

# ACIDIFICATION PROCESS IN THE AREA OF THE ABANDONED ĽUBIETOVÁ - PODLIPA CU-DEPOSIT, SLOVAKIA

## PROCES ACIDIFIKÁCIE V OBLASTI OPUSTENÉHO CU-LOŽISKA ĽUBIETOVÁ - PODLIPA, SLOVENSKO

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### Abstract

Acidity in surroundings of the abandoned Ľubietová-Podlipa Cu-deposit depends predominantly on the geochemical behaviour (weathering) of particular minerals (mainly pyrite). The article presents the results of measurements of basic physicochemical parameters – pH and Eh in technogenic sediments and in surface and drainage water of a dump-field. Although the dump material shows a significant amount of mobility-able metals and thus also a potential to form acidity, a massive AMD formation in future is not probable.

### Abstrakt

Acidita v okolí opusteného Cu-ložiska Ľubietová - Podlipa závisí predovšetkým od geochemického správania sa (zvetrávania) niektorých minerálov (hlavne pyritu). V článku sú prezentované výsledky meraní základných fyzikálno-chemických parametrov – pH a Eh v technogénnych sedimentoch a v povrchovej a drenážnej vode haldového poľa. Haldový materiál síce stále vykazuje značné množstvo mobilizovateľných kovov a teda aj istý potenciál tvoriť kyslosť, podľa výsledkov výpočtu rizika, k masívnejšej tvorbe AMD nebude v budúcnosti pravdepodobne dochádzať.

**Key words:** dump-field, technogenic sediments, soil, acidity, neutralisation potential

## 1 INTRODUCTION

Surroundings of mine workings in Ľubietová represents an area having been changed by historical exploitation of copper ores [3]. Changes in pH and Eh in technogenic sediments cause a release of heavy metals from the solid phase, where they are in a form of heavier soluble minerals or a sorption complex, to groundwater and surface water [1,10]. The mobility of heavy metals in solutions and complex compounds is shown by the fact that the contents of many of heavy metals in technogenic sediments and soils and in products of oxidation of sulphides in the area of dumps is sometimes lower than the contents in soils under a dump-field, as well as the formation of numerous secondary minerals (mainly copper minerals) carbonates, phosphates, sulphates and oxides [4]. These secondary mineral phases originated mainly in the process of precipitation from solutions

circulating in technogenic sediments and soils, but also due to the oxidation of primary minerals. Their formation controls and slows down migration of heavy metals, due to their stability under surface conditions [2].

Important soil properties include soil reaction which is used to indicate the acid-base reactions in soils. We distinguish between active and changeable forms of soil reaction. The active soil reaction is determined by oxonium cations and hydroxide anions present in a soil solution. It is determined from a H<sub>2</sub>O soil solution. The exchangeable soil reaction is given except for free H<sup>+</sup> and OH<sup>-</sup> ions also by H<sup>+</sup> and Al<sup>3+</sup> ions adsorbed by a soil colloidal complex, which are released into the soil solution by the action of hydrolytic neutral salts (NaCl, KCl, CaCl<sub>2</sub>). Generally, it is determined in 1M of the KCl solution [20].

Numerous chemical and biochemical reactions take place only under certain specific conditions of soil reaction. These chemical and biochemical reactions affect the decomposition of mineral and organic substances, formation of clay minerals, solubility (mobility) of substances and hence their bioavailability for living organisms, availability of nutrients, adsorption and desorption of cations, biochemical reactions, soil structure and physical properties [9]. The production of H<sup>+</sup> ions in soils is affected by acid rain and degradation of sulphides. Oxidation of sulphide minerals represents a complex of biogeochemical processes [15]. The rate of acidification depends on several factors such as the effect of bacteria, air O<sub>2</sub>, the presence of water, etc. Signs of acidification are usually subdued by buffering and neutralizing ability of surrounding rocks (carbonates, clay minerals and organic matter), but beyond the buffering and neutralizing capacity of the environment, acute acidification begins to manifest [17].

Nand and Verloo [14] characterized the mobile fraction of metals as the sum of the soluble portion of metal in the liquid phase and the portion which indeed remains in the solid phase, but can gradually move into the soil solution. Rieuwerts et al. [16] emphasizes the importance of the mobility of metals for the possibility to estimate their concentrations in the soil solution, surface, drainage and groundwater. The total metal concentration depends on the content of metal in the solution, which in turn depends on the sorption to natural sorbents (such as clayey minerals, hydrogoethit, zeolites, ...) and the metal release into the soil solution [21].

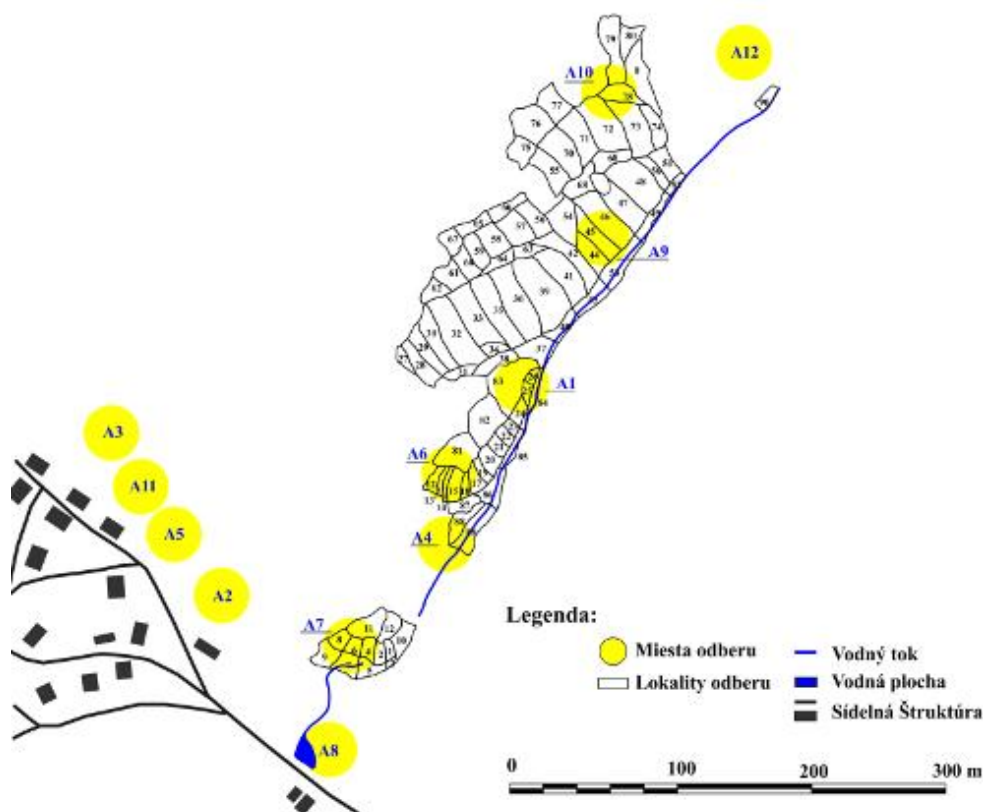
The acidification is significantly influenced by the rock composition of the surrounding terrain and especially the material of dump-fields. The vast majority of rocks in the area of the studied dump-field is created by rocks of a terrigenous crystalline complex of Permian age [8]. Main representations of them are greywackes and arkoses, colourful slate and conglomerates. These rocks have only a minimum neutralizing potential. Carbonates, which may enter the reaction as a neutralizing agent, are represented only by calcite veins, ankerite and rare siderite.

The determination of the risk of acidification is a guide to determine the degree of risk of environmental contamination of the country by heavy metals. The aim of this study is to determine the risk of occurrence of acid mine water (AMD) whose production by the material of mine dumps could lead to a release of ore components into percolating water, an increase of the degree of their bioavailability and thus the acidification and contamination of landscape components by heavy metals.

## 2 METHODOLOGY

From the surface of the dump-field, 90 samples of technogenic sediments numbered 1-89 and 12 samples numbered A-1 through A-12 were taken across the surface in a regular network. Each sample incurred by the homogenization of 8-10 samples among which each have a weight of approximately 2 kg. The sample A-12 represents the reference surface with no mineralization outside the dump-field (Fig. 1). The resulting sample had a mass of about 3 kg. The heavy fraction of the samples was studied by the scanning microscope JEOL JSM-840 at the State Geological Institute Dionysus Stur, Bratislava.

The samples of surface and drainage water (sample V-1 and V-13) were collected in four periods: after rains (in June 2006 – samples identified with the index “a” and in March 2008 – samples identified with the index “c”) and in dry seasons (in February 2007 – samples identified with the index “b”, in May 2008 – samples identified with the index “d”). The surface water samples were collected from the mountain creeks and marshes in the vicinity of mining dumps as well as from the creek flowing through the municipality of Ľubietová. Water sampling sites are indicated in Fig. 2.



**Fig. 1** Location of sampling technogenic sediments and soils from the site Ľubietová - Podlipa.

Active and changeable pH was also determined in surface water of a broader area of the dump-field as well as in drainage water percolating through dump sediments, and was measured in the suspension of 20 g of the sample and 50 ml of distilled water, or 1M KCl, according to the methodology by Van Reeuwijk [22] used for soils using the pH meter EcoScan pH 5/6 by the company EUTECH Instruments. The monitoring points are indicated in Fig. 2.

The measurement of the oxidation-reduction potential (Eh) was carried out by means of the in situ measuring instrument WTW Multi 3420 with the combined redox-electrode SenTix ORP with the reference system Ag/AgCl, containing the 3M KCl electrolyte solution. The Eh reading was converted to the standard hydrogen electrode.

The measurement of pH and Eh of water (Samples V-1 to V-13) was carried out “in situ” directly while taking water samples. The Eh measurement of sediment samples (samples 1 to 90, A1 to A12) was carried out in an aqueous suspension, and the working procedure was as follows:

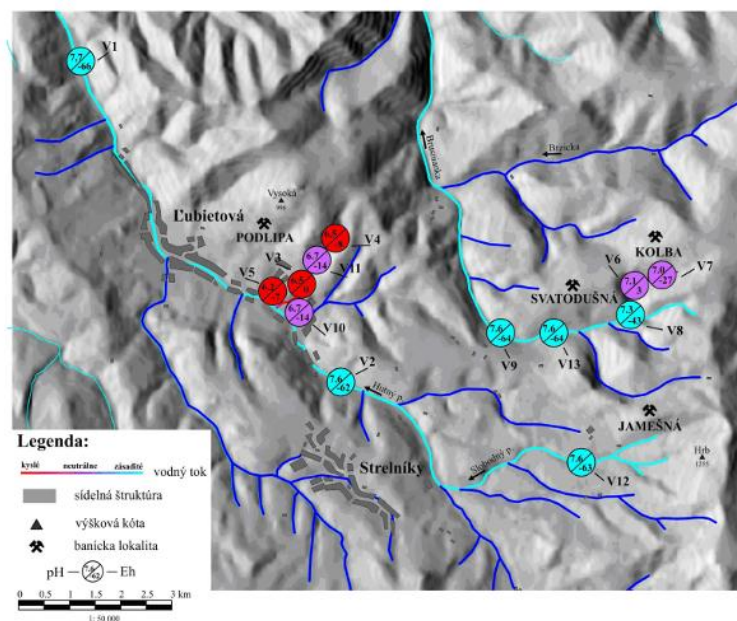
The samples of soils and technogenic sediments were homogenized. A 20g weighed portion of the samples of soil and technogenic sediments was poured with 50 ml of distilled water in a 200ml flask. After 20 min of shaking out, the contents of the flask was poured into a 200ml beaker and while stirring constantly the suspension, pH and Eh were determined.

For the determination of the total acidity (AP) and neutralization potential (NP), it was necessary to know pH and Eh of sediments, contents of sulphur and carbon. For the prediction of acid mine products in mine waste, the U.S. EPA methodology was used: Acid Mine Drainage Prediction EPA530-R-94-036 from 1994, which was applied for the needs of research in the Western Carpathians by Lintnerová and Majerčík [11].

The analysis of total ( $S_{tot}$ ), sulphidic ( $S_s$ ) and sulphate sulphur ( $S_{SO_4}$ ) was performed from a 1g weighed portion of the samples in the Geoecological Laboratories of the Geological Survey, Spišská Nová Ves. Carbon (total carbon –  $C_{tot}$ , organic carbon –  $C_{org}$ , and inorganic carbon –  $C_{inorg}$ ) was determined in the laboratories of the Geological Institute of the Slovak Academy of Sciences with IR-spectroscopy of carbon using the device Ströhlein C-MAT 5500. The values of contents of  $CO_2$  and  $CaCO_3$  were determined by the recalculation from the values of  $C_{tot}$ ,  $C_{org}$ , and  $C_{inorg}$ . The analytical data was processed by the GIS system.

$\Sigma Fe$  and  $Fe^{2+}$  were determined in the Testing Laboratories GEL, Turčianske Teplice by titration.

The samples of surface and drainage water were stabilized with  $10 \text{ ml.l}^{-1} \text{ HNO}_3$  and analyzed in the Water Research Institute, Bratislava.



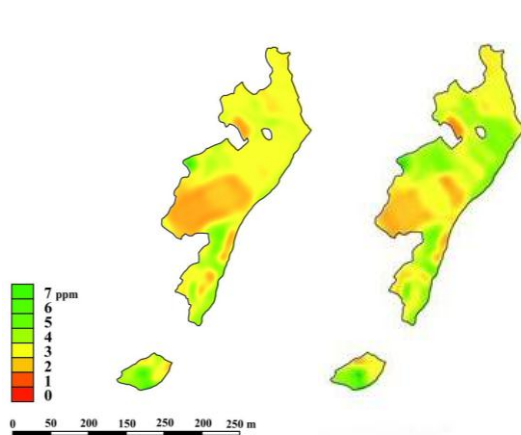
**Fig. 2** Location of monitoring sites of samples of surface and drainage water around Ľubietová indicating measured pH values.

Processing the map image attachments were made using Grass GIS, a modular tool for processing spatial data. Plotting the data was carried out with the `v.surf.rst` module ensuring spatial interpolation of data (regularized spline with tension, RST).

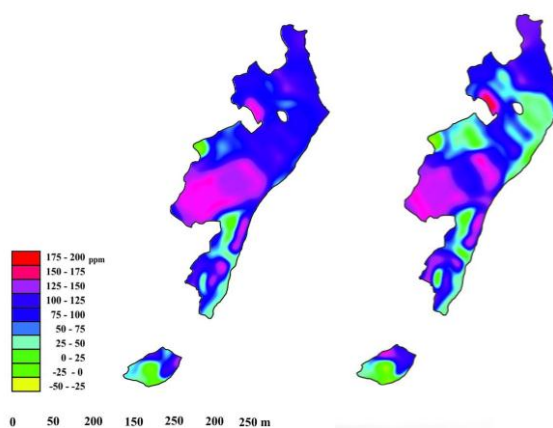
### 3 Results

The active pH value in samples from the dump-field Podlipa (and a reference surface) varies within the range of 3.75 – 6.32 and the changeable pH value from 3.58 to 6.48 (Tab. 1, 3). The average of the active pH value of the reference area is 4.93 and the average of the changeable pH value is 3.47 (Tab. 1). The acidity of the dump-field on the basis of the leachates in distilled water and in the 1M KCl solution is shown in Fig. 3 a, b.

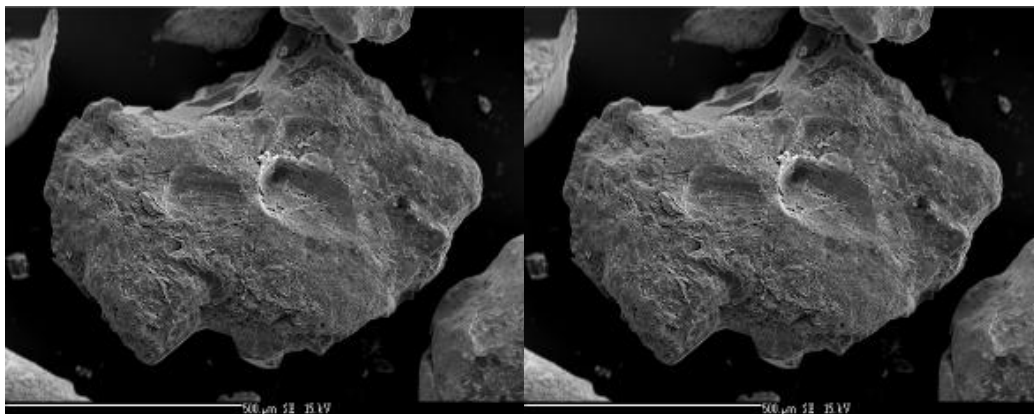
The chemical reactions of soil are as follows: a) acid – pH 4 or less, b) neutral – pH 6.5 to 7.4 and c) alkaline – pH 7.5 and above [7]. Under this classification, the acidic soil reaction was (with minor exceptions) confirmed throughout the entire study area, especially on landfill platforms of terraces (compare Fig. 1; lower acidity of slopes is probably due to a greater leaching of material with rainfall water



**Fig. 3** Acidity of technogenic sediments in the dump-field Podlipa; figures indicate pH values in the a) water leachate, b) 1M KCl leachate.

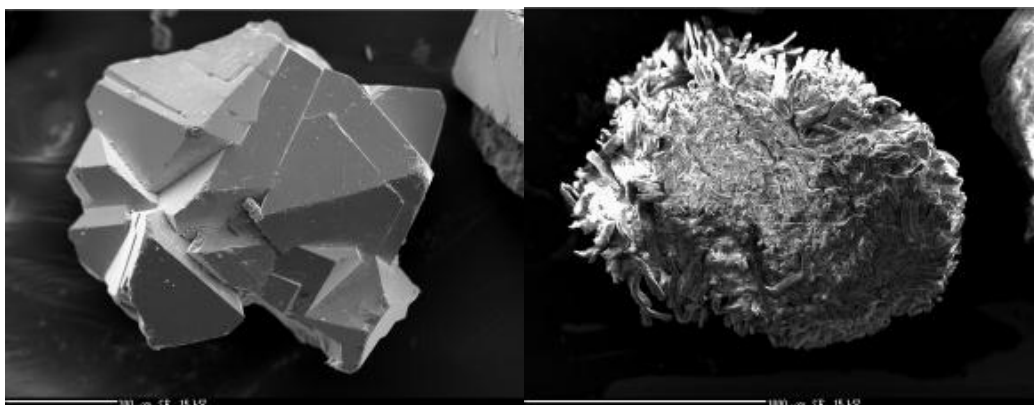


**Fig. 4** Values of Eh of technogenic sediments and soil in the dump-field Podlipa; figures indicate Eh values in the a) water leachate, b) 1M KCl leachate.



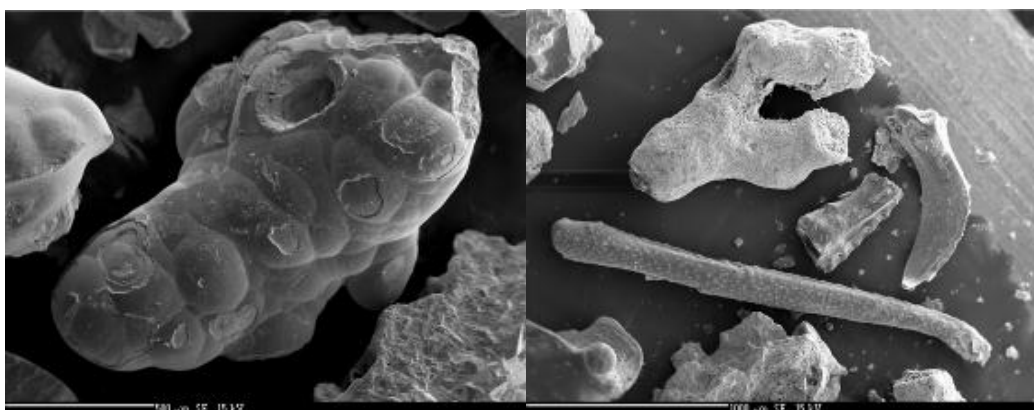
**Fig. 5** Porous pure copper

**Fig. 6** Pyritic pentagon dodekaeder –  $\text{FeS}_2$



**Fig. 7** Aggregate of fused crystals of euchroite -  $\text{Cu}_2(\text{AsO}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}$

**Fig. 8** Aggregate of lepidocrocite –  $\text{FeOOH}$



**Fig. 9** Nodules of malachite

**Fig. 10** Organic remains of animal and plant origin in sediments of landfill material

The oxidation-reduction potential (redox potential - Eh) is a parameter that allows you to define aerobic (oxidation) and anaerobic (reduction) processes in soil. The most important from the factors that determine the conditions for such processes are soil moisture, soil reaction (pH),  $\text{O}_2$  content in the soil air and solution, organic matter content, presence of elements – Fe, Mn, N, S, and activity of micro-organisms [7]. The lower the value Er, the more intense the reduction processes taking place in the soil and vice versa. The values higher than 600 mV indicate soil oxidation processes; the values lower than 200 mV indicate the dominance reduction processes in soil.

The Eh measured value is not stable, it fluctuates at a very small distances and varies depending on the amount of rainfall. The Eh values in the water leachate vary in a wide range from 5 to 156 and in the 1M KCl leachate from 16 to 174 (Tab. 1).

The most oxidizing conditions indicate the measured Eh values (up to 133 mV in the water leachate and 173 mV in the 1M KCl leachate) on the platforms and top parts of the dump-field (Tab. 1; Fig. 4). The highest values of Eh are in the sample from the reference area A-12. The lowest Eh values (-84 in the water leachate and -58 in the 1M KCl leachate) were measured in the waterlogged lower zone of heaps (Tab. 1; Fig. 4).

In the dump material, the following were identified: silicate minerals, oxides, as well as pure metals (Fig. 5), oxidized and non-oxidized sulphide minerals (Fig. 6), arsenates (Fig. 7), hydroxides (Figure 8), secondary sulphides, secondary Cu carbonates (Fig. 9) and residues of organic matter (Fig. 10).

Weathering kinetics of these minerals depends on pH, temperature and mainly on the reaction surface. The weathering of carbonates and certain silicates is able to deliver neutralizing agents to the system, which are able to consume the acid released from the oxidation of sulphides and thus buffer the system to the point so that the resulting pH is close to neutral values [12].

**Tab. 1** Characteristics of samples A-1 to A-12 of technogenic sediments from the dump-field.

Sample	H <sub>2</sub> O		1M KCl		%							
	pH	Eh <sub>(mV)</sub>	pH	Eh <sub>(mV)</sub>	S <sub>tot</sub>	S <sub>SO4</sub>	Ss	C <sub>tot</sub>	C <sub>org</sub>	C <sub>inorg</sub>	CO <sub>2</sub>	CaCO <sub>3</sub>
A-1	5.14	77	4.61	109	0.25	0.10	0.15	0.74	0.20	0.54	1.97	4.48
A-2	5.89	34	5.40	63	0.02	0.01	0.01	0.86	0.38	0.48	1.75	3.99
A-3	4.87	94	4.21	131	0.10	0.03	0.07	0.62	0.34	0.28	1.02	2.32
A-4	5.46	59	5.33	66	0.33	0.13	0.01	0.34	0.26	0.08	0.29	0.66
A-5	5.77	42	5.37	64	0.05	0.01	0.05	0.78	0.35	0.43	1.57	3.57
A-6	5.17	74	5.06	83	0.42	0.15	0.27	0.40	0.27	0.13	0.47	1.08
A-7	7.93	-84	7.34	-58	0.03	0.02	0.01	1.63	0.10	1.53	5.61	12.71
A-8	5.42	36	5.22	42	0.01	0.01	0.01	0.45	0.13	0.32	1.17	2.66
A-9	5.03	83	5.01	85	0.03	0.03	0.01	0.40	0.37	tr.	tr.	tr.
A-10	5.25	71	5.14	78	0.04	0.02	0.02	0.48	0.46	tr.	tr.	tr.
A-11	6.11	22	5.95	30	0.11	0.04	0.07	4.31	4.18	0.13	0.47	1.08
A-12	4.21	133	3.47	173	0.02	0.01	0.02	4.05	4.03	tr.	tr.	tr.

It is interesting that the lowest pH value was measured in the area of the reference surface – sample A12. This is probably due to the fact that despite the absence of sulphides there are no carbonates there; inorganic carbon contents (C<sub>inorg</sub>) are below the limit of quantification (Tab. 1). The highest contents of carbon within the dump-field were found in the sample A-7 (C<sub>tot</sub> 1.63 %, recalculated to CaCO<sub>3</sub> up to 12.71 %; Tab. 1), where also the highest pH<sub>H2O</sub> value of 7.93 was recorded.

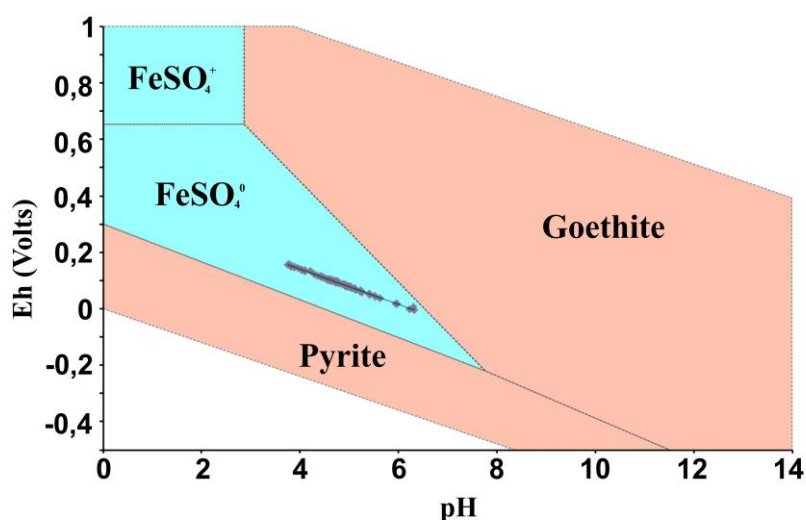
**Tab. 2** Calculation of reliability of the value R<sup>2</sup>.

	Measurement		Calculation	
	H <sub>2</sub> O	1M KCl	H <sub>2</sub> O	1M KCl
R <sup>2</sup>	0.9968	0.9992	0.9945	0.9959

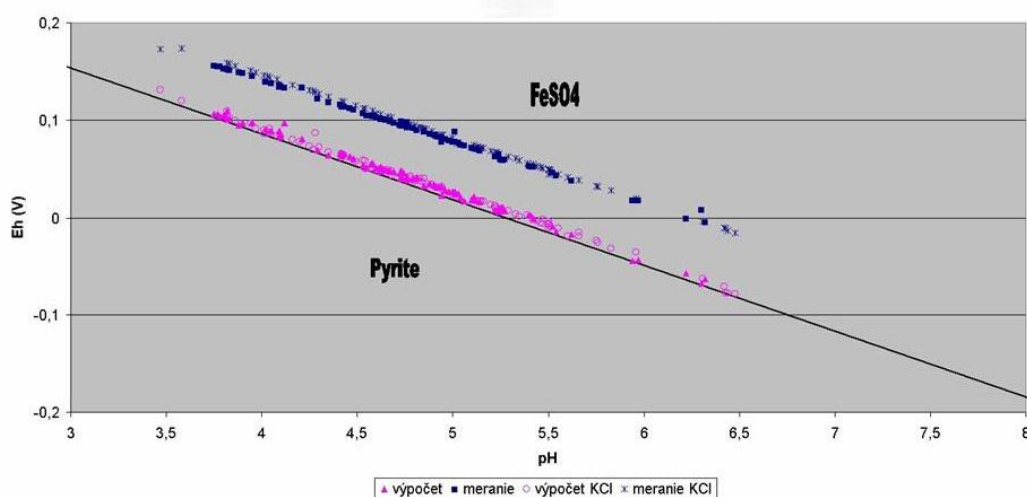
The pH-Eh diagrams of the stability of compounds with the contents of Fe in the system Fe<sup>3+</sup> – SO<sub>4</sub><sup>2-</sup> – H<sub>2</sub>O in Figs. 11 and 12 show the form of occurrence of Fe in the dump material from the Podlipa and Reiner deposits. The diagram

shows a strong correlation between pH and Eh. High values of  $R^2$  reliability equations (Tab. 2, Fig. 11) show a very accurate determination, especially the determination of pH and Eh in an leachate.

The activity diagram of the components in the system  $\text{Fe}^{3+} - \text{SO}_4^{2-} - \text{H}_2\text{O}$  describes the stability of solid phase for active and changeable pH values. Based on in situ measurements of physico-chemical parameters (pH and Eh) and by calculating Eh [18, 19] it was found out that the main form of iron occurrence in sediments and soils of the dump-fields Podlipa and Reiner is the sulphate form –  $\text{FeSO}_4$  (Fig.12). This data is inconsistent with the data indicating that a high incidence of sulphide sulphur was confirmed in the material of dump-fields [5]. This discrepancy can be explained by the fact that Fe occurs in sulphide form only in fresh rock fragments that do not enter the reaction during the measurement of pH and Eh due to the time factor (60 minutes). The possibility of Fe occurrence also in sulphide form is indicated by the calculated values of  $R^2$  which are unlike those obtained by in situ measurements of pH and Eh at the boundary of stability of fields  $\text{FeSO}_4$  and  $\text{FeS}_2$  (Fig. 12).



**Fig. 11** Activity diagram of components in the system  $\text{Fe}^{3+} - \text{SO}_4^{2-} - \text{H}_2\text{O}$ , describing the stability of solid phases of activities  $[\text{Fe}^{3+}] = 1.9136\text{e-}02$  and  $[\text{SO}_4^{2-}] = 2.5259\text{e-}02$  [6] for samples of technogenic sediments from the dump-fields in Ľubietová.



**Fig. 12** Activity diagram of components in the system  $\text{Fe}^{3+} - \text{SO}_4^{2-} - \text{H}_2\text{O}$ , for active pH ( $\text{pH}_{\text{H}_2\text{O}}$ ) and for changeable pH ( $\text{pH}_{\text{KCl}}$ ) of the samples of the dump material from Podlipa and Reiner.

The pH value of surface water around the village of Ľubietová approaches usually neutral values. Nevertheless there are some differences. Even though both surface water flows and mine water in the area of the Svätodušná dump-field show probably slightly alkaline reaction due to the different lithology (especially the higher contents of dolomite in the rock complex), but also due to the different composition of the primary ores (e.g., a lower representation of pyrite),

surface and drainage waters from the Podlipa area are slightly acidic in nature (Tab. 3, Fig. 2), primarily resulting from weathering of ore minerals (mainly pyrite, but also chalcopyrite) in dump sediments and soils. This characteristic was also confirmed by multiple measurements: the data collected during the dry season and the rainy season differs substantially rarely only.

**Tab. 3** Values of pH and Eh in samples of surface and mining water.

Sample	pH	Eh (mV)	Sample	pH	Eh (mV)
V-1a	7.7	-69	V-7a	7.0	-27
V-1c	7.7	-66	V-7b	7.1	-29
V-2a	7.6	-62	V-8a	7.7	-66
V-3a	6.7	-12	V-8b	7.3	-43
V-3b	6.2	14	V-9a	7.6	-64
V-3c	6.5	0	V-9a	7.7	-67
V-4a	6.5	-6	V-10a	6.7	-14
V-4b	7.5	-58	V-10b	6.2	14
V-4c	6.54	-8	V-11b	6.7	-14
V-5a	6.2	-11	V-11c	6.9	-21
V5b	6.1	-8	V-12a	7.6	-63
V-6a	6.4	1	V-13a	7.6	-64
V-6d	7.1	3	V-13b	7.4	-60

To determine the risk of acidity, the set of samples A-1 to A-12 is used, which represents the entire dump-field. The pH value in sediments and soil of these samples set out in the leachate by distilled water varies between 4.21 and 7.93 (Tab. 1). Sulphide sulphur is in most samples in a higher amount than sulphur sulphate, indicating a relatively high content of not yet oxidised primary sulphides.

**Tab. 4** Values of total created acidity (AP), neutralization potential (NP) and net neutralization potential (NNP).

Sample	AP	NP	NNP
A-1	7.81	44.8	37.0
A-2	0.62	39.9	39.3
A-3	3.12	23.2	20.1
A-4	10.31	6.6	-3.7
A-5	1.56	35.7	34.1
A-6	13.12	10.8	-2.3
A-7	0.93	127.1	126.2
A-8	0.31	26.6	26.3
A-9	0.93	0	-0.9
A-10	1.25	0	-1.3
A-11	3.43	10.8	7.4
A-12	0.62	0	0.6
Average	3.7	27.1	23.5

The total acidity formation (AP) corresponds to the amount of acid that can potentially be produced by the dump material. At the Podlipa site, AP ranges from 0.3125 to 13.125 (at average 3.7, Tab. 4). The value of neutralization potential (NP) indicating the content of neutralizing substances in a dumping site, capable to neutralize the acidity produced by the dump material is different in each section of the dumping site (0 to 127.1,  $\bar{x} = 27.1$ ; Tab. 3) and in the



negative correlation to the AP. A high NP (127.1) is only in the sample A-7 (Tab. 4), in which the highest content of  $C_{tot}$  (which after recalculation corresponds to  $12.71 \text{ kg.t}^{-1}$  of  $\text{CaCO}_3$ ; Tab. 1) was determined.

The net neutralization potential (NNP) corresponds to the amount of a neutralizing substance that must be added to neutralize the acidity produced by the dumping site ( $\text{NNP} = \text{NP} - \text{AP}$ ). The NNP values in the dump-field Podlipa (Tab. 2) show that the neutralization of mine tailings requires as much neutralizing agent as it corresponds, on an average, to  $23.5 \text{ kg of CaCO}_3$  per 1 ton of the dump material. The best NNP value shows the risk of the occurrence of acid mine water (AMD). If the value is close to 1, the risk of the AMD formation is high. Where the ratio is equal to or greater than 3, the risk of formation of AMD is negligible [20] (Sobek et al. 1978). The average value of the NNP at the Podlipa dump-field is 23.5 (if we exclude the extreme value of 126.08, the average value will change to 14.62; Tab. 4), so the risk of the AMD formation can be ruled out.

#### 4 DISCUSSION

Spatial distribution of heavy metals in the dump-field is a reflection of their geochemical properties: content, solubility, acidity (migration potential) and sorption properties. Lack of carbonates (as the primary natural neutralizing agent) causes that in 5 from 12 samples (A-1 to A-12), corresponding to average samples from 12 parts of the dump-field, the NPP values are negative (neutralizing agents are missing at all), and only two values (from the samples A-3 and A-11) are very low (7.4 and 20.1). Unlike Sobek et al. [20], who states that if the NNP values are greater than 3, the risk of AMD formation is negligible in terms of the US EPA methodology [13], the NNP values from -20 to 20 (kg of  $\text{CaCO}_3.\text{t}^{-1}$  of the dump material) in terms of the potential formation of acidic substances classified as a „*range of uncertainty*“ as it is impossible to make it clear whether or not the formation of AMD occur. The pH value in leachates in distilled water usually fluctuates around 5.3.  $\text{pH} < 5$  which indicates that the sample contains potential acidity, while the values measured in carbonates generally oscillate between 8 – 10. The values above 10 can be considered to be alkaline ones [20].

#### 5 CONCLUSIONS

The ongoing process of oxidation of primary sulphide minerals at the deposit is indicated by coatings of secondary copper minerals (carbonates and oxides) and confirmed by the observed values of pH and Eh in leachates from technogenic sediments. The dump material still shows a considerable amount of mobilized metals and a certain potential to generate acidity. As a result, the surface water in the area of the dump-field Podlipa is slightly acidic, while the water from the nearby dump-field Svätodušná shows a slightly alkaline character due to the presence of carbonates (calcite, ankerite and siderite).

The dump material still shows a considerable amount of mobilized metals and a certain potential to generate acidity.

Although a relatively high level of total sulphide sulphur in technogenic sediments indicates a considerable content yet unoxidised primary sulphides, the overall result of the study of acidity formation suggests that the formation of AMD is not likely to occur in the future.

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## RESUMÉ

V článku sú prezentované výsledky meraní základných fyzikálno-chemických parametrov – pH a Eh v technogénnych sedimentoch a v povrchovej a drenážnej vode haldového poľa opusteného Cu-ložiska Ľubietová – Podlipa. Výsledky výpočtu rizika potvrdily, že acidit okolí zkúmané plochy závisí predovšetkým od geochemického správania sa (zvetrávania) niektorých minerálov (hlavne pyritu), a že haldový materiál stále vykazuje značné množstvo mobilizovateľných kovov a teda aj istý potenciál tvoriť kyslosť, ale ďalej výsledky poukazujú, že k masívnejšej tvorbe AMD nebude v budúcnosti pravdepodobne dochádzať.