< 0.5	< 1.5	55.8
Westrandgraben	100%	31% HCl	90.86	< 0.5	< 1.5	65.1
Westrandgraben	70.8 %	31% HCl	67.20	< 0.5	< 1.5	71.8
Eichow	47 %	31% HCl	62.06	< 0.5	< 1.5	63.6



So, products from iron ochre revealed an equivalent treatment success compared to commercially available products.

Residues

The residues from chemical conversion can be separated by solid-liquid separation after the conversion process. Solids were analysed and compared with the German soil classification regulations (LAGA codes) for soil emplacement and backfilling with the following conclusions:

- Most of the iron content is in the liquid
- Zinc and arsenic remain in the residue and are concentrated
- Soil emplacement classes Z1.2 or Z2 for the residues are suitable, meaning that a restricted open soil emplacement (class Z1.2) or a soil emplacement with technical safety measures (class Z2) are possible

Cost estimation

Cost estimations can be performed after realisation of the second stage of the pilot project. Because of the predicted cost increases for landfilling and/or iron ochre flushing the economic feasibility of the proposed utilization route is very likely.

Conclusions

The following conclusions can be drawn:

- Utilization of iron ochre by chemical conversion with acid is possible
- Products have comparable treatment properties as commercial products
- Residue amount can be significantly decreased
- Production of auxiliary water treatment materials from mine water treatment waste is most likely economically feasible
- Key figures for the commercial-scale use will be investigated in the next project phase

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