

INVESTIGATION OF THE POSSIBILITY FOR EXTRACTING IONS POSSESSING A CORROSIVE ACTION ON CONSTRUCTION MATERIALS BY WASHING SOLID INCLUSIONS IN A CLAYEY OVERBURDEN

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ABSTRACT. Considerable amounts of solid phase material of different composition and physical and -mechanical properties are disposed of during the coal extraction. In fulfilling the tasks of the circular economy, some of this material, after proper washing, could be utilised in road construction. This paper presents the results from measurement of integral parameters and from chemical composition analysis of the waters, formed as a result of laboratory experiments by simulated rain leaching and by washing of solid inclusions in clayey overburden from mining activities in Maritsa East Mines Ltd. Based on the results obtained, the following issues are discussed: the possible impact on the environment in case of the material leaching by normal and acid rain; the possibility of extraction in the liquid phase of ions, possessing a corrosive action towards construction materials, at contact of raw and washed materials with water; the possibility for washing water re-use.

Keywords: solid inclusions in coal mine overburden, acid rain impact, washing water recycling, carbonates' leaching

ИЗСЛЕДВАНЕ НА ВЪЗМОЖНОСТТА ЗА ИЗВЛИЧАНЕ НА ЙОНИ, ПРИТЕЖАВАЩИ КОРОЗИОННО-АГРЕСИВНО ДЕЙСТВИЕ СПРЯМО СТРОИТЕЛНИ МАТЕРИАЛИ, ПРИ ПРОМИВАНЕ НА ТВЪРДИ ВКЛЮЧЕНИЯ В ГЛИНЕСТА ОТКРИВКА

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РЕЗЮМЕ. При добива на въглища по открит способ се депонират значителни количества твърдофазен материал с различен състав и физико-механични свойства. В изпълнение на задачите на кръговата икономика, част от този материал, след съответно промиване, би могла да се оползотвори в пътното строителство. Настоящата работа представя данни от определяне на интегрални показатели и на химичен състав на водите, формирани в резултат на лабораторни експерименти за моделно излужване от валежи и по промиване на различни твърди включения в глинеста откритка от въгледобива в мини "Марица-изток" ЕАД. На базата на получените резултати са дискутирани: възможното въздействие върху околната среда при евентуално излужване на материала от нормални и кисели валежи; възможността за извличане във водата на йони, притежаващи корозионно-агресивно действие спрямо строителни материали, от непромити и промити твърди включения при контакта им с вода; възможността за обратно използване на промивната вода.

Ключови думи: твърди включения в откритка на въглищни мини, въздействие на киселинен дъжд, рециклиране на промивни води, излужване на карбонати

Introduction

Opencast mining releases huge amount of mining wastes to the land surface as overburden dump materials. Coal mining wastes are one of the major global bulk waste streams. Sometimes the removed overburden occupies large areas of fertile land and leads to soil quality degradation. When they are not properly reclaimed, the dump materials can be a source of fine particulates highly prone to blowing by wind. They can spread over the surrounding fertile land and flora, disturbing their quality and abstaining the growth of fresh leaves. Occurrence of sulphides and/or other geochemically instable materials in the waste rock could result in acid or neutral rock drainage that could make this material an environmental issue. Due to its high acidity the acid rock drainage mobilises heavy metals and thus, it can contaminate the nearby water bodies. The neutral or alkaline rock drainage may also have high pollution potential due to the elevated salinity (Szczerpańska-

Plewa et al., 2010). In addition, some heavy metals can become mobile in neutral pH conditions.

Increase in production capacity of opencast coal mines is achieved by deployment of increasingly larger capacity haul trucks that require appropriately designed and well maintained haul roads. Use of the material representing solid inclusions (after its washing) in the overburden in haul roads or as partial replacement for fine aggregates in other roads will enhance the waste utilisation and minimisation and will also reduce environmental problems. Recently different attempts have been made in this direction (Mary et al., 2016; Mallick et al., 2017).

The objectives of the present study can be summarised as follows: (a) monitoring in laboratory of the possibility for harmful substances leaching from the deposited material as a result of precipitation; (b) identification of chemical indicators related to the possibility of using this material in road construction; (c) exploring the practicability of recycling of the washing water.

Materials and Methods

Samples of materials representing solid inclusions in the coal mine overburden were collected and kindly supplied by the colleagues from the "Department of Opencast Mining of Mineral Deposits and Blasting Activities" (DOMMDBA). Material milling and separation of the needed size fractions was carried out with the help of colleagues from the "Department of Processing and Recycling of Mineral Resources".

Column leaching tests, aimed at monitoring the possibility of leaching harmful substances from the deposited material as a result of rainfall, were carried out in plastic columns (40 x 280 mm) with perforated bottom. One kg of the tested material was placed in each of the two columns. The material in the first column was periodically sprinkled with distilled water imitating pure rain. The material in the second column was periodically sprinkled with acidified distilled water (pH 2, achieved by addition of HNO₃ – p.a.) imitating extreme acid rain. The lower pH compared to the most common acid rain was chosen to speed up the processes. The volume of water/acidified water used was 1600 cm³. Each test was run to provide leaching under unsaturated conditions. The material in the columns was flushed two times per day with portions of 200 cm³. The leachates permeated through the columns were collected and analysed. Electrical conductivity (EC), the pH, and oxidation reduction potential (Eh) were measured by using WTW Multi 3400i measuring instrument and corresponding electrodes. Studies on the Maritza East region have shown higher content of many different heavy metals in the coal, coaly clay and coal ash than the Clarke values (Kostova, 2005). Among them are lead, cadmium, copper, zinc, and iron, chosen by us as indicators of eventual leaching and pollution, since the first four usually do not form precipitates of hydroxides and are mobile under the measured pH values and iron presence can be an indication for the sulphides' leaching. The heavy metals were determined by ICP-OES analysis (method CNILG BM-1:2014, point II). The column leaching test was conducted in eight cycles. The number of cycles was based on measurements of physicochemical parameters of leachate and thus it was obtained that practically the steady state is reached in five cycles. In addition, this number of cycles is in accordance with the usually needed minimum number (Kusuma et al., 2012).

Chemical indicators that have been investigated in relation to evaluating the possibility of using this material in road construction are total iron and total sulphur, water soluble chlorides, water soluble sulphates and material's water solubility. Total iron and total sulphur were determined by the Central laboratory "Geochemistry" at the University of Mining and Geology, Sofia by using the laboratory method CNILG BM-1:2014, point III. The other chemical indicators were determined by following the procedures described by the BDS EN 1744-1:2009+A1:2012. Briefly, for determining the water soluble chloride salts clause 9 of the standard was applied – the use of Mohr's method. The aggregate test portion was extracted at room temperature for 60 min by stirring at solid to water ratio = 1:1. The chloride in the supernatant after settling was titrated with silver nitrate using potassium chromate as an indicator. For determining the water soluble sulphate salts clause 10.1 was used, modified by us. The aggregate test portion was extracted at room temperature for 24 hours by stirring at solid to water ratio = 1:2. The modification consisted

in applying the turbidimetry for determining the sulphate concentration in the supernatant after settling, since the expected sulphate concentration (based on the data about the total sulphur content of the material) was too low to apply correctly the BaSO₄ precipitation method. To determine the water solubility of the material clause 16 of the standard was used. Briefly, 500 g of the material was dried at 110°C, weighted and placed in a contact with distilled water at room temperature for 24 hours by stirring and solid to water ratio = 1 : 2. Then, after solids' settling, the clear water was separated from the solid. The latter was dried at 110°C till constant weigh. The difference between the first and the second weight divided by the first weight and multiplied by 100 gives the water solubility of the material in %.

To explore the possibility of the washing water recycling, a portion of the studied material was placed in contact with tap water at solid to water ratio = 1 : 8 and stirred mechanically for 4 hours. The mixture was left for solids' settling and clarified water was collected for analysis and further use as recycled water. The procedure was repeated totally 10 times, each time with new portion of material and using the recycled clarified water. Conductivity, pH and Eh values were determined each time in the clarified water. Some water macro-components were determined after 1st, 3rd, 6th, and 10th cycle of washing, as well as for the used tap water. Concentrations of lead, cadmium, copper, zinc, and iron were measured in the clarified water after the 10th use. In the Deval washing experiments the studied material was placed in the machine at solid to tap water ratio = 1 : 5, solid to abrasive spheres ratio = 1 : 9, mixed for 3 hours at totally 12000 revolutions and then left till 24th hour. Samples from the clarified water (referred to as Deval washing) were supplied by the colleagues from the DOMMDBA for different analyses, as well as samples from the 1st washing of the material after it was taken out from the Deval machine.

The mineralogical composition of the raw unwashed material, 10-times washed material, fine material removed by Deval washing and of material subjected to spraying with acidic water was determined by XRD (BRUKER D2 Phaser, Cu/Ni radiation, $\lambda=1.54184$ Å, 30 kV, 10 mA, 2 theta – 5-70, time 1720 s). The analysis was done by the laboratory "X-Ray diffraction" at the University of Mining and Geology.

Results and discussion

Analysis of solid samples

The analysis of the raw solid sample showed total iron (Fe) content of 0.450 wt.% and total sulphur (S) content of 0.047 wt.%. These values are considerably lower compared to the pyrite FeS₂ contents of 1-5% capable to form an acid mine drainage (Tiwary, 2001). The data from the mineralogical characterisation of the samples are presented in Figure 1. The material consists mainly of calcite, dolomite, quartz, illite and kaolinite, as it can be seen in Figure 1. Calcite is the dominant mineral in the raw unwashed sample, 10 times washed, and the fine material removed by washing in Deval machine. Dolomite is the main material in the sample that was subjected to "acid rain".

Column leaching experiments

Data on the conductivity, pH and Eh values measured for samples from these experiments are presented in Figs. 2-4 and data for the concentrations of some heavy metals are given in Table 1. Data presented in Figure 2 show that practically a steady state is achieved relatively fast.

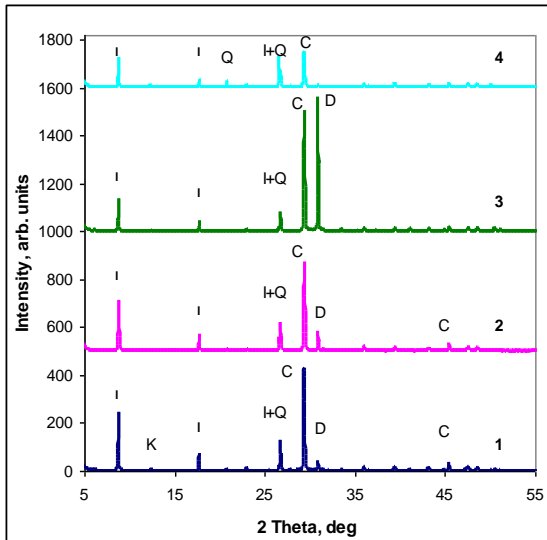


Fig. 1. X-Ray data: 1 – raw unwashed material, 2 – 10-times washed material, 3 – material subjected to spraying with acidic water, 4 – fine material removed by Deval washing; I – illite, K – kaolinite, Q – quartz, C – calcite, D – dolomite

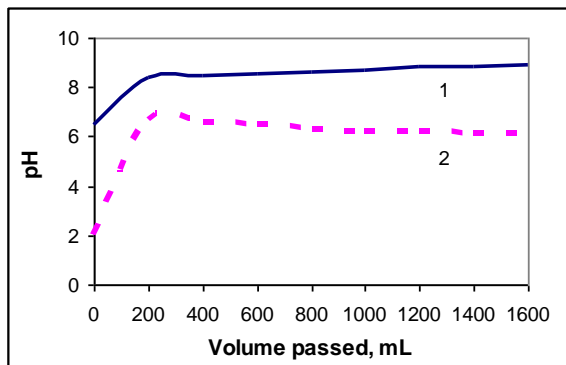


Fig. 2. Change in the pH value of the leachates permeated through the columns: 1 – “clean rain”, 2 – “acid rain”; pH values at 0 mL are for distilled and acidified water

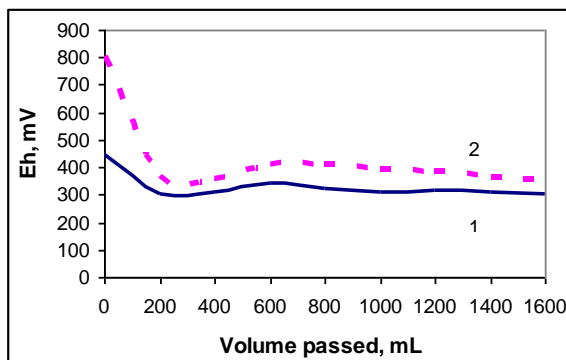


Fig. 3. Change in the Eh value of the leachates permeated through the columns: 1 – “clean rain”, 2 – “acid rain”; Eh values at 0 mL are for distilled and acidified water

Furthermore, the studied material possesses a high neutralising capacity. This finding is not surprising, having in mind the high carbonate content of the material (Fig. 1). Carbonate minerals, such as calcite CaCO_3 and dolomite

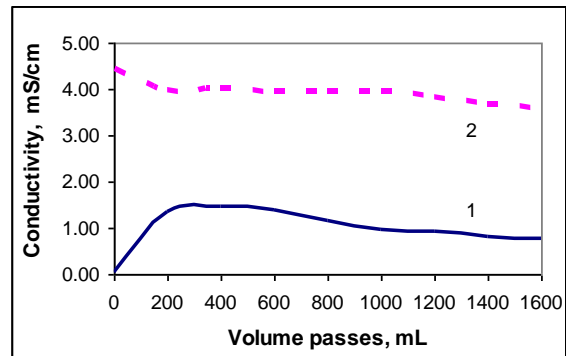


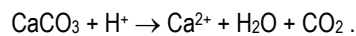
Fig. 4. Change in the conductivity of the leachates permeated through the columns: 1 – conductivity of “clean rain” drainage x 10, 2 – conductivity of “acid rain” drainage; conductivity values at 0 mL are for distilled and acidified water

Table 1. Leached heavy metals

Sample No	1	2	3	4	5
Pollutant					
Fe _{tot} , mg/kg	<0.03	<0.04	0.07	0.16	0.09
Pb, mg/kg	<0.01	<0.01	<0.01	<0.01	<0.01
Cd, mg/kg	<0.005	<0.006	<0.005	<0.005	<0.005
Cu, mg/kg	<0.005	<0.006	<0.005	0.033	<0.005
Zn, mg/kg	<0.005	<0.006	0.033	0.222	<0.005

- 1 – leachate – “clean rain” precipitation – passed 400 mL/kg
- 2 – leachate – “clean rain” precipitation – passed 1200 mL/kg
- 3 – leachate – “acid rain” precipitation – passed 200 mL/kg
- 4 – leachate – “acid rain” precipitation – passed 1000 mL/kg
- 5 – recycled water – after 10th use

$\text{CaMg}(\text{CO}_3)_2$ that are the main constituents of the studied material can neutralise the acid rain and most probably the neutralisation is mainly due to CaCO_3 dissolution following the reaction:



This is confirmed by the relative increase in dolomite main peak (Fig. 1 – curve 3) and the 3-fold decrease in the ratio of calcite to dolomite in the solid sample taken from the upper part of the column sprayed with “acid rain”. At the same time the ratio “dissolved magnesium to dissolved calcium” found in the leachate decreased, pointing also at predominant calcite dissolution (Fig. 5). Dolomite dissolution produces waters with a molar $[\text{Mg}^{2+}] / [\text{Ca}^{2+}]$ ratio of 1. Dissolution of equal moles of dolomite and calcite contributes 0.5 mole of Mg^{2+} and 1.5 moles of Ca^{2+} , producing waters with a $[\text{Mg}^{2+}] / [\text{Ca}^{2+}]$ ratio of 0.33. The $[\text{Mg}^{2+}] / [\text{Ca}^{2+}]$ ratio less than 0.11 points that more than 75% of the carbonate mineral dissolved is calcite (Szramek et al., 2007). Silicate minerals can also participate in the neutralisation process but the reaction is slower (Kusuma et al., 2012). When the amount of carbonate and silicate minerals in the material is sufficient, an acid drainage due to acid rain will not be formed, as it can be seen in Fig. 2 – curve 2. This results also in conditions where the most toxic Pb and

Cd do not leach and the leached amounts of Fe_{tot}, Cu and Zn are very low – Table 1, samples 3 and 4. The concentrations of all studied heavy metals in leachates obtained with “clean rain” precipitation are below the detection limit – Table 1, samples 1 and 2. Most probably, in this case dolomite dissolution predominates – Fig. 5. The solubility of dolomite increases compared to that of calcite at temperatures below 25°C as a result of the temperature-dependent relative solubility of these minerals (Szramek et al., 2007).

As it can be seen in Figure 3, after an initial decrease in the Eh value, pointing at a certain reduction process, whose identification needs further studies, the Eh value practically reaches a steady-state.

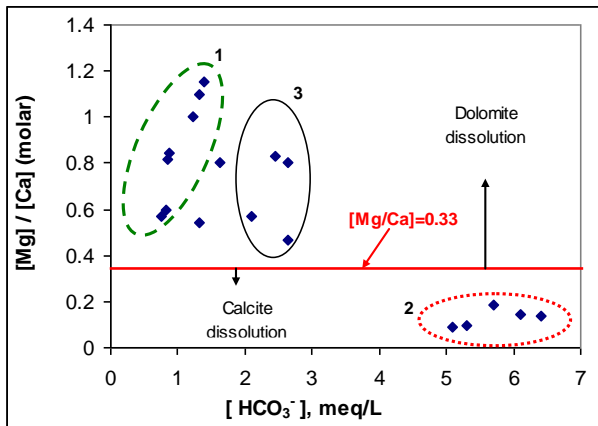


Fig. 5. Mg²⁺ / Ca²⁺ ratios versus HCO₃⁻ values: 1 – leachate from “clean rain”, 2 – leachate from “acid rain”, 3 – water from 1st, 3rd, 6th and 10th washing; points outside the cycles – water from Deval washing

The electric conductivity reflects the total amount of dissolved ions in the leachate. For leachate obtained with “clean rain” initially the conductivity increased pointing at fast dissolution of more easily soluble compounds in the material and then practically reached a steady-state (Fig. 4 – 1). The considerably higher conductivity measured in “acid rain” leachates (Fig. 4 – 2) can be attributed to the presence of hydrogen ions in the system and their specific conductivity mechanism resulting in high measured EC values.

Chemical indicators related to the material use in road construction

The measured concentration of water soluble chlorides was 0.010 wt.%. The concentration of water soluble sulphates was 0.015 wt.%. These values are well below the threshold values of 4 wt.% water soluble sulphates and 8 wt.% water soluble chlorides required by the Bulgarian legal documents for aggregates for unbound and hydraulically bound materials for use in civil engineering work and road construction (BDS EN 13242:2002 +A1:2007) and for materials for embankments, underlying layers, stabilised banquetts with a top layer of crushed stone (Ministry of Regional Development and Public Works, 2014). The same documents place a legal requirement of less than 1 wt.% total sulphur. The material's water solubility was 0.028 wt.%. The figure is much less than the threshold value of 2 wt.% for coarse aggregates from crushed limestone, re-crystallised limestone, marble and marl (Rostovski et al., 2010).

Possibility of washing water recycling

The possibility for multiple use of clarified washing water in closed cycle depends on its physicochemical parameters, such as pH and Eh values related to precipitation of low soluble compounds and EC values that are indicative for the dissolved salts. In addition, information about the concentrations of chloride and sulphate ions that are corrosion – aggressive both to steel and concrete could be useful from a practical point of view. Data on the conductivity, pH and Eh values measured in recycled water samples are presented in Fig. 6.

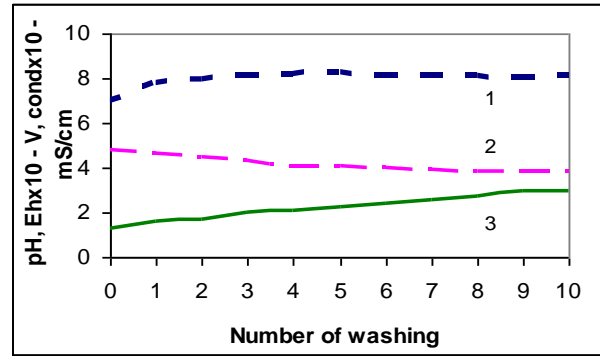


Fig. 6. Change in the pH, Eh values and conductivity of the recycled washing water: 1 – pH; 2 – Eh x 10, V; 3 – conductivity x 10, mS/cm; the values at 0th washing are for the used tap water

Initially an increase in the pH and decrease in the Eh values were observed (Fig. 6) that most probably are due to the dissolution of some carbonaceous material. Further, these parameters practically reach a steady state that could be related to the carbonates' equilibriums (of dissolution and precipitation). Conductivity values, measured by us, are within the same range (0.049-0.480 mS/cm) that have been measured in water samples prepared by contacting overburden dump materials from coal mines at similar solid to water ratios and times (Dutta et al., 2018). As it can be seen in Fig. 6, increasing the number of cycles of water use leads to an increase in the EC. This is indicative for the accumulation of salts in the water – mainly chlorides and sulphates (Table 2). However, the accumulated salts and especially the corrosion aggressive ions are in relatively low concentrations which cannot cause corrosion problems of steel or concrete (Panayotova, 2007).

Table 2. Leached corrosion aggressive ions

Pollutant, sample	Cl ⁻ , wt. %	SO ₄ ²⁻ , wt. %
Water for washing	0.001	0.001
Lab, 1 st washing	0.004	0.003
Lab, 3 rd washing	0.009	0.009
Lab, 6 th washing	0.011	0.012
Lab, 10 th washing	0.014	0.024

It is worth noting that the water used by us (from the drinking water supply network in Sofia) is generally with low mineralisation and conductivity. Such type of flushing water can be used in a closed cycle multiple times. However, the accumulation of salts in recycled water will be much faster and more noticeable when the water used for flushing has a higher initial mineralisation and conductivity, as for example is the case with the tap water in many villages in Yambol region, Southeast Bulgaria (Panayotova et al., 2010).

Characteristics of Deval washing water

Data on some physicochemical parameters, macro-components and some micro-components of washing water from Deval washing tests are presented in Table 3.

Table 3. *Physicochemical parameters, macro-components and some micro-component of washing water from Deval washing*

Parameter	Deval washing	1 st washing
pH	8.10	8.21
Eh, mV	245	414
Conductivity, $\mu\text{S}/\text{cm}$	240	134
Na^+ , mg/L	10.9	4.0
K^+ , mg/L	6.1	3.2
Ca^{2+} , mg/L	20.2	18.1
Mg^{2+} , mg/L	9.8	4.9
HCO_3^- , mg/L	93.7	68.4
Cl^- , mg/L	17.6	11.2
SO_4^{2-} , mg/L	21.4	12.2
Pb^{2+} , mg/L	<0.01	<0.01
Cd^{2+} , mg/L	<0.005	<0.005

By comparing data presented in Table 3 and Figure 6, it can be seen that physicochemical parameters of water samples obtained in experiments aimed at studying the washing water recyclability and Deval washing experiments are in the same range. Since in the 1st washing of samples in the Deval machine fresh tap water was used, the conductivity decreased and the Eh value increased. The molar $[\text{Mg}^{2+}] / [\text{Ca}^{2+}]$ ratios of Deval washing and 1st washing are indicative for predominant dolomite dissolution (Fig. 5). The fine material removed from the solid sample by Deval washing, which material practically represents the total suspended particles in the water sample, practically does not contain dolomite (Fig. 1 – 4), thus supporting the idea of dolomite dissolution. The concentrations of corrosion aggressive chlorides and sulphates were 0.009 wt.% and 0.005 wt.% respectively, showing that corrosion problems are not to be expected if the clarified water from this washing is re-used.

Conclusions

Based on the studies carried out, the following conclusions can be drawn:

1) Normal rain and snow water contacting with the material representing solid inclusions in the overburden from opencast coal mining in Maritsa East Mines Ltd will not generate acid rock drainage and will not leach heavy metals from the material. Moreover, the material is capable to neutralise acid rain, thus contributing to the protection of the surrounding land and water bodies by heavy metal ions pollution.

2) Dolomite is the main leached carbonate mineral in neutral water contacting with the studied material at ambient temperature. At acidic water contacting with the studied material, calcite is the main leached carbonate mineral.

3) From the chemistry point of view, the material is suitable for use in civil engineering work and road construction. It contains acid drainage forming minerals and minerals releasing corrosive-aggressive ions in amounts much less than permitted by the relevant legislation.

4) Tap water used for the materials' washing can be re-used multiple times after its clarification, subjected to the condition that initially used water is not highly mineralised.

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