The toxicity of cyanide in water, air and soil is an excepted fact. However to find serious exposure limits is a difficult task. Data for the evaluation is often old and difficult to use in contemporary requirements, on the other hand, studies about the toxicity of cyanide are getting more complicated due to the growing knowledge of its hazardousness.

One of the basic arguments for the definition of exposure limits in air is the detoxification rate of cyanide in the human body. Two values are still in discussion in recent literature. The rate of 17 µg/kg body weight/min is based on studies from Loevenhart (1918) [1], who tested the impact of NaCN seriously ill patients, ignoring the fact that free cyanide is not stable in solutions at high pH. The rate of 1 mg/kg body weight/min is found in a more recent publication from Schulz (1982) [2], although no explanation was found for citations of fatalities after consumption of similar cyanide concentrations in the same paper. Hence, an amount of cyanide being metabolised in the body must be below this value.

The volatilisation rate of HCN in different pH values is a crucial point in the estimation of the hazardousness of cyanide in the environment and further treatment opportunities. The photoelectrocatalytic treatment, using TiO₂ on conducting glass (FTO) was investigated by the authors in previous studies. Treatment of solutions with a pH value of 10.5 resulted in a low degradation rate, compared to experiments with other substances [3]. In plotting the degradation rate against the distance of the redox potential to the energy of the valence band, a correlation is found (Fig. 1)

\[
p = \frac{kVF}{i_{\text{photo}}}
\]

\(p\): ratio between the rate constant of the oxidation of the oxidisable additive \((k)\) and the rate of water oxidation in a batch reactor with the total volume \(V\) of the solution.

\(F\): Faradaic constant.

\(i_{\text{photo}}\): photocurrent produced with irradiation of UV-light.

Fig. 1: Linear free energy relationship - constant \(p\) against the difference of the energy of the valence band to the redox potential of different species
The assumption of a relationship between the reaction rate and the difference of the energy of the valence band to the redox potential can be confirmed if the reaction rate changes with \((\text{EVB} - \text{E}_{\text{redox}})\). If the oxidation of cyanide proceeds via the direct route

\[
\text{CN}^- + \text{H}_2 \text{O}^+ \rightarrow \text{CN}^+ \]

it should be pH independent and the difference to the pH dependent valence band level increases. Experiments for the investigation of this relationship were done with TiO2 layers on FTO glass and a steel counter electrode in a photoelectrocatalytic setup, using UVA light (Fig. 2).

![Fig. 2: Total and detailed Cyanide loss in a degradation experiment, using 400 mg/l Cyanide solutions in buffered solutions of different pH values.](image)

Besides the strong increase of volatilisation, the increase of cyanide oxidation with decreasing pH is confirmed. Experiments were done in a closed setup with cyanide-contaminated air suction through an absorption flask (1M NaOH). Experiments with other materials will follow to investigate the acidic region and to prove the relationship on other species.

Additional investigations of the processes in photoelectrocatalysis at different pH will help to improve the detoxification capability of TiO2 in gold mining. Furthermore, the cyanide management in gold processing has to be improved to minimise the intake of NaCN. With a new discussion of cyanide-limits in gold mining based on recent investigations of the toxicity, the further reduction of cyanide contaminations will require advanced technologies for the degradation and the analysis as well.

References