Iron-Hydroxide-Removal from Mining Affected Rivers

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Abstract
Oxic and ferric iron hydroxide rich river waters are evolving in the Lusatian mining district due to discharge of ferrous iron rich ground waters. These river waters are characterized by small hydroxide flocs which show a very slow sedimentation. To stop pollution of downstream ecosystems flocculation and sedimentation of the hydroxides has to be accelerated. Addition of flocculants like polyacrylamides into the rivers is effective but shall be avoided because of unknown ecological consequences. Liming is also effective but demands technological infrastructure and ongoing supply with lime milk. To reduce technical infrastructure and to integrate ferric hydroxide retention in the river systems, alternative technologies are being developed. It is the aim to supply the stakeholders with easy to maintain techniques for the years to come to protect the downstream parts of the rivers from severe iron hydroxide pollution.

Key words: iron hydroxides, polluted rivers, remediation technology, groundwater discharge

Introduction
The Lusatian mining district is one of the three large lignite mining districts in Germany. After reunification a large part of the mines was closed due to economic and ecological reasons. The remaining mines are still in operation. After closing the mines in the nineties the pitlakes were flooded and the former groundwater level is currently being reestablished in and around the abandoned mines. Today the groundwater level has reached its natural level in many parts of the mining area and the groundwater starts to discharge into the local river systems again.

The mining dumps but as well the surrounding unworked sediments contain sulfides, which have been partly oxidized during the period of groundwater drawdown. The oxidation products partly remained in the unsaturated zone and were dissolved in the rising groundwater. Sulfide-rich but temporarily aerated swamps release additional amounts of ferrous iron to the groundwater. The groundwaters thus became rich in ferrous iron showing concentrations up to 400 mg/L even outside the dumps [3].

By discharging into the rivers the ferrous iron rich anoxic groundwaters mix with the oxic river waters. The ferrous iron loads oxidize in the presence of oxygen and form iron hydroxides. Iron hydroxide formation releases protons by hydratation of ferric iron. Due to the natural buffer capacity of most river waters of the region of 1 to 1.5 mmol/L most waters keep their neutral pH. Nevertheless it takes several hours up to several days to completely oxidize the whole iron load [1]. Thus the river waters in the mining area are characterized quite often by a combination of ferrous and ferric iron, total iron loads reaching more than 100 mg/L.

Hydroxide formation results in an elevated turbidity of the river water and high sedimentation rates which impair the living conditions of the Macrozoobenthos. The sludge reduces photosynthesis and oxygen uptake as well as food supply for the fish population. The riverbeds are clogged by the sludge. Last but not least the optic impression of the surface waters is considered to be a major drawback for the evolving tourism in the region.

It is the common aim of the mining industry and the authorities to prevent the deterioration of large parts of the rivers by iron hydroxide loads. Two strategies are currently tested and implemented:

1) The iron loads are stopped downstream of the sources right in front of areas which have to be protected from the iron sludge. A well known example is the Spreewald area, an alluvial forest of high touristic and ecological value downstream of the mining region. The advantage of this

strategy is that a few “core areas of hydroxide retention” next to the dominant zones to be protected would be sufficient to stop the hydroxide load. The disadvantage is that many of the upstream rivers will stay polluted with the iron hydroxide sludge, will suffer under low ecological conditions and just serve to transport iron hydroxide loads. Iron hydroxide sludge has to be removed from these parts of the rivers periodically to avoid clogging of the river beds [2]. This is why the local population and authorities demand the retention of the iron “at its source”.

2) So a more desirable strategy might be the retention of the iron loads next to their sources still in the underground (Hildmann et al. 2015) or at least in the upstream parts of the rivers next to the areas of exfiltration. In this way the downstream rivers could be protected from the iron loads. However ferrous iron release from groundwater into the rivers occurs in a diffuse manner and is distributed widely along large parts of the riverbanks. Therefore it is difficult to detect and to treat the “hot spots” of exfiltration. Local measures, like pumping wells and ditches next to the rivers are tested to keep the iron rich groundwaters away from the rivers. Many of these local measures would have to be taken to stop the overall iron load.

State of the art technologies for iron removal rely on the control of the flocculation process by liming, by catalysed ferrous iron oxidation in contact with already existing flocs at elevated pH-values between 8.0 and 9.0 and by the use of flocculants. By creating large flocs in technical plants fast sedimentation of the produced solids within 1 to 2 hours is possible (Bilek, 2013). Yet the conditions in the river waters differ from those in classic treatment plants which treat water which is typically rich in ferrous iron:

- The river waters are already oxidized and the pH is still in the neutral range in most cases even after complete iron oxidation due to their natural buffer capacity and the low groundwater/river water mixing ratio.
- Neutral pH-values and abundant oxygen result in fast iron oxidation kinetics at least in summer. Hydroxide formation is more or less completed within a few hours.
- The flocs stay small due to pH-values below 7.5, low density of solids and no artificial flocculants present. Therefore their sedimentation rate is rather slow. Field observations show that sedimentation may take several days up to two weeks even in still water [1].
- Conditions for sedimentation are bad due to the tractive forces of the rivers and due to the constantly changing flow velocities and fluxes during the year.

This shows that the possibilities to influence the flocculation and sedimentation process by classic technical means are limited. Iron hydroxides stay in suspension for many kilometers and pollute large parts of the rivers.

Liming the rivers and even adding flocculants can increase the sedimentation of the iron hydroxides. However out of ecological considerations, local large pH-increases and addition of flocculants in natural environments should be avoided. Besides that application of flocculants leads to sludges with rather high water contents which rapidly clog the riverbeds and are not favorable for further sludge processing. By creating rather dense iron hydroxide sludges their volume can be kept low and removal intervals from the river beds can be kept larger.

Sometimes artificial basins next to the rivers are available which can be used as sedimentation ponds for the whole river. Due to the large retention times of several days large basins or stillwater areas are required to guarantee permanent ferric iron hydroxide sedimentation.

Currently new technologies are under development to accelerate the sedimentation process and to minimize the size of additional sedimentation pond volumes which have to be provided along the affected rivers even without adding large amounts of chemicals. It is the aim to provide methods to retain and remove the iron hydroxide loads which need less technological effort and should be applicable also for small rivers. They should be better integrable into the natural environment of the affected river systems than classical treatment plants.

One way to intensify the flocculation is to temporarily increase the turbulence of the water by applying mixing energy. This technique serves to intensify the contact between the already existing flocs. The probability of coagulation is increased that way. On the other hand turbulence does not have to be too large. Otherwise already existing flocs will be disintegrated again.

Another technique which may be applicable to intensify sedimentation and increase sludge density is the high density sludge technique, which is well known in mine-water treatment [Aube´, Coulton, 2003]. Iron-hydroxide sludge, which already settled, is pumped back into the reaction zone to serve as a reactive surface for the oxidation and coagulation reactions. The presence of hydroxide solids in turbulent water in combination with additional liming is used to accelerate ferrous iron oxidation and coagulation of already existing small flocs. Sedimentation of the larger flocs now is faster and a much more dense sludge can be created. This process is currently adopted to river waters and its potential to increase the flocculation and intensify the sedimentation process is tested.

Methods

In a first step **laboratory tests** have been performed to identify various combinations of pH-control, mixing energy input and sludge recirculation. In these tests the river water was firstly mixed with various amounts of lime, stirred with various velocities and then was transferred to settling vessels to examine the settling process. The sedimentation process was observed for about 1.3 days. After certain time intervals the supernatant water of each batch was sampled repeatedly for the remaining total iron content. The iron hydroxides were completely redissolved in nitric acid and analyzed in aqueous phase with ICP-OES.

A **bench scale treatment plant** (*figure 1; left*) consisting of two reactors was set up to test various combinations of liming, application of mixing energy and increased floc density. In the first reactor lime, air and mixing energy could be added. In the second reactor also mixing energy could be applied and higher sludge densities were achievable by adding sludge. The settling process was observed in column-like vessels, which were filled with the runoff from the reactors after a steady state flow through process was established.

A **pilot plant** next to a river is currently set up to test the most promising combinations in the field (*figure 2*).

Natural river water was used for all tests because also other suspended components besides iron hydroxides like clay and organic particles are found in the water and may influence the flocculation and the precipitation process.The water shows a pH between 6.6 and 7.0 and a total iron concentration of 3 to 20 mg/L. Its total solids content ranges between 20 and 50 mg/L, its electric conductivity lies between 900 and 1100 µS/cm. The used river water is representative for many mining influenced waters of the region.

Results

The laboratory tests showed that increase of the pH helps to increase the size of the flocs and thus improves the settling process even if all iron is already present as ferric hydroxide colloids (Koinzer, 2014). Even a small pH-increase from 6.7 (original river water) up to 7.0 allows for a significantly faster removal of total iron from the water column (*figure 3*).

In a second test the influence of turbulence was tested. At first the influence of the duration of mixing with a propeller mixer (2, 5 and 15 minutes; 300 rpm) was investigated at various pH-values. *Figure 4* shows the remaining total iron concentrations in solution of pH 7.5 at various times after stopping the mixing process. It can be seen that also mixing leads to a faster removal of iron. Iron removal is faster when mixing 15 minutes instead of 5 minutes whereas mixing for 30 min did not improve the settling process any further (results not shown). This result was confirmed for all pH-values between 6.7 and 8.5.

In bench scale air injection, a propeller mixer with 450 r.p.m. and a paddle mixer 20 r.p.m. were tested as a means of crating turbulence (*figure 1 and 5*). Mixing energy input was higher with the propeller mixer than with the paddle mixer (Moritz, 2015). The tests showed that better results were achieved with the fast working propeller mixer than with the slow working paddle mixer. Air injection showed comparable results to the propeller mixer. Increasing the pH improved the sedimentation rate in any case and under any combination of propeller mixer and paddle mixer. Increase of energy input improved flocculation and sedimentation in any case.

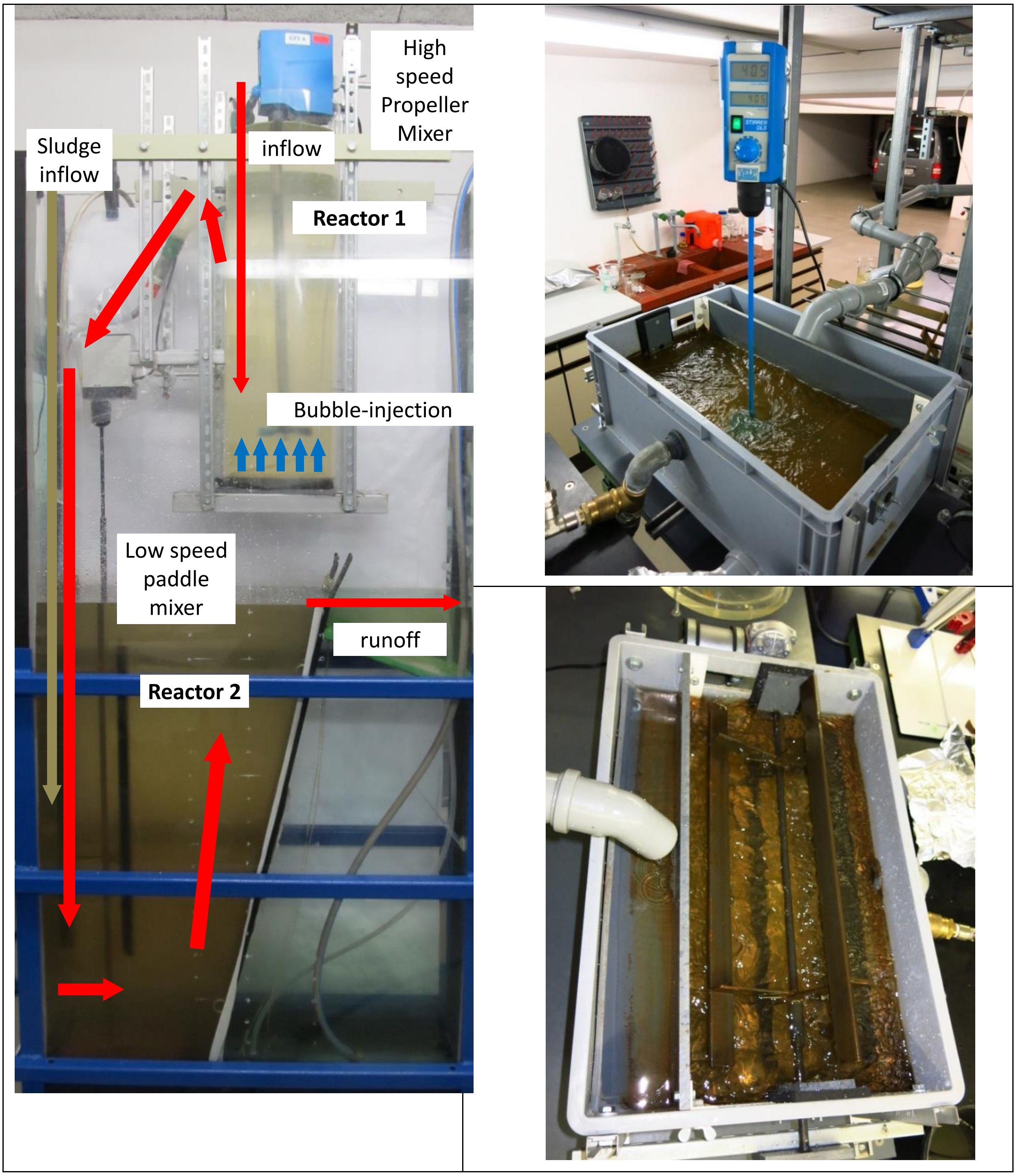

Figure 1 *Left: Bench scale plant with two coupled reactors to test the sequential influence of mixing energy input on flocculation process. Right top: Propeller mixer (405 r.p.m.). Right bottom: horizontal paddle mixer (8 r.p.m.)*

Figure 2 *Pilot plant in the field to test various combinations of mixing, liming and sludge recycling.*

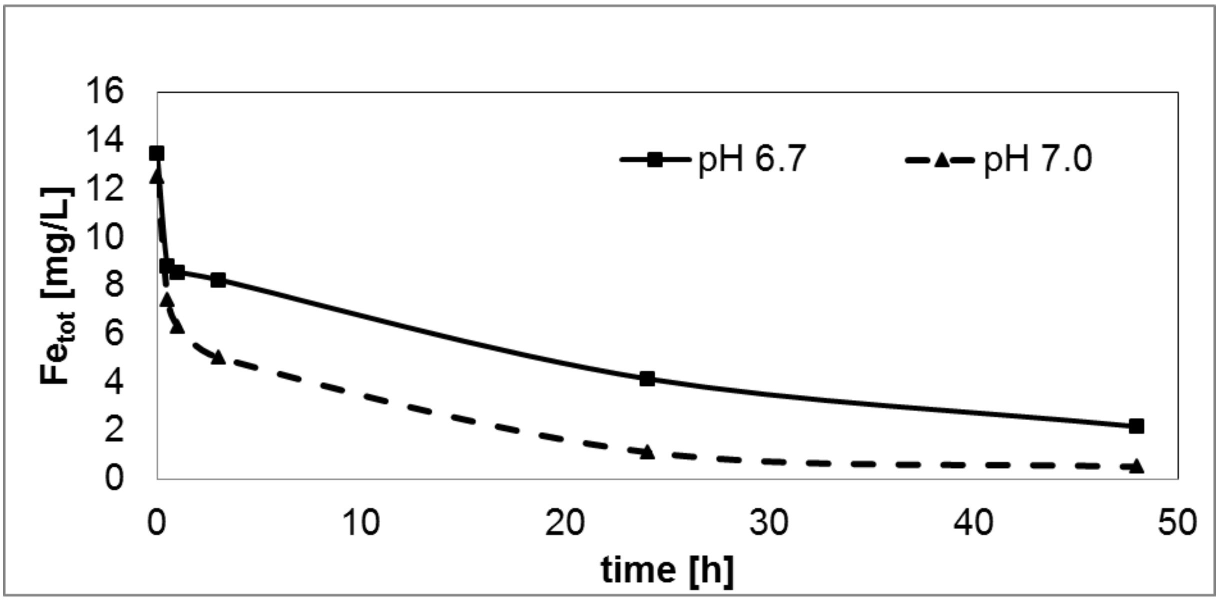

Figure 3 *Investigation of sedimentation at different pH-values. Change of total iron concentration with time.*

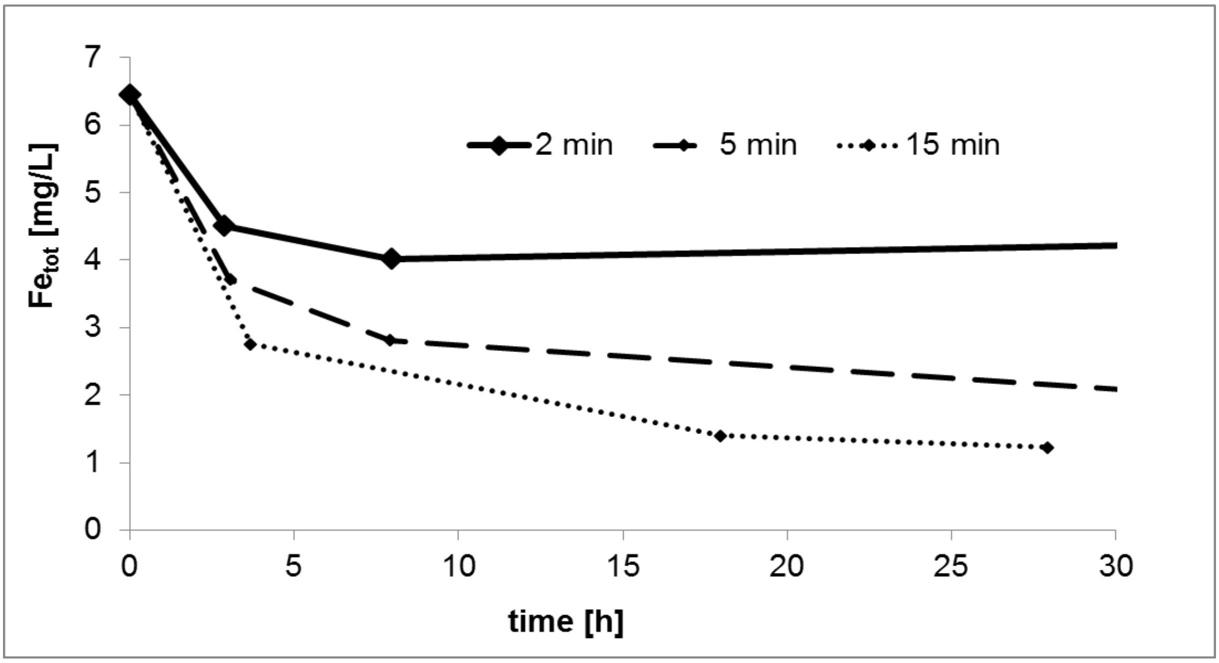

Figure 4 *Investigation of influence of stirring duration. Raw river water (pH 6,7) without lime addition was used.*

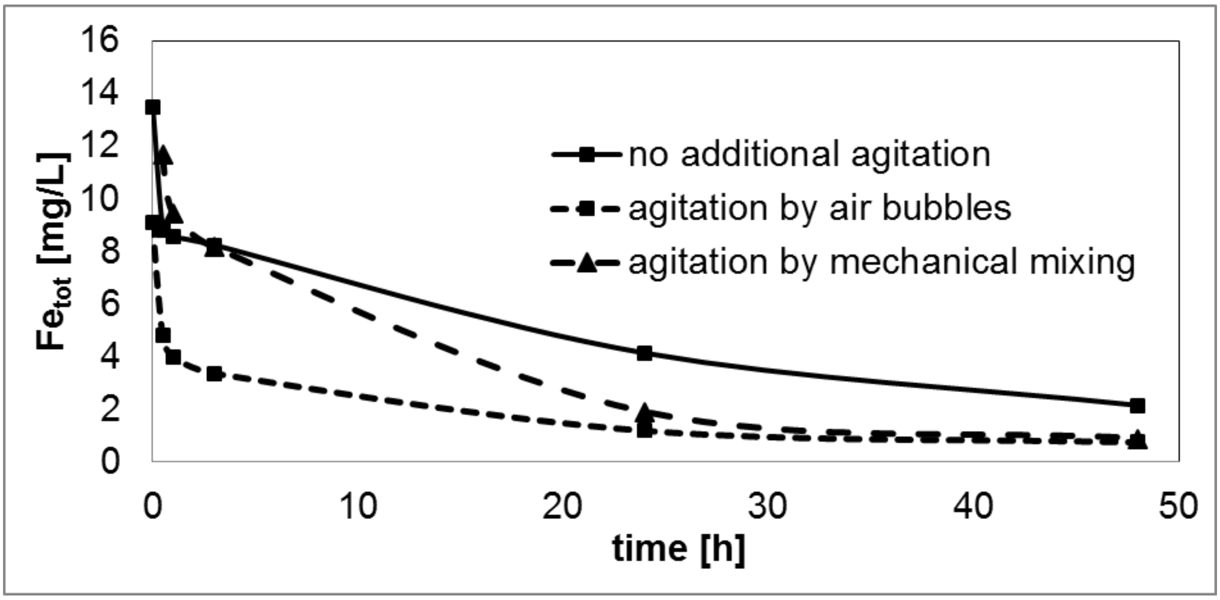

Figure 5 *Investigation of different ways of energy input. Change of total iron concentration with time.*

The bench scale plant was also used to test sludge recycling using mining affected raw waters with high ferrous iron contents up to 100 - 160 mg/L. A large improvement was achievable by sludge recycling in combination with liming. The flocs became much larger (diam. 2-3 mm) and settled within 30 min. *Figure 6* shows the mass balance calculated for the field application.

However, sludge recycling without liming did not improve total iron removal for the low concentrated river waters (Fe(III) ~16 mg/L). No growth or coagulation of the existing flocs was observable. The addition of lime proved to be a prerequisite to support coagulation. It is assumed that the change of the surface charge of the hydroxides due to pH-change is the prerequisite for further floc growth.

The remaining total iron concentration could not be lowered below 1.0 to 0.5 mg/L with any of the tested techniques in all laboratory and bench scale tests. After having reached an iron concentration of 1.0 to 0.5 mg/L only very little additional concentration decline was observable in all tests (*figure 3 to 5*). It is assumed that further reduction of the total iron concentration is only possible with filtration techniques. Yet it is not necessary to lower the iron concentration below this concentration because all current regulatory limits for discharge are met with these concentrations. Furthermore total iron with this concentration is not visible any more.

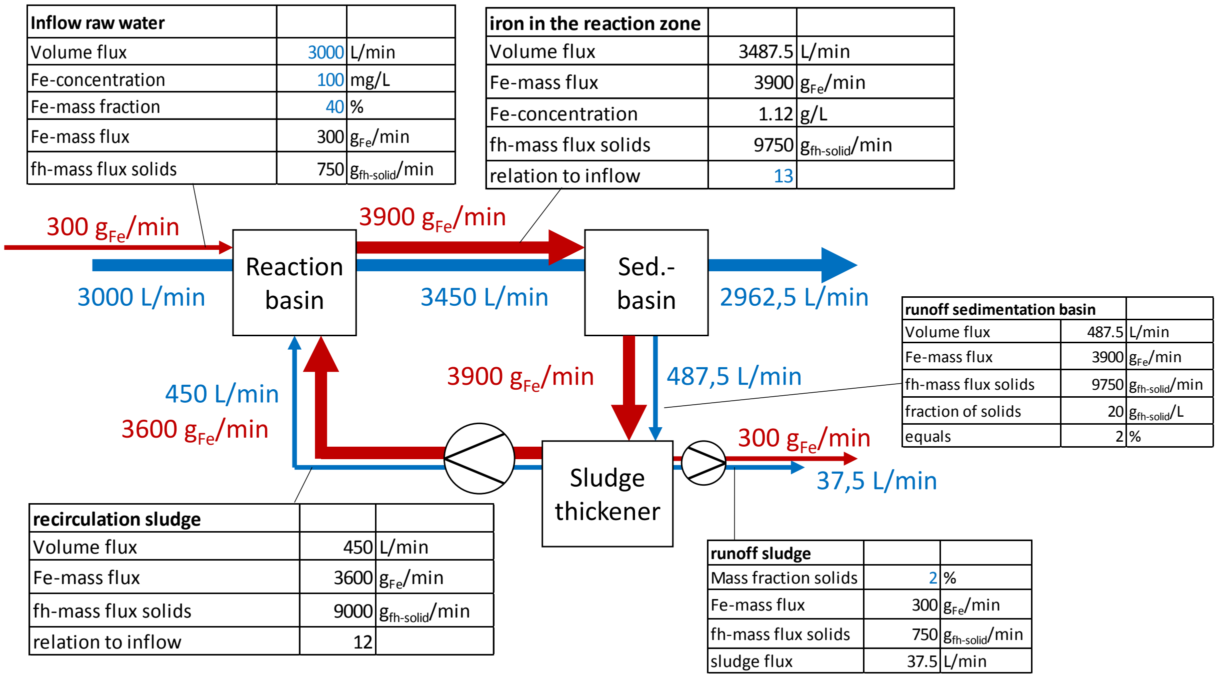

Figure 6 *Example of volume and mass fluxes of iron using the high density sludge technique (fh: Ferric hydroxide)*

Conclusions

Sedimentation of iron hydroxides in natural environments has to be accelerated to facilitate the maintenance of ferric hydroxide polluted rivers. To increase floc size and reduce sedimentation time liming is even useful for fully oxidized waters, which are characterized by ferric iron hydroxide colloids and neutral pH-values. Flocculation and sedimentation are intensified by increased pH. Application of mechanic energy can also be used to accelerate flocculation and sedimentation. Flocculation is increasing with higher energy input.

Mixing energy can by applied to the water by different methods (among them stirring with propeller and paddle mixer and air injection). Sludge recycling does very much improve ferric hydroxide retention as long as it is combined with lime addition. Otherwise no improvement was detectable so far. The most effective and energy saving technique will be identified in pilot tests in the field.

It seems that ongoing growth of flocs is inhibited by their surface charge which repels other particles. It is assumed that changing the pH results in a change of the surface charge of the hydroxides and thus enables further coagulation. This is why increase of pH is not only helpful to accelerate ferrous iron oxidation but also to coagulate already existing ferric iron hydroxide flocs.

The results imply that distinct zones of turbulence (e.g. created by rapid of cascade like structures) in the riverbeds could be used to agitate the river waters to increase flocculation. Sedimentation of these flocs could be focused in stillwater areas. Maintenance of the river beds could be limited on zones of iron hydroxide sludge formation. The pilot tests in the field will serve to investigate this approach in more detail.

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