

## Environmental Hazards Associated with Heavy Metals at Ľubietová Cu-deposit (Slovakia)

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This article reports the results of our studies about environmental hazards which are connected to presence of heavy metals at Ľubietová Cu deposit (Slovakia), whose distribution depends on geochemical behaviour of the elements. The heavy metal contamination of soils and technogenous sediments shows an irregular spatial distribution at the dump-field.

The study of heavy metal content in surface water, drainage water and groundwater was carried out both during dry and during rainy periods. Surface water, as well as groundwater, is mainly contaminated by Fe, Cu and As. The health risk is mainly posed by the mineral water Linhart because of its radioactivity and its high Fe, Cu, Cd and Pb contents. Speciation of As and Sb in the country components (soil, sediments, water, plants) showed that there are present both As<sup>3+</sup>, Sb<sup>3+</sup> as well as the less toxic As<sup>5+</sup> and Sb<sup>5+</sup> species. Our studies also concerned plant tissues degradation in heavy metal contaminated conditions.

Calculation of the average value of Total Acidity Production (TAP) and of the average value of Neutralization Potential (NP) is also discussed. Results from this calculation suggest that the potential of the acid mine drainage water formation is limited. Free sorption capacity of natural sorbents (clay minerals and hydrogoethite) for some heavy metals was also proved. The attitude of the water to precipitate cementation copper on the iron surface makes possible to realize a Fe<sup>0</sup>-barrier for elimination of heavy metals.

### 1. Introduction

Located in the north-eastern side of Slovenské Stredohorie Mts. and exploited since the Bronze Age, Ľubietová deposit was one of the most important Cu-mines in Europe in the XV and XVI centuries.

Hydrothermal Cu (Ag) mineralization at Ľubietová ore-field is developed within a 4–5 km long and 1.5 km wide range, with a N-S direction, and it is formed as a part of quartz-sulfides carbonate vein mineralization at three abandoned deposits: Podlipa, Svätodušná and Kolba (with admixture of Co/Ni-mineralization). The main dump-field, Podlipa (Figure 1), covers an area of about 2 km<sup>2</sup> and it was exploited by 18 galleries with a vertical section of 130 m. Its ore mineralization is located in a terrigene crystalline complex of Permian age, consisting of greywackes, arkoses, schists and conglomerates. A scattered mineralization was also described in the southern low Cretaceous rocks.

Paragenesis of the vein mineralization is represented by quartz, siderite, chalcopyrite, Ag-bearing tetrahedrite, arsenopyrite, pyrite, barite and rare galena. In the well developed cementation zone, the main Cu-minerals were cuprite and native copper. Podlipa area is also known for some very rare secondary minerals such as libethenite and mrázekite. At dumps, malachite and pseudomalachite are the most common minerals.

Weathering processes of reactive minerals in surrounding and mainly acid rocks mobilize heavy metals and toxic elements (e.g. Cu, As) from primary minerals and then form secondary minerals (mainly Fe hydroxides, Cu-oxides and carbonates), causing contamination of technogenous sediments, soils and surface water, drainage water as well as groundwater (Younger et al., 2002).

Knowing migration and bioavailability of toxic elements is basic in order to plan an efficient remediation. The possibility to install a  $Fe^0$  permeable reactive barrier, in order to decontaminate groundwater and surface water of heavy metals, was planned after characterizing pollutants (by realizing a detailed mapping of contamination), groundwater flow regime and sub-surface geology. A trench, downstream from the area to be cleaned up, will be filled with a reactive material, able to degrade pollutants to not toxic or to less toxic substances. Natural gradient of groundwater flow path, which allows the barrier to work, will cause polluted water to pass through the barrier itself, where occurring redox reactions will reduce concentration of some pollutants. The possibility to install anaerobic and aerobic wetlands upstream from the barrier is also going to be considered. Developed during last years for elimination of chlorinated solvents (the first example in Italy is dated from 2004–2005), nowadays  $Fe^0$ -barriers also represent an effective remediation technique for groundwater decontamination of inorganic compounds.

The aim of this paper consists in reporting results of our studies about contamination of soil, technogenous sediments, groundwater, surface water and plants by heavy metals and present the results of the As and Sb toxicity study based on speciation of mentioned toxic elements, as well as the risk of acid mine drainage water

formation. The article presents also some proposals of country remediation procedures.

## 2. Materials and methods

Technogenous sediments from the dumps, soil samples (about 10 kg in weight) from 15–20 cm in depth (with a sampling step of 25 m<sup>2</sup>) and surface water (stream water, drainage water, and groundwater) were collected in order to characterize components of landscape contamination. 10 mL of HCl were added to each water sample of 1.000 mL in volume. A reference site was selected by comparing territories loaded by heavy metals and the surrounding, not contaminated, natural environment. Located outside of the geochemical anomalies of heavy metals, the reference site is represented by Permian greywakes, similar to material at the dump-field. Plant samples were also collected from the contaminated dumps.

Samples of technogenous sediments from dumps and soils were dried and 0.25 g of sample was heated in  $HNO_3$ - $HClO_4$ -HF to fuming and

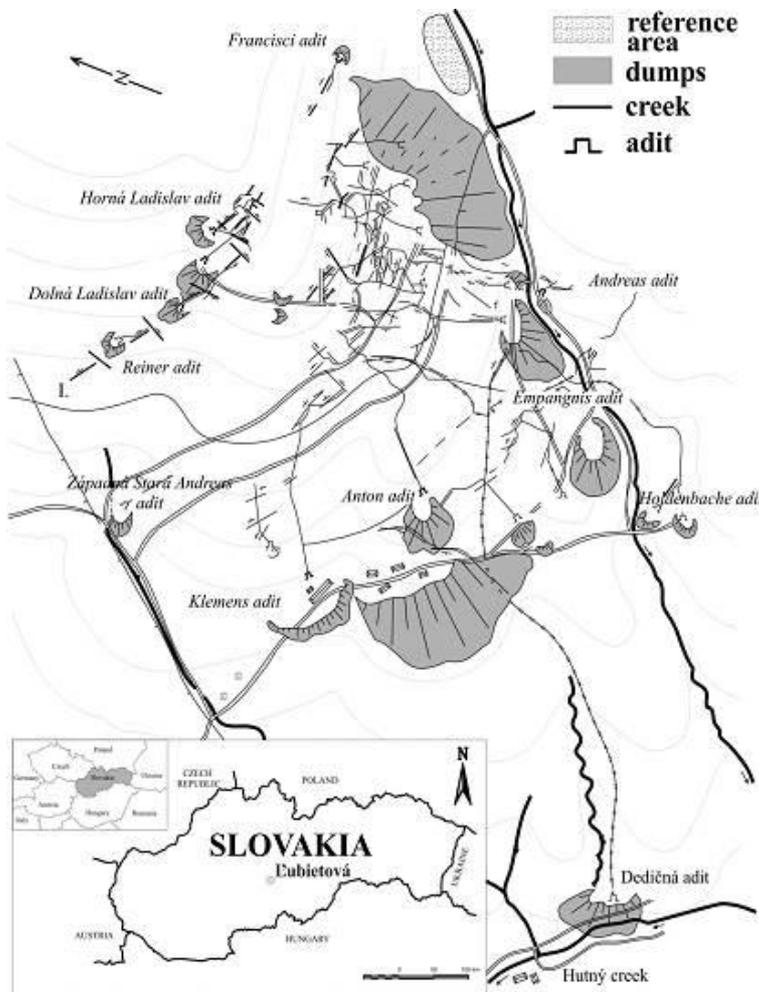


Figure 1: The map of Podlipa area

taken to dryness. The residue was then dissolved in HCl. Solutions were analyzed by ICP-MS at the ACME Analytical Laboratories (Vancouver, Canada).

Minerals in the clay fractions were prepared according to Šucha et al. method (1991) and determined by x-ray diffraction in the laboratories of the Geological Institute of the Slovak Academy of Sciences using X-ray diffractograph PW 1710 Philips. In clay mineral samples were heavy metals analyzed by ICP-MS, then macerated 14 days in natural drainage water of the studied locality containing heavy metals and then analyzed for heavy metals content again. pH of sediments was determined from suspension both with distilled water and 1M KCl after 3 h of maceration.

Sulphur, total carbon, organic and inorganic carbon content in the sediments was IR analyzed by using furnace Ströhlein C-MAT 4000 at the laboratories of the Geological Institute of Slovak Academy of Sciences. A static test for Total Acid Potential (TAP) was realized according to Morin and Hutt (1997) and Sobek et al. (1978).

Water samples were analyzed by Atomic absorption spectrophotometry (AAS) at the National Water Reference Laboratory for Slovakia (Water Research Institute, Bratislava). Speciation for As was performed on the basis of different reaction rates of  $As^{3+}$  and  $As^{5+}$  using Eh-pH stability plots of As-H<sub>2</sub>O-S from Ryu et al. (2002) and Ferguson and Gavis (1972). Speciation for Sb was performed by stability diagrams elaborated by Vink (1966). The experimental study on Cu precipitation on surface of iron chips (testing of a Fe<sup>0</sup>-barrier) mixed with dolomite (ratio 9/1), in order to capture Fe released during cementation process, was realized at the laboratory of Comenius University in Bratislava by Dr. B. Lalinská according to Bartzas et al. (2006) in columns. In order to verify the reactive mean, a laboratory solution was prepared, by using the compounds Fe(NO<sub>3</sub>)<sub>3</sub> · 9 H<sub>2</sub>O, ZnCl<sub>2</sub>, CuCl<sub>2</sub> · 2 H<sub>2</sub>O, H<sub>3</sub>AsO<sub>4</sub>, 3 CdSO<sub>4</sub> · 8 H<sub>2</sub>O and pH was ruled by titrating with NaOH to 6.3.

A selection of plant was performed in order to allow a comparison identical species between polluted places and the reference site. At every site, ten samples of hardwood species (*Betula pendula*, *Quercus petraea*, *Salix fragilis*), coniferous species (*Pinus sylvestris*, *Abies alba*, *Picea abies*) and herbs (*Juncus articulatus*, *Mentha longifolia*, *Acetosella vulgaris*) were sampled in order to get average samples. Five coniferous individuals of approximately same age were sampled for branches (in case of *Picea abies* also needles) from the fourth or fifth spike, with around the same segment length (10–15 cm). About *Pinus sylvestris*, two years old needles were analyzed. Roots of the same length and with 2–3 cm diameter were obtained from the surface soil level. A similar sampling was used for hardwood species: 3–4 y old branches were sampled from the lower limbs. Samples were dried at laboratory temperature and then homogenized.

### 3. Results and discussion

Heavy metal contamination of technogenous sediments from the dump-field is influenced by hydrothermal Cu-mineralization. The heavy metal distribution in technogenous sediments of the dump-fields is variable reflect the primary concentration in separate parts of the dump-fields as well as their geochemical relations, first place their migration ability. The main pollutants are Cu (up to 20.360, Figure 2), Fe (up to 2.58 %), As (up to 457 mg.kg<sup>-1</sup>, Figure 2), Sb (up to 79.3 mg.kg<sup>-1</sup>) and Zn (up to 80 mg.kg<sup>-1</sup>) and we also find U (up to 10 mg.kg<sup>-1</sup>) and Th (up to

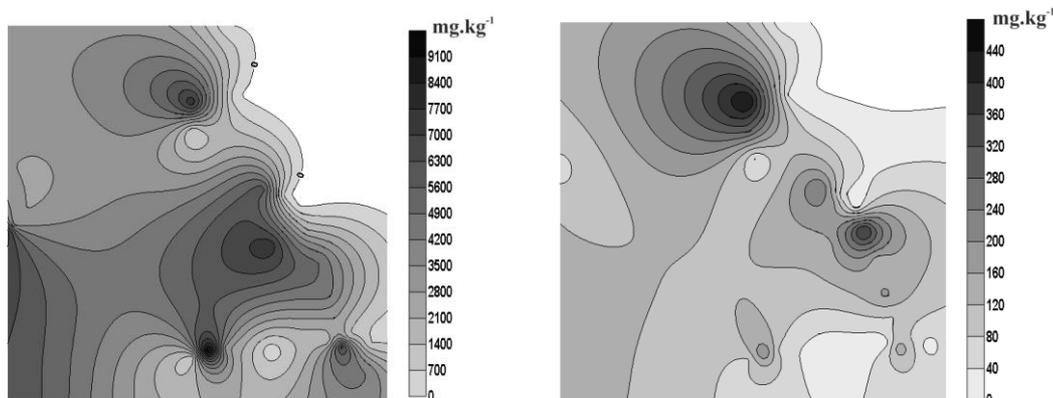


Figure 2: Map of Cu (left) and As (right) distribution in soil and technogenous sediments at Podlipa

35 mg.kg<sup>-1</sup>) from Permian rocks. Distribution of heavy metal contamination depends on ore minerals content in sediments as well as on geochemical features of individual metals (solubility, formation of secondary minerals, migration, sorption etc.).

Knowing Total Acid Production (TAP) of the dump-field is important in order to evaluate the possibilities for a remediation. TAP was calculated according to Morin and Hutt (1997):

$$\text{TAP} = (\% \text{ Stot}) \cdot 31.25 \quad (1)$$

where TAP is provided in any of three equivalent units: kg CaCO<sub>3</sub>, equivalent/metric tone (t) of sample, t CaCO<sub>3</sub> equivalent/1000 t of sample and S<sub>tot</sub> is the total carbon content. TAP values from the dump-field Podlipa range between 0.625 and 10.31 (average 3.7).

In order to define the risk of the acidity production, it is also necessary to know the neutralization potential (NP), which defines the content of the neutralization matter in the dump-field which is able to neutralize the dump produced acidity. NP values within the individual parts of the Podlipa dump-field range between 0.66 and 127.1 kg·t<sup>-1</sup> (average 27.1 kg·t<sup>-1</sup> CaCO<sub>3</sub>). Values of Net Neutralization Potential (NNP) expressed as: NNP=NP – TAP show a very limited potential of the acid mine drainage water formation (NNP=1.42), thus environmental risk is negligible (sensu Sobek et al., 1978).

The study of the most important possible natural sorbents at the studied locality (clay minerals and hydrogoethite) was carried out in order to secure efficient landscape remediation. XRD analysis of clay fraction showed that it consists of illite and muscovite mixture (the dominant clay minerals), of kaolinite, and minerals of smectite and chlorite group. The present study showed that the best sorbent is the hydrogoethite but its occurrence at the dump-field is very limited. In most cases, clay minerals also show good sorption features. These minerals form at the site the natural geochemical barrier which enables precipitation of heavy metals and their fixation on clay minerals surface. Active carbon is also an effective absorbent of heavy metals, especially Fe, Cu, Al (Petriláková and Bálintová, 2011).

Surface water in the creek draining the valley along the dump-field is gradually contaminated by heavy metals leaching from technogenous sediments of mining dumps. Drainage water contains relatively high Cu (up to 2.060 µg·L<sup>-1</sup>), Fe (up to 584 µg·L<sup>-1</sup>), Zn (up to 35 µg·L<sup>-1</sup>) and sometimes also Co (up to 10 µg·L<sup>-1</sup>) and Pb (up to 5 µg·L<sup>-1</sup>) concentrations. The highest As concentration is 6.11 µg·L<sup>-1</sup>.

Heavy metal content in waters is in most cases higher during dry periods than during rainy periods (Figure 3). Presence of *Acidobacteria* or of sulphate reducing bacteria was not proved. Both surface acidity and groundwater acidity are close to neutral pH (6.4–7.6).

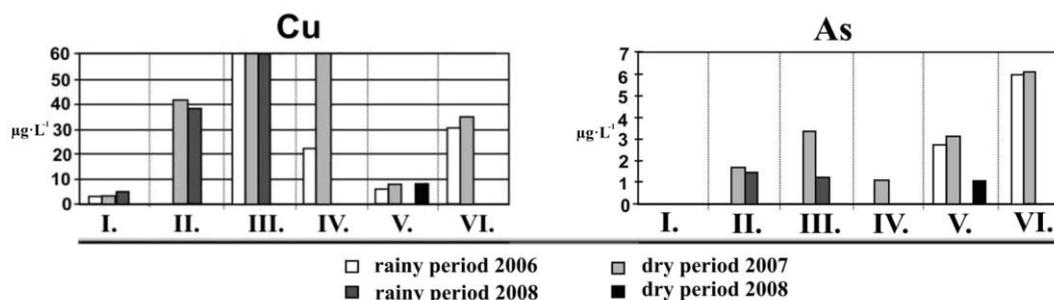


Figure 3: Cu content in surface water during dry and rainy seasons in 6 selected samples

Groundwater analyses showed that the most polluted mineral water comes from the spring Linhart: its total radioactivity is 6.498 Bq·L<sup>-1</sup> and its Fe (380 µg·L<sup>-1</sup>), Cu (181 µg·L<sup>-1</sup>), Pb (1 µg·L<sup>-1</sup>) and Cd (82.0 µg·L<sup>-1</sup>) exceed Government Regulations No. 296/2010, No. 354/2006 Coll.

Speciation of As and Sb using pH-Eh diagrams according to Pokrovski et al. (2002) and Vink (1996) showed that both As<sup>3+</sup> and Sb<sup>3+</sup>, and the less toxic As<sup>5+</sup> and Sb<sup>5+</sup> species, are present. As<sup>5+</sup> and Sb<sup>5+</sup> species prevail in sediments whereas As<sup>3+</sup> and Sb<sup>3+</sup> forms are dominant in the water. Arsenic is mainly present in waters as H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, HAsO<sub>4</sub><sup>2-</sup> and HAsO<sub>2</sub><sup>0</sup> forms (Greenwood and Earnshaw, 1990), whereas As<sup>3+</sup> is much more mobile than As<sup>5+</sup> (Manning and Goldberg, 1997) in weathering oxidation zone. High As content in

the water, at the studied locality, is controlled by tetrahedrite and arsenopyrite decomposition and by As sorption on amorphous Fe-oxides and hydroxides, on clay minerals and hydrogoethite (Andráš et al., 2009).

Speciation for Sb showed that part of the anthropogenic sediment samples and soils fall into the stability field of  $\text{SbO}_3^-$  water solution, the second part in senarmontite stability field. In underground water, Sb is mainly present as  $\text{Sb}_4\text{O}_6$ . Only in one single sample we could find Sb in the form of elementary  $\text{Sb}^0$  and Eh as well as pH values of one sample are at plot on the border between water solution and stibnite –  $\text{Sb}_2\text{S}_3$ . Also in surface water the dominant form of antimony is  $\text{Sb}_4\text{O}_6$ . Forms  $\text{SbO}_3^-$  and elementary  $\text{Sb}^0$  are very rare.

The experimental study concerning Cu precipitation on surface of Iron particles proved that, though cementation process is not fast, it causes a gradual displacement of  $\text{Fe}^{2+}$  ions and precipitation of  $\text{Cu}^{2+}$  ions on the surface of iron, both in form of Cu-oxides, Cu-carbonates and in form of native copper.

The attitude of the drainage water to precipitate cementation copper on the iron surface makes possible to realize a  $\text{Fe}^0$ -barrier for elimination of heavy metals from drainage water and groundwater. Laboratory tests showed the efficacy of the reactive material (mixture of Fe chips and dolomite, ended to capture Fe released during cementation process) in water decontamination from As (99.97 %), Cu (98.98 %), Zn (98.13 %), Cd (99.64 %). Because Fe starting content had been increased, we can hypothesize a significant reduction.

The experiment allowed to test the efficacy of the reactive material in order to decontaminate water from some **potentially toxic elements (Cu, As, Sb, Zn, Cd e Fe), and it was realized at an efficient way as far as As (99.97 %), Cu (98.98 %), Zn (98.13 %), Cd (99.64 %)** adsorptions are concerned.

The study of plant contamination by heavy metals showed that plants from the different zones of the studied area show a different level in contamination of individual tissues. The intensity of plant contamination by heavy metals is up to plant species concentrations of heavy metals, which in plant tissues decrease at the following rate: Fe, Zn, Pb and Cu. The study showed the highest Fe, Pb, As, Sb and Zn concentrations in roots. The important role of roots system in environmental protection also confirmed Tomaškin (2007). Cu mainly contaminates leaves and needles, causing formation of dead stains on lower leaves at stem, purple and violet stem coloring (*Acetosella vulgaris*), roots atrophy and leaf chlorosis with green veins. Fe contamination causes atrophy of plant tops and root coarsening. Zn causes leaf chlorosis with green veins (*Picea abies*, *Betula pendula*), dead stains on leaf-tips (*Acetosella vulgaris*) and rudimental root systems (*Picea abies*). Ni and Co cause formation of white stains (*Salix fragilis*). The highest Cd contents are in roots, lower in leaves and in stems and fruits, and they cause leaf chlorosis, root darkening (*Quercus petraea*), formation of violet-brown stains on leaves (*Acetosella vulgaris*), irregular growth of leaves and roots, cell extent and stagnation of cell division. The lowest Cd contents are in seeds.

Year shoots in live branches of *Betula pendula* (Figure 4) and *Pinus sylvestris* (Figure 5) from the dump-field are narrow (10/100  $\mu\text{m}$  vs. 2000  $\mu\text{m}$  wide year shoots from the reference area).

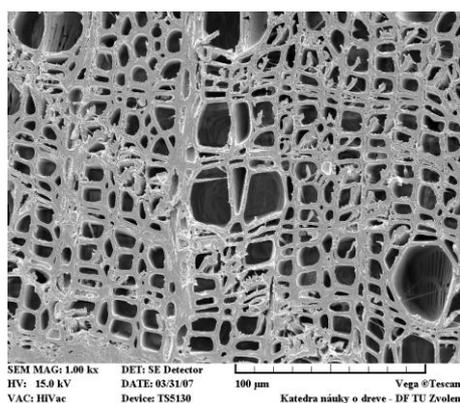


Figure 4: *Betula pendula*: formation of extraordinary tight current year shoots (SEM image)

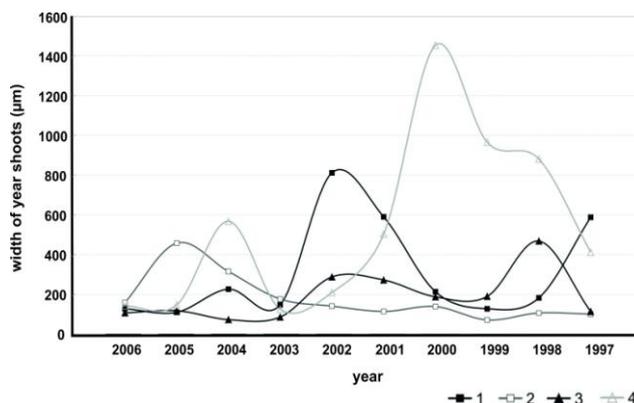


Figure 5: Comparison of the current year shoots in analyzed samples of *Pinus sylvestris* from the dump-field (1–living twig, 2–dead twig) and reference site (3–living twig, 4–dead twig)

#### 4. Conclusions

The study showed variable spatial distribution of contamination in sediments due to selected heavy metals. Surface water (and drainage water), as well as groundwater, are substantially polluted above all by Cu, Fe and As. In the sediments, the less toxic  $\text{As}^{5+}$  and  $\text{Sb}^{5+}$  species are prevailing whereas in the water are dominant the more toxic  $\text{As}^{3+}$  and  $\text{Sb}^{3+}$  forms. The attitude of the water to precipitate cementation copper on the iron surface makes possible to realize a  $\text{Fe}^0$ -barrier for elimination of heavy metals (Cu, As, Zn, Cd). Mixture of iron with dolomite enabled removal of Fe released to solution. The present natural sorbents are predominantly the clay minerals (illite, muscovite, caolinite, smectite) and hydrogoethite. The clay minerals and hydrogoethite are good sorbents of heavy metals. In the case of the Fe, As, Sb, Ag, Pb, Zn, Mn, Mo, Bi, U was proved also the free sorption capacity. The average pH of sediments measured both in distilled  $\text{H}_2\text{O}$  and 1M KCl is 5.3. Calculation of the average value of Total Acidity Production (TAP) is 3.7 and of the average value of Neutralization Potential (NP) is  $27.1 \text{ kg.t}^{-1} \text{ CaCO}_3$ . Results from this calculation suggest that the potential of the acid mine drainage water formation is limited. The Net Neutralization Potential ( $\text{NNP} = \text{NP} - \text{TAP}$ ) value 1.42 indicates negligible environmental risk. Concentrations of the heavy metals in plant tissues decrease at the following rate: Fe, Zn, Pb and Cu. Comparison of individual types of plant tissues show that the highest concentrations of heavy metals are in roots, than in leaves and stems and the lowest concentrations are in flowers, seeds and in fruits.

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