Characterization of dry residues of surface waters from the Maritsa East coal basin

Характеристика на сух остатък от повърхностни води от въглищен басейн Марица Изток

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Key words: lignites, dry residue, sulphate phases.

Introduction

Phase-mineral and chemical composition of dry residues, resulting of evaporation of seasonal surface waters interacting with coal, may provide information about initial element migration. The aim of this study is to determine the migration of elements in such waters within the Maritsa East lignite basin.

Materials and methods

Surface waters were collected in summer (July 2013) from 4 different places (drainage points in Troyanovo 3 mine and Mednikarovo dump site) within the Maritsa East coal basin. The pH and electric conductivity (EC) of waters were measured in the laboratory. Concentrations of Cu and Zn in waters were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using Horiba Jobin Ivon Ultima 2. Equal quantity (400 ml) of every water sample was evaporated in drying furnace at 50 °C to dry residue. The quantity of resulting dry residue in each sample was as follows: N1, Troyanovo 3 mining area – 3.22 g; N2, Mednikarovo dump site – 1.63 g; N3, drainage point 1 Troyanovo 3 – 2.24 g and N4, central drainage point Troyanovo 3 – 2.97 g. The precipitated matter was observed under stereomicrosope and photographed. Morphology and chemical composition of crystallized phases were studied using JEOL Superprobe 733 scanning electron microscope (SEM) equipped with EDS. Mineral phase composition was characterized by powder X-ray diffraction (XRD) using a PANalytical Empyrean equipped with a multichannel detector (Pixel 3D).

Results

Powder X-ray diffraction revealed 3 major minerals formed in all samples: gypsum (14.8–53.5%), hexahydrite (11.2–44%) and löweite (6.7–41.3%). Ferrinatrite (1.4–16.8%), rhomboclase (0.6–0.75%), sideronatrite (7.8%) and boussingaultite (17.2%) were identified in some of the samples (Table 1). Diffraction data of all samples suggest presence of amorphous phase(s). SEM-EDS study detected other minor (Na-Ca, Na-

Table 1. Phase composition of dry residues (DR) from surface waters

Mineral phase	Sample No.	Method
Gypsum, $CaSO_4.2H_2O$	N1-4	XRD, SEM-EDS
Hexahydrite, $MgSO_4.6H_2O$	N1-4	
Löweite, $Na_{12}Mg_7(SO_4)_{13}.5H_2O$	N1-4	
Ferrinatrite, $Na_3Fe^{3+}(SO_4)_3.3H_2O$	N1-2	
Boussingaultite, $(NH_4)_2Mg(SO_4)_2.6(H_2O)$	N4	
Sideronatrite, $Na_2Fe^{3+}(SO_4)_2(OH).3H_2O$	N4	
Rhomboclase, $H_5Fe^{3+}O_2(SO_4)_2.2H_2O$	N2, 4	
Celestine, $SrSO_4$	N1-4	SEM-EDS
Barite, $BaSO_4$	N1	
Hallite, NaCl	N1-2	
Sylvite, KCl	N1	
Na-Ca sulphate (?)	N2	
Na-Al sulphate (?)	N4	
Na sulphate (?)	N1, 3	
Al sulphate (?)	N1, 4	
Si-S phase (?)	N1	
Fe oxide/hydroxide	N1,4	
Cr-Mn-Ni-Au phase (?)	N3	
Amorphous phase (?)	N1-4	

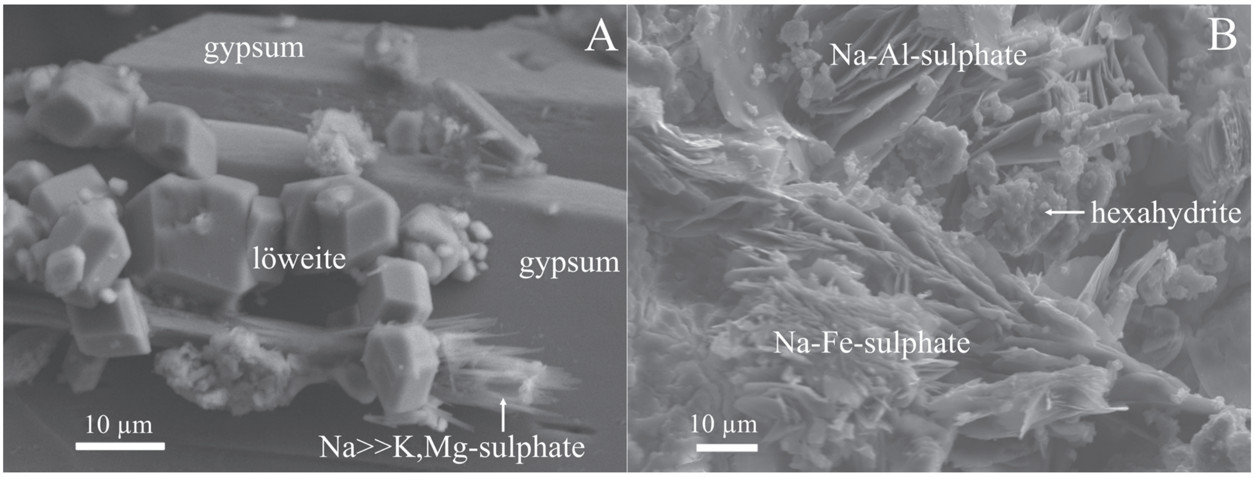

Fig. 1. SEM images of newly formed minerals from evaporated surface waters: *A*, löweite and (Na, K, Mg) sulphate (Na>>K) on gypsum crystals; *B*, aggregate of hexahydrite with unidentified Na-Al and Na-Fe sulphates. Secondary electrons.

Al, Na, Al unidentified sulphate crystal and Si-S amorphous? phases) and accessory (celestine, barite, halite, sylvite, Fe oxide/hydroxide, Cr-Mn-Ni-Au phase?) minerals. Elongated prismatic, acicular, tabular, rhombohedral (Fig. 1A), needle-like, flake-like and cubic crystals, cryptocrystalline granular masses and amorphous crusts were observed. Flake-like crystals mostly form rosette-like aggregates (Fig. 1B). Prismatic crystals form bundle- or radial aggregates. Hexahydrite mostly occurs as anhedral partly crystallized aggregates.

The composition of dry residues is mainly represented by S, Ca, Na, Mg, and Fe. Microprobe analyses of some mineral phases show presence of minor constituents as Al, Mn, K, Si, Sr, and Cl. Concentrations of Zn (1.75–2.59 mg/l) and Cu (0.046–0.256 mg/l) were measured in water samples, but were not detected in precipitated phases. Aluminum occurs as own sulphate phases together with Na. Carbonate phases are not observed unlike those reported in dry water-soluble residues of Maritsa East coals by Vassileva (2004). Dry residues of samples N1, N2, N4 precipitated from waters with pH 2.83–3.96 and have high content of gypsum. Sample N3 precipitated from water with pH 7.52 and has the lowest content of gypsum, but is enriched with Mg and Na-Mg hydrated sulphates (85% of the sample). This composition is probably a result of interaction of water mostly with clay layers and lack of organic acids. Sources of S, Ca, Na, Mg, and Fe are autogenic minerals in coals (gypsum, pyrite, and calcite), clay partings, organic matter and acids, and rain waters. In sample N4 NH_4-containing mineral is determined (baussingaultite) in considerable amount. Its formation may be related with nitrogen migrating from organic matter/acids and atmosphere.

Conclusions

Seasonal surface waters formed during rainfalls interact with coal and partings leaching the most mobile constituents – S, Ca, Mg, Na, and Fe. They have predominantly low pH and contain traces of Mn, Sr, Ba, Zn, Cu, Cl, and K. Lack of carbonates may be due to their foremost precipitation or limited interaction of surface water with activity surface of the bottom layer (coal or clay partings).

Acknowledgements: This study is financially supported by the DNTS China 01/7 grant of the Bulgarian Science Fund. The authors thank “Mini Maritsa Iztok” geological department for their assistance in sample collection on site.

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