

# Investigations into seepage water acidification of a tailing dam of the tin ore processing

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**Abstract.** The changes in the chemical composition of water and solid phases in the zone of seepage water and ground water of a tailing dam of a tin ore processing plant are described. To clarify the causes of a steep decrease of the pH value and in connection with this a partly considerable increase in concentration for several elements, geochemical and mineralogical investigations of waters and tailings were carried out in the dam area. Mineralogical investigations of the tailings from the slope area clearly showed symptoms of dissolution and corrosion. The causes of the current state and several possibilities for the regeneration of an almost neutral pH in seepage water, connect with a reduction of the element discharge, will be shown and explained.

## Task

Tailing dams of the ore processing usually contain elevated contents of sulphide minerals. Their oxidation often takes place in a relatively short time and produces compounds, some of them with a very good water solubility. Depending on the ore paragenesis present, these tailings dams have an almost unlimited reservoir of several heavy metals and arsenic. Therefore, tailings dams' seepage waters are polluted by these elements over long time periods.

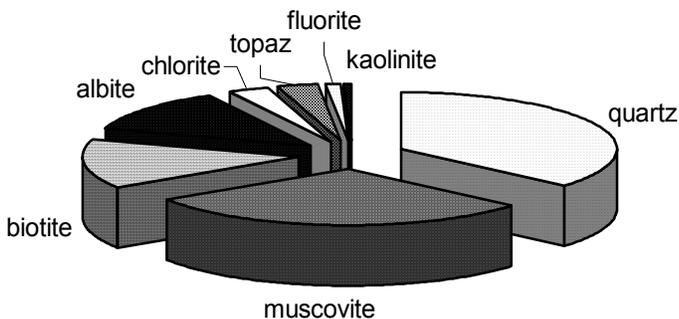
Long-term monitoring of two tin ore processing tailing dams of comparable content, which are located in Ehrenfriedersdorf, unexpectedly showed differing developments. The younger and larger dam 2 (1969—1990), which is located on a gentle slope, emanated water of an almost unchanged quality over a period of ten years. Contrary to this, water from the older dam 1 (1942—1969), which is situated in a valley cut, without obvious reasons and in a very short time showed a steep decrease of the pH value from 6.8 to 4 together with an increase in several elements' concentrations (Fe, Al, Mn, Zn, As). This phenomenon could not be ob-

served at the main and the eastern infiltration ditch of the tailing dam 2, which otherwise contains the same material.

The determination of the reason(s) for the change in quality of the seepage water of Tailing Dam 1 was of fundamental importance in view of the anticipated “remedy” for water cleaning and its necessary time span as well as for the possible influence of the ageing process of tailing dams. Possible ageing effects as causes for the acidification and the increased discharge of As and heavy metals would then have to be expected in future for a larger number of younger tailing dams.

## Mineralogical and geochemical investigations of the tailing material

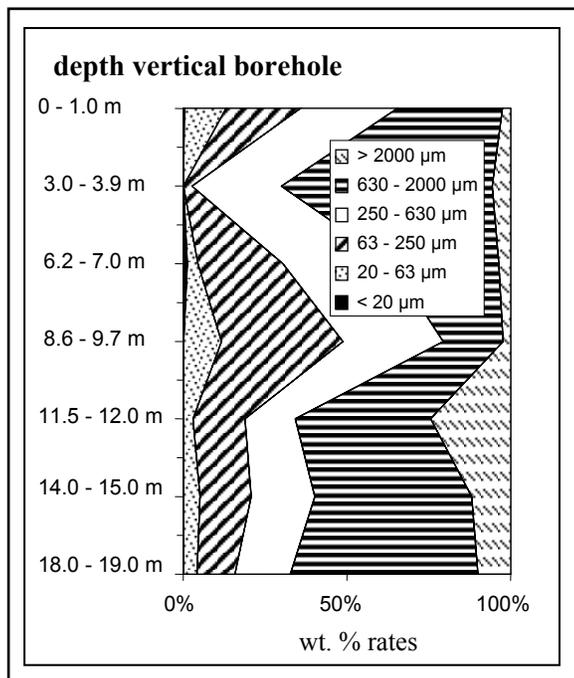
The tailing material mainly consists of quartz and micas (ca. 96%). Feldspars, fluorite, tourmaline, and chlorite, as well as remains of sulphides (arsenopyrite, pyrite, löllingite) are present in smaller amounts (Fig.1).



**Fig. 1.** Mineralogical phase composition of tailing of Tailing Dam 1.

The sand and silt fraction is mainly composed of the stable minerals quartz and mica, whereas the prevailing components of the clay fraction are weathering products like clay minerals (especially kaolinite) and iron hydroxides.

The grain size distribution of the tailing material can be found in the following Fig. 2.



**Fig. 2.** Grain size profile of vertical borehole (from Krellmann 2001).

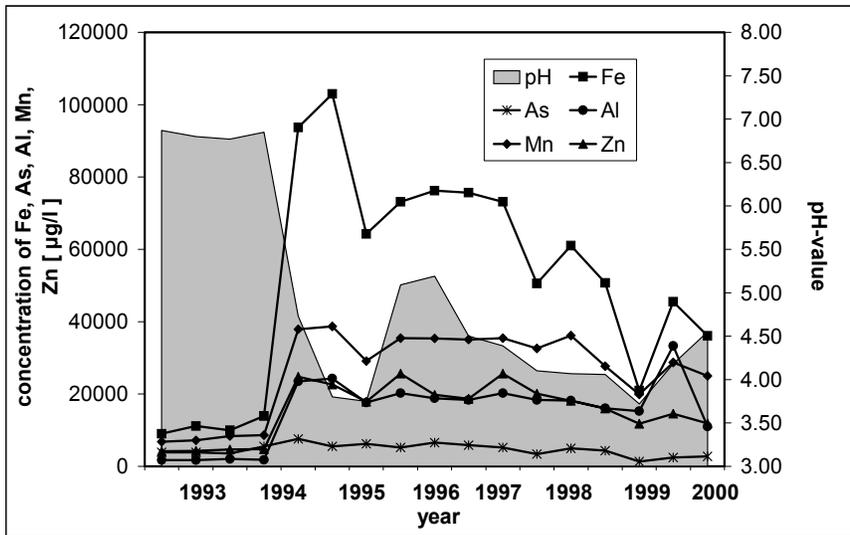
The weathering processes are mainly controlled by the oxidation of the sulphides and  $\text{Fe}^{2+}$  (which also produces  $\text{H}^+$  ions), as well as the hydrolysis of the silicates in acidic conditions. The weathering of the feldspars is already in an advanced state. Remains of the feldspars (mainly albite) are left as light coloured crusts on most of the dark micas. Intense oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and its subsequent precipitation by hydrolysis preferably occurs in the outer zone of the dam and on the groundwater level, well marked by the strong red-brown colouring of these zones.

The material discharge by the seepage water is decisively influenced by the bonding capacity of the elements, but also by the pH value and the redox potential. Investigations of a depth profile of gauge well 4A<sub>new</sub> were carried out by sequential extraction technique according to Salomon and Förster (1984). Because of the heterogeneous material distribution the measurement results showed large variations for the elements under consideration, comparable to the overall composition. The oxidation of the dominating sulphide arsenopyrite has advanced considerably. In a depth of 4—17 m iron and arsenic are present in sulphide bond only in a very small amount (< 1%). Of prime importance is the water soluble portion, which is presented in Table 1 together with the *aqua regia* soluble content (DIN 38414).

**Table 1.** H<sub>2</sub>O and *aqua regia* soluble contents of As, Al, and heavy metals in material from Tailing Dam 1 (from Krellmann 2001).

	Al	Fe	As	Co	Mn	Ni	Zn
H <sub>2</sub> O-soluble	8 – 159	3.8 – 196	14 – 80	0.02 – 1.8	1.9 – 17	0.17 – 5.6	0.49 – 36
<i>aqua regia</i> soluble	21,000 – 2,800	29,000 – 63,000	820 – 13,700	5.6 – 14.6	374 – 988	11.7 – 51.6	180 – 1,809

The pH value and several element concentrations were measured at the captation zone for the seepage waters (measuring point 33) between May 1993 and March 2000. Between August 1993 and April 1996 the pH value, which until then had only been slightly varying, dropped from 6.8 to 4, a phenomenon that was accompanied by an increase in concentration of main components and trace elements, like Fe<sup>2+</sup>, Al, Mn, As, and Zn (Fig. 3). Nickel and cobalt have only been measured from March 1996 onwards, hence an increase in their concentration can only be assumed.

**Fig. 3.** Time dependent concentration trend of pH, arsenic, aluminum and heavy elements (Mn, Zn, Fe; from Krellmann 2001).

## Geochemistry of the groundwater in the tailing dam

Gauge wells in the tailing dam enabled measurements of the groundwater level and samples to be taken (Fig.5). Geochemical analyses showed a clear increase of the overall mineralisation ( $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ) as well as of the concentrations of Fe, Al, Mn, As, Ni, Co, Zn occurring alongside a decrease of the pH value from 9 to 6.3 in the direction of flow of the groundwater (Fig.4). This tendency only changed in the area of the dam slope between the gauge well (4A<sub>new</sub>) and the seepage water captation zone (measuring point 33). Together with the decrease of the pH value from ca. 6 to 4 the concentrations of the elements diminished irregularly. Whilst the values of Fe and As showed a sharp decrease, the changes for Al, Mn, Ni, and Zn were only moderate. Reasons for this could be a higher flow velocity of the seepage water because of the coarser grain fraction in this area and the lateral influx of seepage waters, which may dissolve the dam water because of its lower pollution. Also the lower compression of the dam slope offers much better pathways for the influx of air, thus intensifying the oxidation processes.

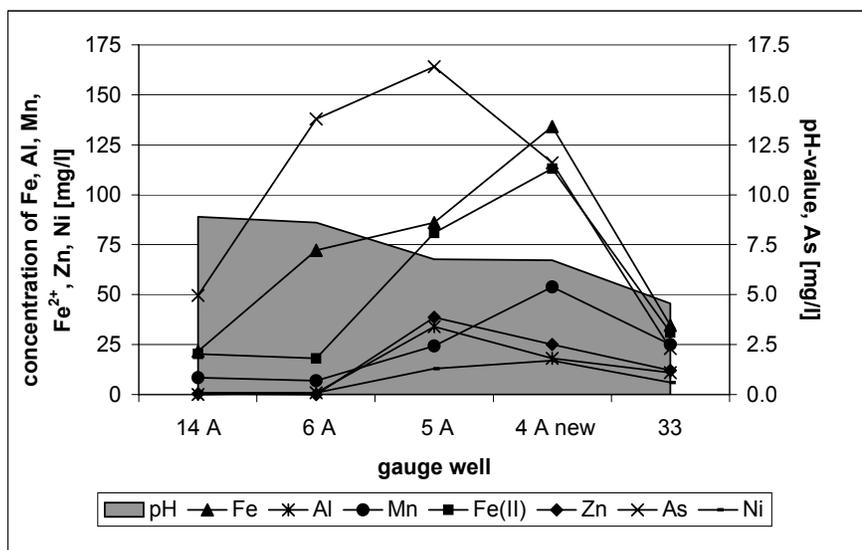


Fig. 4. Variation of pH value and trace elements concentration in the ground water of the Tailing Dam 1.

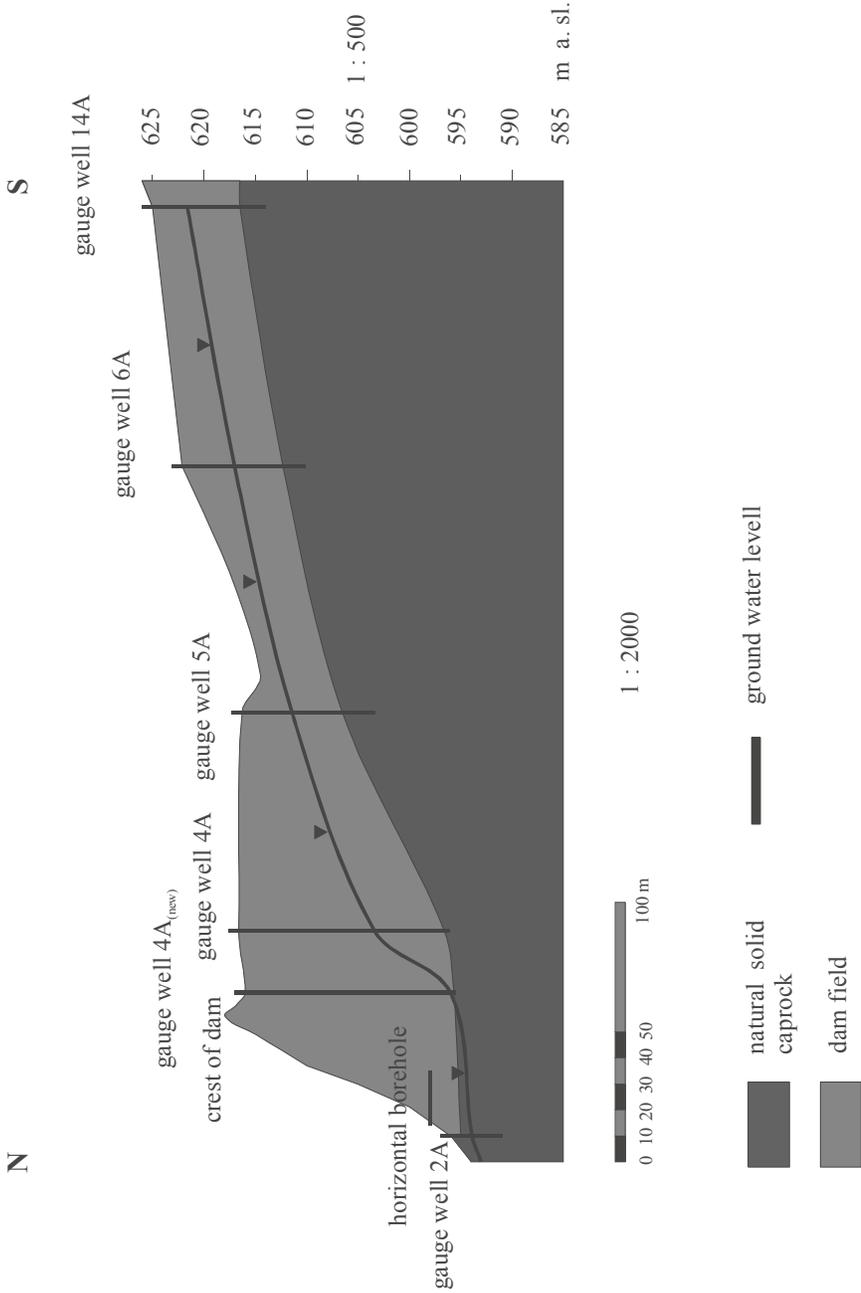


Fig. 5. Profile of Tailing Dam 1 (from Krellmann 2001).

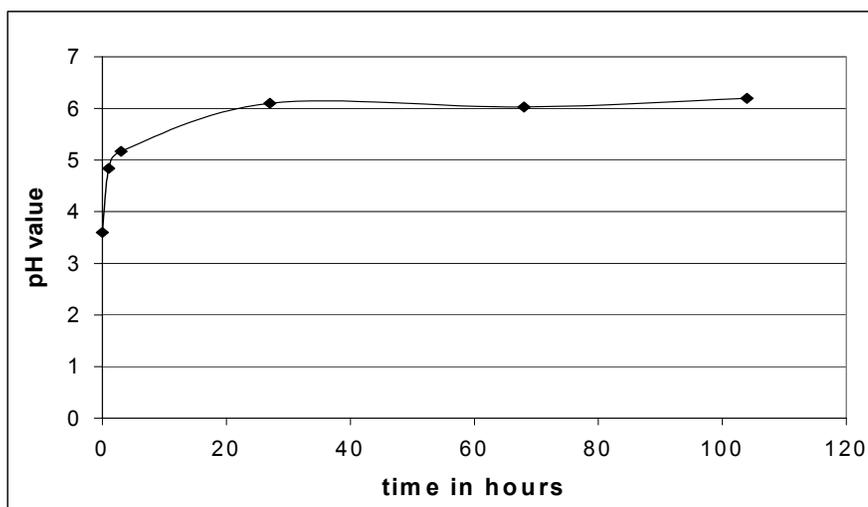
## Possible causes for the decrease of the pH value

Several possible causes for the decrease of the pH value and the change of the water quality, which is closely linked to this, can be named:

- Intensification of the sulphide oxidation inside the dam
- Depletion of the silicate buffer of the tailing material
- Geochemical reactions with increased “acid production”
- Changes in the hydrological regime

Of these, the first one, namely the intensification of the sulphide oxidation, appears to be hardly probable as the main reason for the acidification of the seepage water being emanated, because the sulphide concentrations are already very low. Contrary to this, the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and its subsequent hydrolysis to iron hydroxides offers a reaction that is in accordance with the change of the pH value towards stronger acidity as well as with the considerable decrease of the concentration of iron (111—140 to 34—78 mg/l). The content of As is reduced by adsorption at the flocculating iron hydroxides parallel with the diminution of the Fe concentration. The elements that are not affected by this process (Mn, Al, Ni, and Co) show a much slighter decrease in composition, which can be explained as a “dilution” by laterally inflowing waters.

If this is to be seen as the dominating process for the diminution of the pH value, changes in the buffering capacity of the area under consideration must have taken place. However, laboratory experiments with tailing material showed that in batch experiments with seepage water (pH 4) after ca. 20 hours an almost constant pH value of 6 is reached (Fig.6).



**Fig. 6.** Buffer effect of the tailings in shacking experiment with seepage water from the Tailing Dam1.

Besides evidence of a sufficient buffering capacity of the tailing material the experiment provided some indication as to the necessary reaction time. If this is undershot, decrease of the pH value of the emanated seepage water is the result.

In the years 1993—1996 a ditch was dug at the dam base during clean-up operations of the seepage water captation zone. As a result of these works the seepage water emanated at a level 1.5 m lower than before. The pH buffering was subsequently limited because the loss of the water tailback in the dam base had reduced the dwell time of the water and the originally existing reaction time accordingly.

## Conclusions for steps to be taken

The certain exclusion of an ageing effect as the cause for the decrease of the pH value and the increase of the discharge of As and heavy metals also precludes similar reactions for younger tailing dams. The deterioration of the seepage water quality in the dam under investigation is caused by changes in the hydrological regime, which provokes the decrease of the pH value towards higher acidity and alongside this the increase of the element discharge. From these findings the following steps for the reduction of the water pollution with As and heavy metals can be proposed:

- Reduction of the water throughput through the dam by branching off of accruing groundwater before its entry into the dam body with suitable drainage systems and sealing of the tailing dam surface against meteoric water
- Increase of the dwell time of the seepage water in the dam body in order to improve the pH value buffering by the restoration of the original water outlet level by building in packing material at the dam base

## References

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