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MECHANISM OF RHABDOPHANE-(LA) AND LANTHANITE-(LA) FORMATION DURING REDUCTION OF BIOAVAILABLE NUTRIENTS IN WATER BASED ON SEM AND XRD STUDY

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Abstract. This study presents results of SEM and XRD investigation of products formed after La-rich bentonite application into water containing PO_4^{3-} and CO_3^{2-} ions. The main product of the investigated reaction with phosphate and carbonate anions is rhabdophane-(La) and lanthanite-(La), respectively. Studied material has adaptation in many water reservoirs only for phosphorus ions reduction. Further studies might find application in case of reduction others hazardous ions. They could be precipitated in the same fast and effective way, to other stable, nontoxic mineral phases.

Keywords: rhabdophane-(La), lanthanite-(La), bentonite, phosphorus ion, carbonate ion, water reservoirs

Introduction

The natural and anthropogenic nutrient pollution occurs in many water reservoirs and is very common. The main nutrient that is observed in all known water environments is represented by phosphorus (PO_4^{3-}). Higher concentration of phosphorus in e.g. lake or river may be responsible for “algae boom”. For that reason bentonite might be used in many different water environments. Application in large scale of La-rich bentonite is the best technique for reducing bioavailable phosphorus in water. The reduction product is a mineral phase- rhabdophane-(La) ($\text{LaPO}_4 \cdot \text{H}_2\text{O}$) (Robb *et al.* 2003). Characteristic of the reaction is a very fast time of the reaction and stability of the product in a wide range of pH as well as Eh conditions. In addition, the molar ratio of lanthanum to phosphate is 1:1 ($\text{La}^{3+} + \text{PO}_4^{3-} \rightarrow \text{LaPO}_4$). Lanthanum phosphate is analogous to a highly insoluble, naturally occurring mineral known as rhabdophane. Similar situation has been observed in case of CO_3^{2-} , where the main product is lanthanite-(La) (Szopa 2010).

The rapid increase in anthropogenic activity has accelerated the eutrophication process significantly, markedly altering the geochemical cycle of phosphorus, carbon and other elements. According to the above, ap-

plication of the modified bentonite to water reservoir with eg. carbon-rich nutrient might bring similar effect.

Material & Method

The bentonite forms small, up to 4 mm long particles. They are beige as well before and after addition to water. The chemical composition of modified bentonite is (wt%): SiO_2 61.36, Al_2O_3 14.73, MgO 2.76, Fe_2O_3 3.64, CaO 1.79 and La_2O_3 0.058 (Haghseresht *et al.* 2009). The modified bentonite contains approximately 49 mg of lanthanum per gram of the material. For this research the modified clay was used with a carbon nutrient-rich (CO_3^{2-}) water sample. After the stirring of mixed solution for 0.5 hour, it was kept for 1 day at room temperature and after that the residuum at 50°C for another 1 day. The effects of the reaction were investigated by using scanning electron microscope (SEM) equipped with EDS (EDAX) detector and X-ray diffractometer (XRD) X'Pert Philips PW 3710 at the Faculty of Earth Sciences, University of Silesia.

SEM investigation

The SEM study of the investigated material shows presence of a few different types of mineral

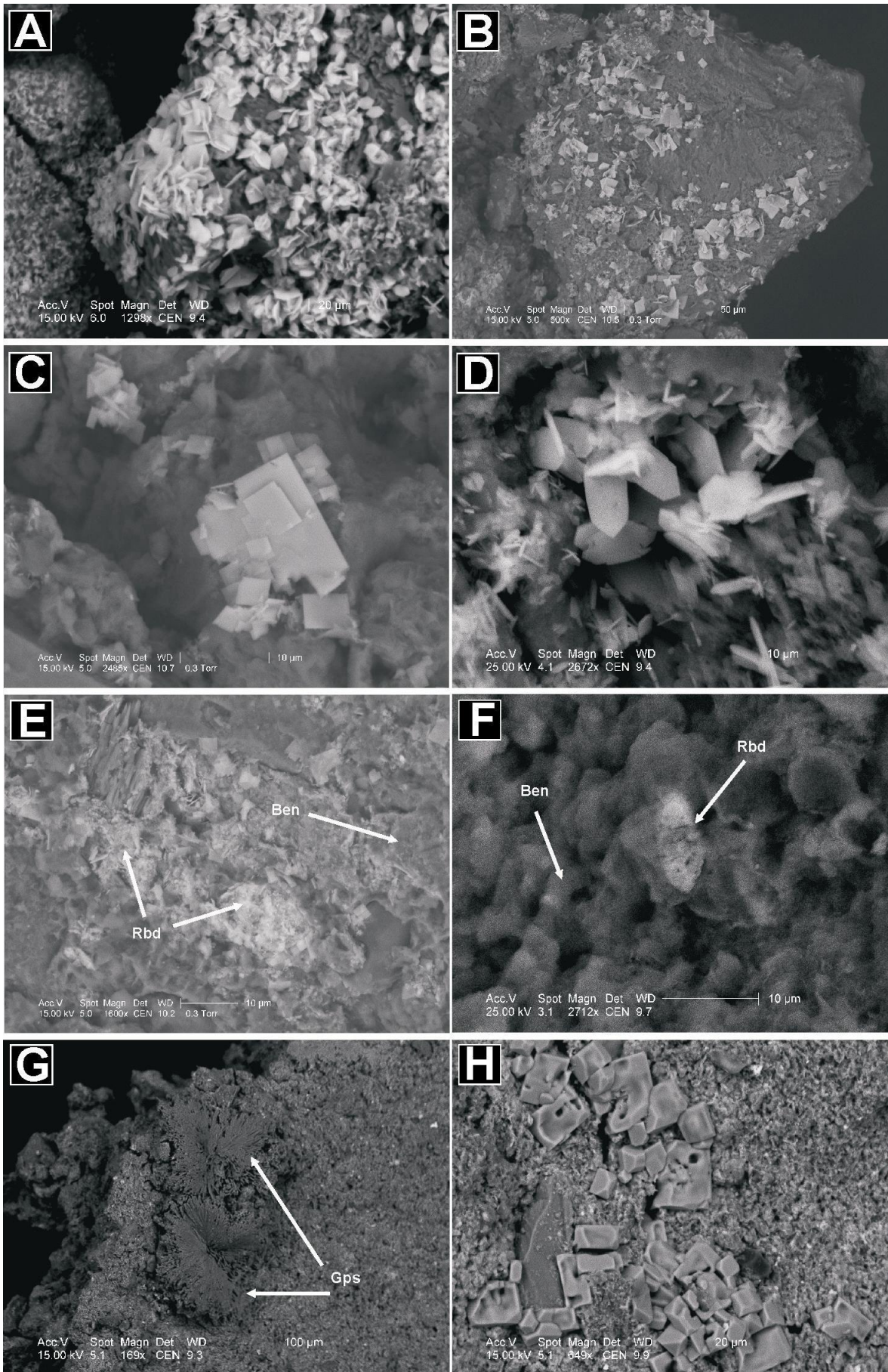


Fig 1. BSE images showing: (A, B) general view on La-rich carbonate (lanthanite-(La)) (white, gray) crystals which are situated on bentonite grain (dark gray); (C, D) zoomed idiomorphic La-rich carbonate (lanthanite-(La)) crystals; (E, F) irregular, xenomorphic La-rich carbonate (rhabdophane-(La)) crystals (light gray) on bentonite grain (dark gray); (G) calcium sulphate (gypsum) crystal formation on bentonite and (H) cubic, partially dissolved chloride of sodium (halite) crystals on bentonite grain. Explanations: Rbd- rhabdophane; Ben- bentonite; Gps- gypsum.

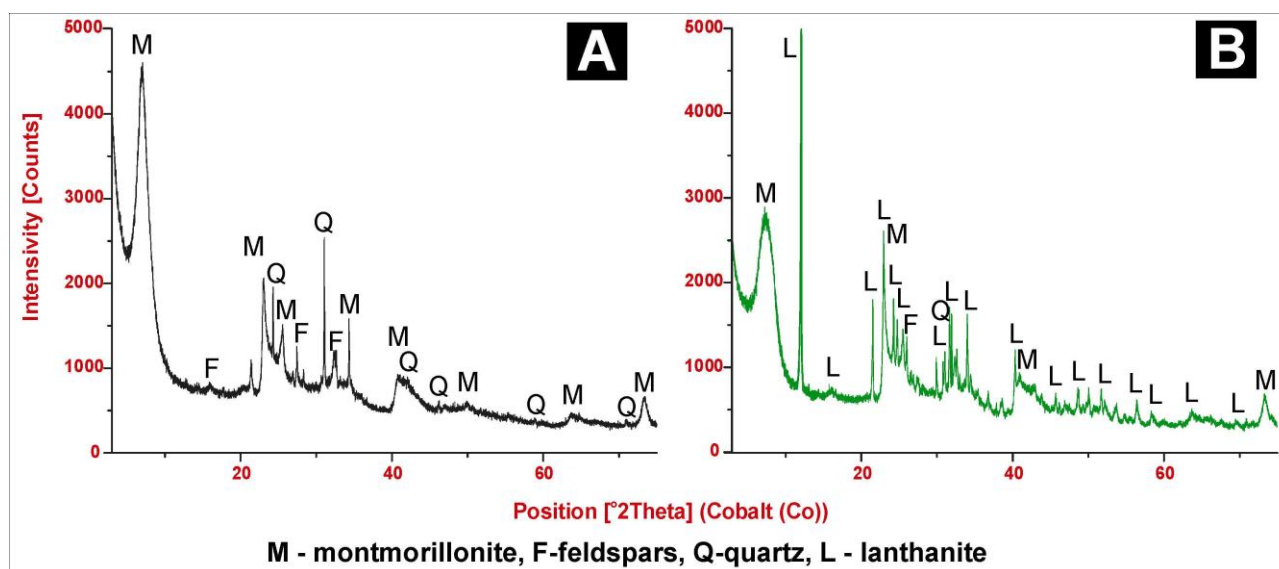


Fig 2. X-ray diffraction patterns of investigated material: (A) before and (B) after interaction with the nutrient-rich (CO_3^{2-} , PO_4^{3-}) water sample.

phases in the investigated sample. Predominant phase is lanthanum-rich carbonate (Fig. 1 A-D) formed on a clay aggregates. The population of the carbonates reveal crystals differ in size and chemistry. The platy, flattened crystals with rhombic (?) outline are up to 20 μm in size (Fig. 1 C). Other visible population is represented by hexagonal (?) and platy crystals (Fig. 1 A, D) which are up to 10 μm in size.

Phosphate La-rich phase is also present. It forms irregular and small grains (up to 4-5 μm) (Fig. 1 E, F). They are also present on the bentonite grains.

Additionally sulphate of calcium and sodium chloride were noted. In both cases the crystal forms idiomorphic forms. The sulphate has rosette-type crystals, which are ca. 120 μm in diameter (Fig. 1 G). The sulphate crystals are situated directly on bentonite grains. No La-rich carbonate or phosphate was observed on the sulphate crystals.

The chloride is present as cubic crystals which are up to 40 μm long (Fig. 1 H). Some of the chloride crystal show dissolved walls. Sometimes the La-rich carbonate is present on/between chloride crystals.

XRD investigation

The XRD data reveal presence of montmorillonite as the main mineral phase (Fig. 2 A, B). The impurities related with the La-rich bentonite are represented by quartz and feldspar as the main mineral impurities (Fig. 2 A). The X-ray data confirmed that the most common mineral phase participated in the bentonite sample is lanthanite-(La) ($\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$) (Fig. 2 B). It is also the predominant and new formed mineral phase.

Mechanism of phosphate and carbonate formation

Bentonite granules are generally mixed with *in situ* water and applied to a water body as a slurry (Fig. 3). Aerial application of bentonite pellets is also possible. As the slurry settles, phosphate and/or carbon anions in the water column are bound to the lanthanum cations contained within the bentonite clay. Once bentonite has settled on the sediment water interface, it forms a thin layer, usually less than 1 mm in thickness. After the application water is rich in La^{3+} cations. The ions react with anions which are presented in the water. In case of the phosphorus ions, the final product of the reaction is rhabdophane-(La)($\text{LaPO}_4 \cdot \text{H}_2\text{O}$). The reaction of lanthanum (La^{3+}) cations with carbon (CO_3^{2-}) anions can be wrote down as: $2\text{La}^{3+} + 3\text{CO}_3^{2-} \rightarrow \text{La}_2(\text{CO}_3)_3$. The final product is lanthanite-(La) with the general formula: $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$.

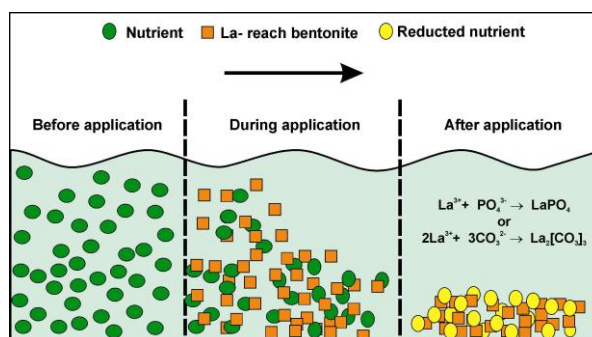


Fig 3. Scheme showing the interaction of bentonite with nutrient-rich water sample. For details see the main text.

The XRD does not reveal presence of any phosphate in the studied sample. It might be caused by very small amount of the phase in the investigated material. In

that case, it is an effect of heating the sample after water application. The same situation is observed with sodium chloride (halite ?) and calcium sulphate (gypsum ?). The last two minerals are common but form crystals locally in the dried bentonite. The gypsum (?) and halite (?) crystallization process is syngenetic with phosphate and carbonate formation but not depends on lanthanum ions content in the water.

Conclusions

As in case of rhabdophane-(La), the new forming carbonate- lanthanite-(La), by the reduction reactions is effective and fast, what should have got adaptation in environmental sciences. Beside open water bodies, the application of the bentonite may be used in industrial filters – not only in high concentration of P but also C. Further studies should be done with undesirable ions e.g. AsO_3^- , NO_3^- or others, which may be hazardous for living organisms.

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Abstrakt

Niniejszy artykuł traktuje o możliwości redukcji nutrientów (np. PO_4^{3-} , CO_3^{2-}) za pomocą bentonitu wzbogaconego w lantan. Jak dotąd jedynym zastosowaniem wspomnianego bentonitu jest redukcja jonów fosfonowych w środowiskach wodnych (np. jeziora, rzeki, zastoiska) do stabilnego i nietoksycznego związku mineralnego jakim jest rabdofan-(La). Na podstawie analiz SEM oraz XRD wykazano, że badany materiał umożliwia również redukcję jonów węglanowych do stabilnej i nietoksycznej fazy mineralnej-węglanowej (lantanit-(La)). Dalsze studia nad bentonitem lantanowym, poczynione względem innych, niepożądanych jonów (np. jonów azotanowych czy arsenianowych) mogą przynieść odpowiedzi względem ewentualnego i dalszego, środowiskowego zastosowania bentonitu lantanowego.

Słowa kluczowe: rabdofan-(La), lantanit-(La), bentonit, jony fosforanowe, jony węglanowe, zbiorniki wodne