Advanced chemical oxidation for arsenic treatment at a flooded uranium mine with a bio-geochemically reduced mine water pool

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Abstract

Mine water from the flooded WISMUT mine at Pöhla-Tellerhäuser requires long-term treatment regarding arsenic and radium before river discharge. The mine water pool is characterized by geochemically reduced conditions with dissolved methane and hydrogen as well as overall redox potentials of 0 - 100 mV. Sulfate concentrations are < 5 mg/l, and uranium concentrations dropped below the regulatory limit (0.2 mg/l) only five years after flooding was complete. Those conditions, however, induce quasi constant mine water arsenic and radium concentrations of 1.5 - 2 g/l and ~4,000 mBq/l, respectively. Speciation analysis of dissolved arsenic revealed arsenite and arsenate as major species with a dominance of arsenite (>65% of total arsenic), while thioarsenates were detected in traces. Mine water treatment is performed by iron oxide and barium sulfate precipitation, leading to co-precipitation and adsorption of arsenic and radium. Reducing conditions, however, hamper ferric hydroxide formation and thus restrict the treatment performance of the precipitation plant. Generally, mixed ferrous-ferric hydroxides are known to be less effective with respect to pollutant binding and cause problems in sludge treatment. For technology optimization, oxidation of dissolved arsenite, ferrous iron and other reduced mine water solutes was tested using aeration and hydrogen peroxide dosage prior to ferric iron precipitation. Moreover, pH was adjusted to pzc for promotion of ferric iron flocculation and arsenic co-precipitation. Lab and field tests revealed hydrogen peroxide pre-oxidation in combination with pH adjustment to pH ≤ 7 most effective in decreasing dissolved arsenic concentrations. The residual concentrations of dissolved arsenic in the reaction chamber effluent were diminished from 250-400 µg/l to < 50 µg/l by reducing the ferrous fraction of the total iron concentration from ~ 10 % to 1-2 %. Advanced chemical oxidation speeds up colloid coagulation preceding flocculation and results in a stable and substantially complete arsenic removal from reduced mine water.

Key words: Uranium mining, mine water treatment, microbial reduction, arsenic and iron species, ferric hydroxide precipitation, chemical oxidation, laboratory test, field test

Introduction

After East German uranium industry was decommissioned in 1990, an unprecedented close-out and remediation programme was launched immediately thereafter. The programme is run by Wismut GmbH, a governmentally owned remediation enterprise, headquartered in Chemnitz, Saxony. The corporate purpose of Wismut GmbH is to decommission its former uranium mining and milling facilities and to rehabilitate the devastated land for further use.

While the physical clean-up and rehabilitation activities are chiefly completed, active mine water management is still required at all major remediation sites. By 2016 Wismut operates six water treatment plants to clean up effluents from four flooded underground mines and seepage water from several tailings management facilities. A total annual throughput of ~ 20 Mm^3 of water is treated for uranium, arsenic, radium-226 and heavy metal removal, basically by modified lime precipitation. According to current estimates, water treatment is expected to continue beyond 2040. Changes in water composition and the permanent need for cost optimization necessitate adjustments in water treatment methods on a regular basis. The paper illustrates most recent experiences regarding the water treatment approach practiced at the flooded uranium mine at Pöhla-Tellerhäuser, with a particular focus on arsenic removal from bio-geochemically reduced mine waters.

Site history

Between 1967 and 1990, the Pöhla-Tellerhäuser deep mine produced approximately 1,200 t U from polymetallic hydrothermal veins situated in a metamorphic host rock environment. Ore mineralization comprised pitchblende, Co-Ni-arsenides, native arsenic, loellingite, magnetite, pyrite, marcasite, chalcopyrite and native silver; quartz and calcite were the main gangue minerals (Hiller & Schuppan 2012). Mine development comprised a main access tunnel of 8 km total length and two blind shafts reaching a depth of 900 m below ground at the Tellerhäuser mine field.

After decommissioning the mine was flooded between early 1991 and autumn 1995. Floodable mine voids total approximately 1 Mm^3. In 1995, a conventional water treatment plant (WTP) was commissioned for the removal of uranium, manganese, arsenic and radium from the decanting mine waters. Unexpectedly, uranium concentrations declined much faster than modeled for a first flush discharge from a perfectly mixed flow reactor (Paul et al. 2013). Five years after reaching the final post-flooding water level, uranium and manganese concentrations in the mine effluent were even already below regulatory limits (Tab. 1), and treatment for uranium became redundant. Geochemically reduced conditions and the detection of microbial activity in the mine (Gagell 2015) are evidence that microbially induced uranium reduction and precipitation are causing the uranium retention. Unfortunately, those conditions favor at the same time the mobilization of arsenic and radium, which are the major aim of the recent treatment efforts.

The mine water is pH-neutral with low redox potential. In 2015, mean mine water quality has been characterized as follows: pH 7-7.5, Fe 5 mg/l, Mn 0.18 mg/l, As 2 mg/l, U 12 µg/l, ^{226}Ra 4.2 Bq/l, SO_4 < 5 mg/l, TDS 286 mg/l. Both prevention of precipitation reactions and mineral dissolution in the mine induce quasi constant mine water arsenic and radium concentrations which are well above the discharge limits (As 100 µg/l, ^{226}Ra 300 mBq/l). Speciation analysis of dissolved arsenic revealed arsenite and arsenate as major species with a dominance of arsenite (>65% of total arsenic), while thioarsenates were detected in traces. Moreover, dissolved methane and hydrogen as well as overall redox potentials of 0 - 100 mV indicate reduced geochemical conditions in the mine.

Table 1 *Quality evolution of the Pöhla mine effluent after fully-fledged flooding*

Element	Limit value	Mine water quality (mean values)				
		1995	1997	1998	2008	2015
Mn (mg/l)	2.0	3.68	1.60	1.14	0.23	0.18
As (µg/l)	100	487	2,017	2,200	2,091	2,050
U (mg/l)	0.20	1.75	0.20	0.19	0.02	0.012
Ra-226 (mBq/l)	300	1,057	3,910	4,520	4,001	4,210

Today, an annual mine water overflow of ca. 0.13 million m^3 from the deeper, flooded part of the mine is collected in the still open drainage adit and led by pipelines to the WTP, while at the same time approximately 0.25 million m^3 of penetrating surface water are collected separately along the main access tunnel and drained directly to the natural water system.

Water treatment plant

After having tested the efficiency and robustness of a semi-passive constructed wetland approach over a 10 year period with an unsatisfactory overall outcome, mine water treatment is most recently performed by an iron oxide and barium sulfate precipitation unit, leading to arsenic and radium retention by co-precipitation and adsorption. Fig. 1 depicts a flow chart of the WTP. Briefly, the precipitation plant treatment scheme comprises aeration, addition of chemicals, mixing, coagulation, flocculation, filtration as well as sludge separation and storage. It is important to note that the plant has been designed for a remote-control operation mode without permanent workforce at the site. Low density sludge is collected in a storage tank and discontinuously transported to Wismut's Schlema WTP some 25 km away, where it becomes introduced into the local sludge management procedure of thickening, immobilization and disposal at an in-house disposal area.

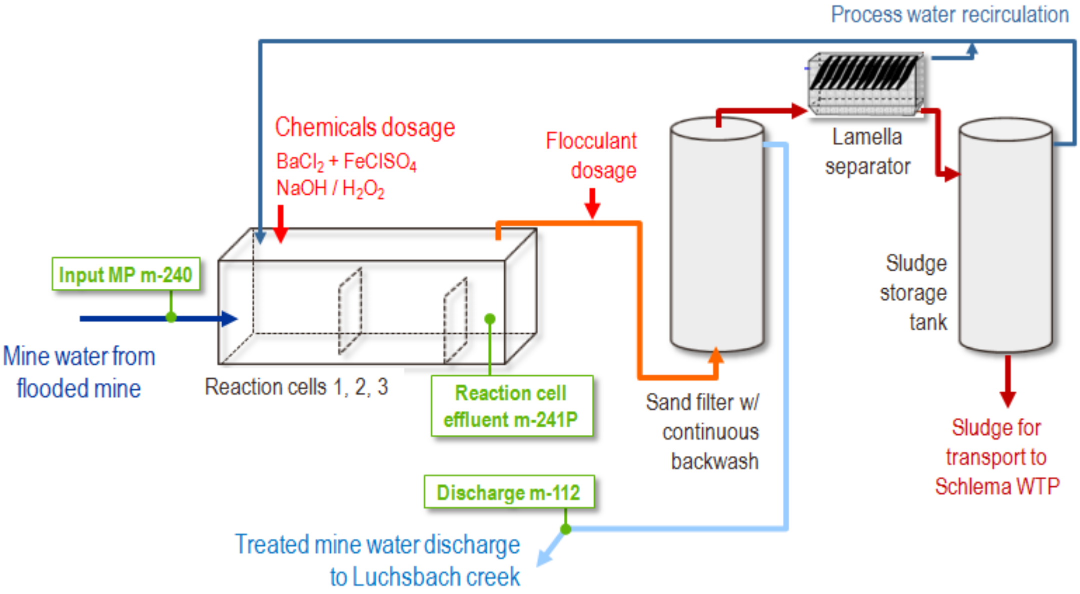

Figure 1 *Principle flow chart of the Pöhla WTP with selected monitoring points*

The Pöhla treatment plant was built in 2013/2014 and has been operated in testing mode since 2014. The treatment capacity of the plant is 10 - 60 m^3/h. At present, the plant is operated at an average flow rate of 12 m^3/h.

The original treatment sequence design comprises

- addition of $FeClSO_4$ (33%) and $BaCl_2$ (24%) with dosage rates of 0.16 - 0.2 l/m^3 and 0.08 l/m^3, respectively (mixing in coagulation basins)
- pH adjustment to pH = 7.5 - 7.7 by addition of 25% NaOH (mixing in coagulation basins)
- flocculant addition (0.05% AP99E (PolyChemie GmbH), 5 l/h) in piping to sand filter
- flocculation and filtration in sand filter with continuous backwash

During the first months of operational testing in 2014, arsenic concentrations in the plant effluent met regulatory limits (100 µg/l) but with values only marginally below it. At the same time, a lag in iron hydroxide flocculation was observed. As illustrated by Fig. 2, flocculation proceeded downstream the sand filter, forming iron hydroxide coatings on pipes, tank walls and probes contacting the filtrate.

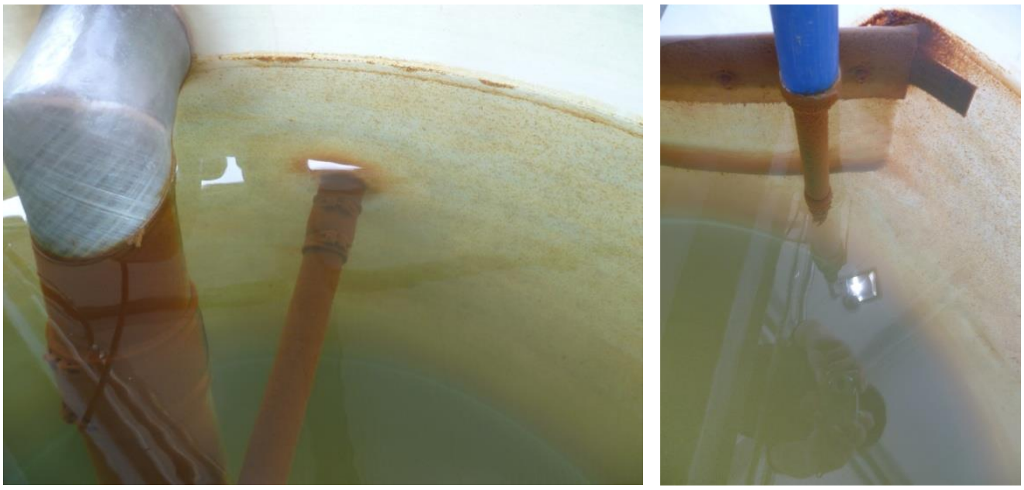

Figure 2 *Photographs of iron hydroxide coatings formed downstream the sand filter from the filtrate*

Monitoring of the treatment process revealed an extension in flocculation time from 15 min to 60 min with an increase in ferrous iron concentration in the coagulation basins from 5 to 25 mg/l. The ferrous concentrations in the coagulation basin occasional exceeded mine water inflow concentrations, indicating a reduction of the ferric iron added for coagulation. Reduced solutes of the mine water (e.g. dissolved methane) and iron reducing microbes may play a role in that.

The presence of ferrous iron during colloid formation and coagulation causes a mixed ferrous-ferric hydroxide formation, which is known to be less effective with respect to pollutant binding. Moreover, mixed ferrous-ferric hydroxides form sticky precipitates causing problems in sludge handling (MEND 1999), which were observed at plant operation as well. Iron hydroxide sorption of the reduced arsenite is generally inferior to that of the oxidized arsenate, too. Thus it was hypothesized, that both limited arsenic retention and unfavorable flocculation depend on an insufficient oxidation state during iron hydroxide colloid formation and coagulation.

Lab investigations for water treatment optimization

For technology optimization, oxidation of dissolved arsenite, ferrous iron and other reduced mine water solutes was tested in the lab using aeration (gassing with pressurized air; 2 hours) and hydrogen peroxide dosage (35% H_2O_2 dosage; 0.2 ml/l; reaction time 30 min). Subsequently, coagulation and flocculation (33% $FeClSO_4$; 195 µl/l; 23% $BaCl_2$; 81 µl/l) was tested at pre-oxidized and at original mine water (mixing time 30 min, settling time 70 min).

Fig. 3 shows pH, redox potential and ferrous iron concentrations of the mine water during pre-oxidation. H_2O_2 addition oxidizes the mine water faster and more extensive than aeration. While ferrous iron is still present after 60 min of aeration, no ferrous is detectable at H_2O_2 addition after 30 min. Moreover, the redox potential at H_2O_2 dosage (~470 mV) exceeds the average redox potential at aeration (~350 mV) by ~100 mV, and the pH stays constant at H_2O_2 addition instead of rising by CO_2 degassing at aeration.

The coagulation tests are discussed for dissolved iron and arsenic concentrations, since both are a measure for completeness of iron hydroxide colloid formation and coagulation. Low dissolved concentrations after coagulation indicate rapid flocculation and high pollutant retention in the treatment process.

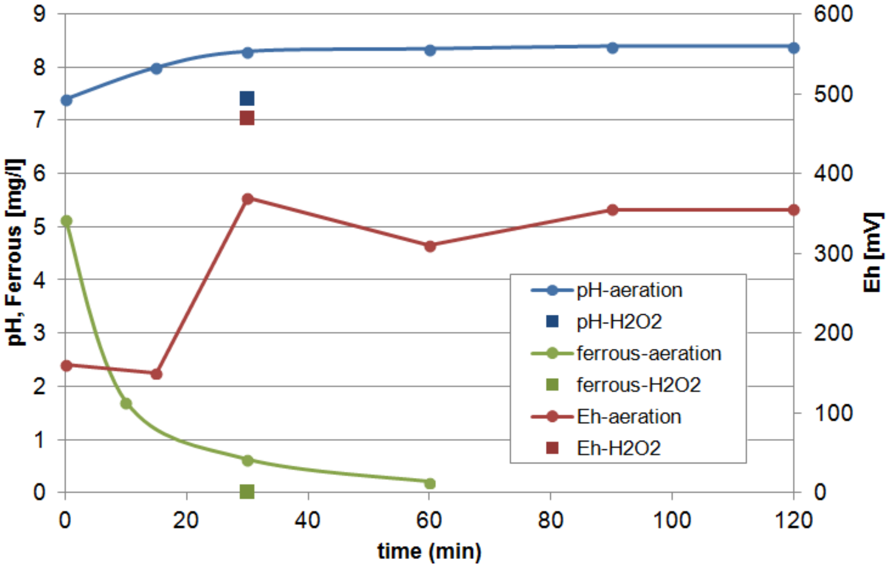

Figure 3 *pH, redox potential and ferrous concentration during pre-oxidation*

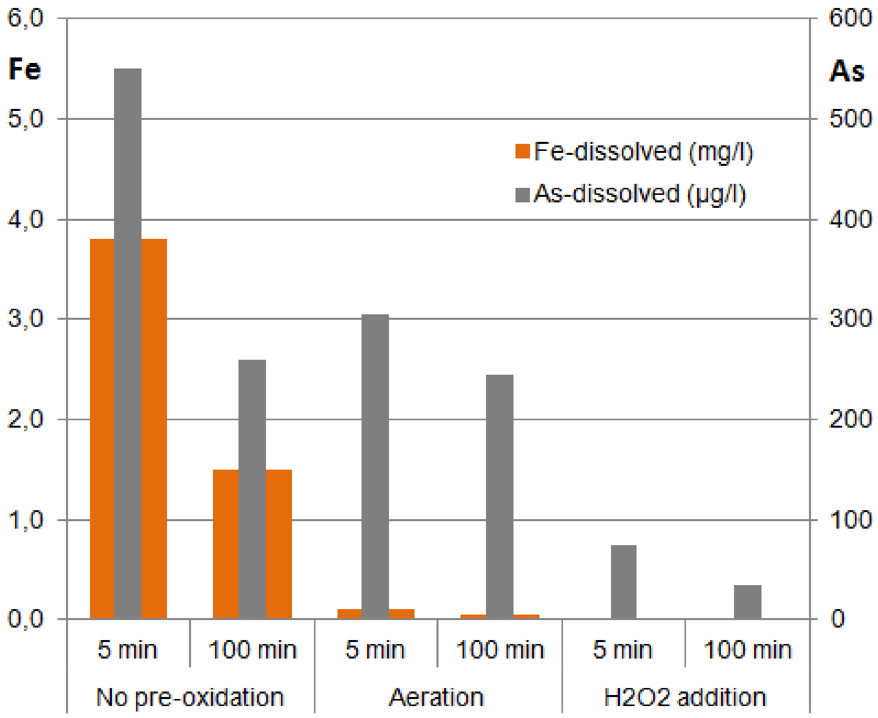

Figure 4 *Dissolved iron and arsenic after coagulation and flocculation at different oxidation states*

As depicted in Fig. 4, the dissolved arsenic concentration was below the effluent limit (100 µg/l) at H_2O_2 addition already after 5 min, while aeration left only little less arsenic dissolved after 100 min than coagulation without pre-oxidation (260 and 240 µg/l, respectively). Colloid formation and coagulation was rapid and complete only at the oxidation state reached by H_2O_2 addition. Obviously, the presence of reduced species and ferrous iron during coagulation and flocculation hampers the precipitation of iron hydroxide and the associated arsenic elimination in the treatment plant.

Field scale testing of treatment optimization

Field scale testing was performed by modification of the operation scheme of the treatment plant. After a period of baseline monitoring (~ 9 month), the effects of pH adjustment to pH 7 (stopping of NaOH dosage), pre-aeration of the mine water (change from pressure to gravity pipeline for mine water inlet) and H_2O_2 dosage (165 – 335 ml $H_2O_{2\ (30\%)}$ / m^3) on arsenic removal were tested. Table 2 indicates the duration and particular operation conditions of the single test periods. Fig. 5 depicts arsenic concentrations (average, min and max) of the plant effluents for each test period.

Table 2 *Field test periods and operation conditions*

No	Period	Modified operation conditions			
		Stopping NaOH dosage	Mine water pre-aeration	H_2O_2 dosage, ml/m^3	Sludge recirculation (partial)
1	01/2014-09/2014			Baseline monitoring	
2a	01/2015-02/2015	x			
3	03/2015-04/2015	x	x		
2b	06/2015-09/2015	x			
2c	10/2015	x		Baseline monitoring for period 4-6	
4	11/2015-01/2016	x		165	
5	03/2016-04/2016	x		165	x
6	05/2016	x		250-335	x

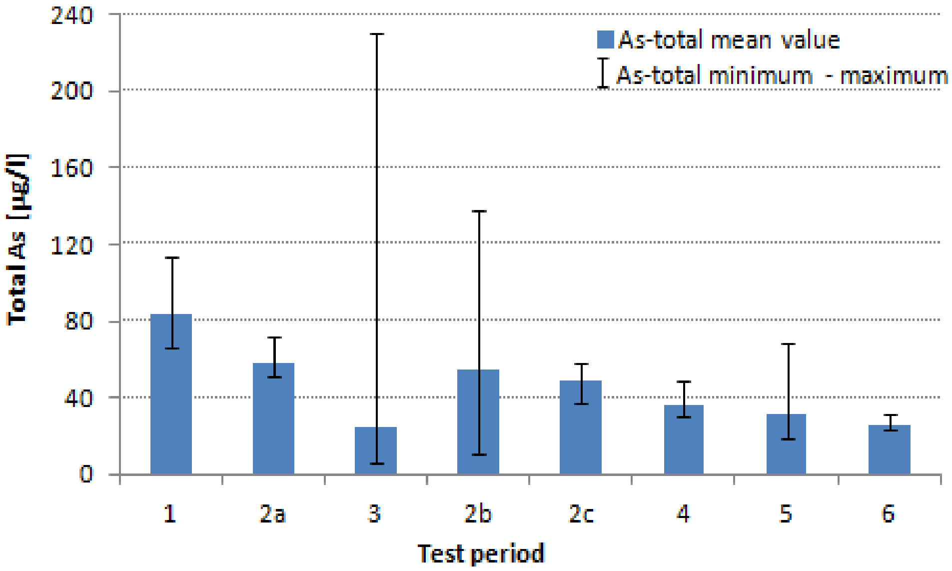

***Figure 5** Total arsenic concentrations in plant effluents (m-112; mean, minimum and maximum values for each of the individual test periods, see table 2)*

As compared to the original operation scheme, all tested modifications of operation conditions yielded a decrease in average total arsenic in the plant effluent.

Adjustment of pH from pH ~ 7.5 to pH ~ 7 (test period 2) decreased mean arsenic concentrations from [As] ~ 85 µg/l to [As] ~ 50 - 60 µg/l. The pH decrease favours the supposed arsenic retention mechanisms: scorodite formation (although totally amorphous at pH ~ 7) and anion sorption to iron hydroxides (increase in number of positive surface charge). In consequence, NaOH dosage was switched off and pH ~ 7 was retained for all subsequent test periods. The increase in data variation ($[As]_{max}$ ~ 130 µg/l) in test period 2b relates to effects of the previous tested mine water pre-aeration, were the decrease in average arsenic effluent concentration but also in data variation were most expressed ([As] ~ 25 µg/l; $[As]_{max}$ ~ 230 µg/l). At mine water pre-aeration in the inlet pipe (connecting the 3.5 km distance from the mine to the treatment plant), a partial oxidation of the mine water had resulted in in-pipe precipitation of arsenic rich iron hydroxide. This caused an expressed but unstable decrease in mean arsenic concentration. Sporadically, the precipitates were flushed out and overloaded the flocculation filter of the treatment plant, yielding arsenic break-through and test period break-off. A more stable decrease in mean arsenic effluent concentrations and low data variation could be achieved by H_2O_2 dosage. While partial sludge recirculation increased data variation in test period 5 ($[As]_{max}$ ~ 70 µg/l), the average effluent concentration of all H_2O_2 dosage test periods stayed below 40 µg/l. At highest H_2O_2 dosage rates (250-335 ml $H_2O_{2(30\%)}$ / m^3; test period 6) the average effluent concentration was as low as 25 µg/l, comparable to mine water pre-aeration but with significantly smaller data variation ($[As]_{max}$ ~ 30 µg/l).

The significant improvement in overall arsenic retention during the test phases with H_2O_2 dosage can be related to the decrease of dissolved arsenic concentrations in the effluent of the coagulation basin prior to sand filtration (m-241P). As shown in Fig. 6, H_2O_2 dosage caused a sudden decrease of dissolved arsenic concentrations in comparison to phase 2c values (As_{diss} ~ 300-400 µg/l). During the test periods 4-6 the mean of the dissolved arsenic concentrations was as low as $[As]_{diss}$ ~ 55 µg/l, i.e. well below the discharge limit of the plant at m-112. Likewise, the As_{diss}/As_{total} ratio of the reaction cell effluent decreased significantly, from 19% in test phase 2c to 4 % (period 4), 3 % (period 5) and 1% (period 6), respectively.

Obviously, advanced chemical oxidation can effectively improve arsenic retention by iron hydroxide precipitation on the field scale as well. The dominance of ferric and arsenate species promotes iron coagulation, adsorption and scorodite formation. Arsenic removal is best at vast iron coagulation, leaving low concentrations of dissolved iron in the effluent. This correlation of dissolved arsenic and iron was found in the reaction cell effluents and is depicted in Fig. 7, compiling data from the test periods 2c (baseline monitoring prior to H_2O_2 addition) and 4 – 6 (H_2O_2 addition at various dosage rates). Low concentrations of dissolved arsenic coincident with low concentrations of dissolved iron. This indicates extensive colloid and particle formation prior to flocculation filtration. Arsenic concentrations can be reliably reduced to values much below regulatory limits and incrustation of plant equipment downstream the sand filter can be prevented.

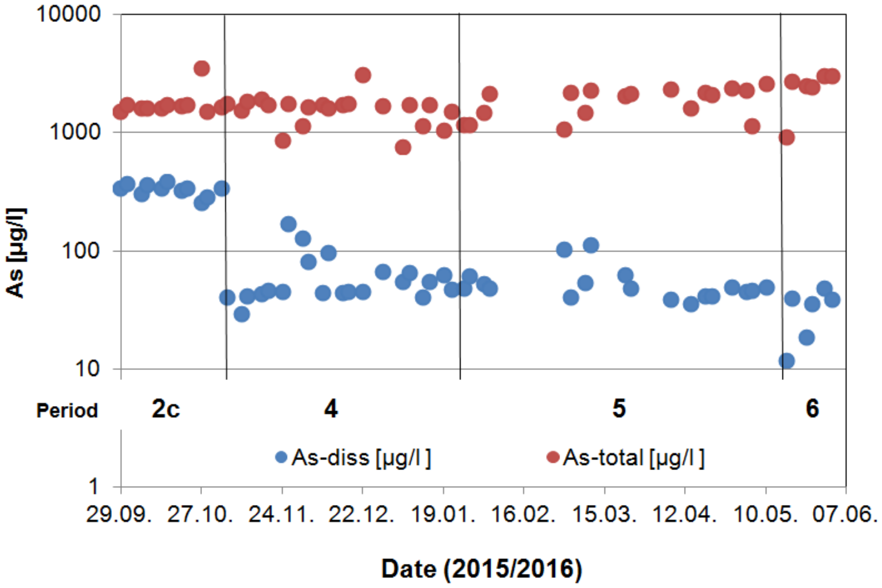

Figure 6 *Total and dissolved arsenic concentrations in reaction cell effluents (prior to filtration, m-241P) during test periods 2c (baseline monitoring prior to H_2O_2 dosage) and 4-6 (H_2O_2 dosage)*

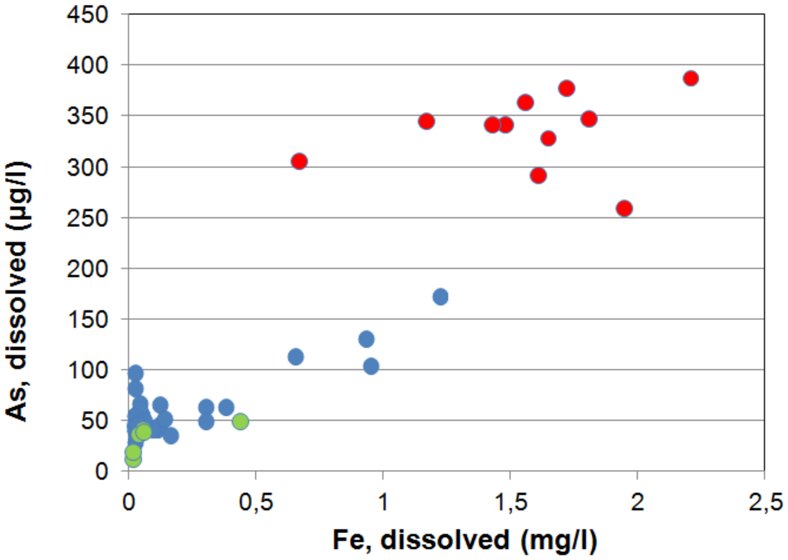

Figure 7 *Correlation of dissolved iron and arsenic concentrations in reaction cell effluents (m-241P) during test periods 2c (baseline monitoring prior to H_2O_2 dosage, red dots), 4-5 (H_2O_2 dosage, blue dots) and 6 (H_2O_2 dosage, green dots)*

Conclusions

The work clearly illustrates the optimization potential of water treatment operations by an approach based on chemical process analysis. The investigations carried out in lab and full scale revealed hydrogen peroxide pre-oxidation in combination with pH adjustment to pH ≤ 7 most effective in decreasing dissolved arsenic concentrations in the reduced mine water at Pöhla. The residual concentrations of dissolved arsenic in the coagulation cell effluent were diminished from 250-400 µg/l to < 50 µg/l by reducing the ferrous fraction of the total iron concentration from ~ 10 % to 1 - 2 %. Advanced chemical oxidation speeds up colloid coagulation preceding flocculation and results in a stable and substantially complete arsenic removal from reduced mine water. The findings of the study will be implemented into the regular long-term water treatment approach at the Pöhla mine site.

Acknowledgements

This work is part of Wismut's environmental remediation program. Special thanks to Holger Klaußner for process monitoring coordination and Andrea Schramm for assistance with data compilation and evaluation.

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