

CHEMICAL-MINERALOGICAL CHARACTERIZATION OF BAUXITES FROM DIFFERENT DEPOSITS

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Abstract: From the aspect of their chemical and mineralogical composition, bauxites are very complex multicomponent raw materials. The paper presents the characterization of bauxite from several different deposits: Brazil, Milići, Čitluk and Kosovo. Chemical characteristics were determined by a combination of different analytical methods: gravimetry, potentiometric titration, atomic absorption spectroscopy (AAS) and UV-VIS spectrophotometry. Mineralogical composition was determined using X-ray diffraction and thermal analysis methods. Chemical and structural characterization is complemented by the results of scanning electron microscopy with EDX analysis. The information obtained was used for the assessment of the quality of investigated bauxites from the aspect of their application in the production of alumina.

Keywords: bauxite, characterization of bauxite, X-ray diffraction, thermal analysis, AA spectrophotometry, UV-VIS spectrophotometry.

1. INTRODUCTION

1.1. Bauxites, basic characteristics of bauxites

Bauxite is the most important aluminium ore. It was first discovered in France (1821) in the vicinity of a place called Les Baux, after which it was named. Although it is often classified as a mineral, bauxite is a sedimentary rock, a polymineral aggregate composed of aluminium hydroxides known as mineral hydrargilite (gibbsite) $\text{Al}(\text{OH})_3$, boehmite AlOOH and diaspore AlOOH . These three minerals are the main components of bauxite. The chemical and mineralogical composition varies within very wide limits. Depending on the mineralogical form of the aluminium present as the basic mineral, bauxites are divided into the following categories: hydrargilite (gibbsite), boehmite, diaspore and mixed (hydrargilite-boehmite and boehmite-diaspore). Apart from aluminium minerals, basic components of bauxite also include the minerals of iron, silicon, titanium, calcium and magnesium. A mixture may

contain traces of minerals of a series of other elements: Na, K, P, Cr, V, Ga, Zn, Pb, Cu, Ni, Mn, Co etc [1].

The Bayer process for alumina production involves the alkaline treatment of bauxite at high temperatures whose aim is to obtain a solution of sodium aluminate and spontaneous decomposition of the obtained aluminate solution in suitable conditions of temperature, with the separation of aluminium hydroxide $\text{Al}(\text{OH})_3$ and NaOH regeneration. Depending on the composition of bauxite, apart from aluminium minerals, other components also react, to a smaller or greater extent, with the caustic solution.

The quality of bauxite, when it comes to its application in production of alumina, is determined based on the silicon module, which represents a ratio between the concentrations of Al_2O_3 and SiO_2 in bauxite. The greater the value of silicon module, the higher the quality of bauxite, and vice versa. Bauxites with modules 10 are considered to be of high quality, those with modules between 8 and 10 can be

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processed, whereas those below 8 are such that their processing is not economically justifiable. The criterion mentioned is applied only to boehmite and diasporite bauxites. Due to lower temperature of leaching for hydrargilite bauxite, the harmful effect of silicon depends only on mineralogical forms which dissolve at these temperatures with NaOH since the temperature of leaching is lower than 150 °C [1].

High quality bauxites are becoming rarer and rarer, which is the reason for intensive investigations of mineralogical and chemical composition of bauxite, with a view to its greater and more profitable application in the production of alumina. Chemical-mineralogical characterization of bauxite prior to its application is particularly significant. This paper presents the results of the characterization of several different bauxite deposits.

1.2. Mineralogical modifications of aluminium and the accompanying elements in bauxites

Bauxite is a multi-component ore with over 100 different mineral forms identified. Aluminium is mainly present in bauxite in the form of hydrated oxides: hydrargilite (gibbsite), boehmite and diasporite.

Hydrargilite (gibbsite) $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is crystallized in a monoclinic system with a limited hexagonal dislocation of ions. The elementary cell consists of 8 aluminium (III) ions and 24 hydroxyl ions, which forms 8 molecules of $\text{Al}(\text{OH})_3$. Gibbsite has a complex structure. It consists of alumohydroxyl layers which are built up of double layers of hydroxyl groups, among which aluminium (III) ions plane is distributed. Alumohydroxyl layers are linked to each other by hydrogen bonds.

Boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) has a leaf-like structure. Each aluminium ion is surrounded by six oxygen anion, distributed on the corners of the octahedron. Double layers which are equally composed of hydroxyl ions and O^{2-} ions are linked by hydroxyl bonds in boehmite. It differs from diasporite in its internal structure, and is softer than diasporite.

Diasporite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) is another polymorphous modification of aluminium oxide hydrated with one molecule of water. It crystallizes in the same way as boehmite, in a rhombic system with a rhombic bipyramidal symmetry, but with different lattice parameters. Aluminium (III) ions are distributed in a dense arrangement of oxygen ions, so that each is linked to three oxygen ions.

Iron is found in bauxites in the form of different minerals, the commonest of them being water-free oxide hematite, Fe_2O_3 and hydrated oxide goethite, (HFeO_2), which differ considerably in colour, crystal structure and behaviour during processing.

Magnetite and limonite are found in smaller quantities.

Silicon minerals are the most important and the most harmful impurities in bauxites. The most common ones are hydrated aluminosilicate kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and quartz (SiO_2). Kaolinite reacts with the caustic solution at lower temperatures, and quartz remains stable up to higher temperatures.

Calcium and magnesium are mainly present in bauxites in the form of different carbonates. The most common of them are calcite (CaCO_3), magnesite (MgCO_3) and dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$). Bauxites also contain mineralogical modifications TiO_2 rutile and anatase, whose content varies between 2 and 3%. Other minerals that may occur are dolomite, muscovite, chabazite, crandallite, etc.

2. MATERIALS AND METHODOLOGY

2.1. Materials

For the experimental part of the research, whose results are presented in this paper, we chose the samples from the bauxite deposits Brazil, Milići, Čitluk and Kosovo. Bauxites were first crushed, dried at 105 °C and then ground to below 200 micron particle size.

2.2. Methodology

The experimental part of this paper was carried out in the laboratory of the alumina factory "Birač" in Zvornik and the University Centre for Electron Microscopy in Novi Sad. Characterization of the selected samples of bauxite was performed using the following methods:

- Preparation of samples for determining basic components: Al_2O_3 , SiO_2 , Fe_2O_3 , TiO_2 , was carried out according to standards JUS B.G8.520 and ISO 6994, by melting with a mixture of Na_2CO_3 + $\text{Na}_2\text{B}_4\text{O}_7$ and dissolving in an acid environment. The solution prepared in this way is used to determine Al_2O_3 , SiO_2 , TiO_2 and Fe_2O_3 .

- Loss of ignition was determined using a gravimetric method according to JUS B.G8.510 (ISO 6606) standard.

- The content of Al_2O_3 was determined by the method of JUS.B.G8.512, potentiometric calculation on the automatic burette EBX TITRIPOL, titration of surplus complexed III with copper chloride.

- The contents of SiO_2 , Fe_2O_3 , TiO_2 , P_2O_5 and V_2O_5 was determined based on the standard "VAMI" spectrophotometric methods, on the Lamb-

da 25 spectrophotometer, supported by WinLab 32 software package.

– The contents of CaO, Na₂O, MnO and ZnO were determined by standard PERKIN ELMER AAS methods on PERKIN ELMER 4000 atomic absorption spectrophotometer.

– X-ray diffraction analysis was carried out on the PHILIPS PW 1710 diffractometer for powder, using Cu-anticathode ($K\alpha=1.540526\text{\AA}$) under the following technical conditions: 40 kV voltage, 30 mA electric current, graphite monochromator, angled recording area 2θ from 5 to 60°, step size of 0.02 s, time per step 1 s. The instrument and recording are operated by software package X'Pert Quantify, whereas X'Pert HighScore programme was used for the interpretation of the obtained diffractograms.

– Identification of the present mineral phases in the bauxites was performed by comparing experimental results with the characteristic values of

interplanar distances selected in the database Powder Diffraction File. Characteristic d-values for the identification of minerals most commonly present in bauxites are shown in Table 1.

– Thermal analysis (DTA, TG, DTG) was carried out using a derivatograph "MOM" Budapest Q1510. The samples were investigated at the 20 °C – 1000 °C temperature range, with 10 °C/min heating rate in the atmosphere of air, with Al₂O₃ as a reference material. The analysis of the resulting thermograms was performed using Winder program.

– Morphological characteristics and the elementary composition of the particles of the samples selected were monitored by means of JOEL JSM 6460 LV EDX instruments, scanning microscope with the acceleration voltage of 20 kV, and the preparation of the samples was performed using BAL-TEC, SCD 005 SPUTTER COATER devices in the laboratory of the University Center for Electron Microscopy in Novi Sad.

Table 1. Characteristic d-values of the minerals most commonly present in bauxites

Mineral	Characteristic d-values of the strongest currents/lines (Å)	Mineral	Characteristic d-values of the strongest currents/lines (Å)
Gibbsite-Al(OH) ₃	4.85; 4.36; 4.32	Anatase-TiO ₂	3.52; 1.89; 2.38
Nordstrandite-Al(OH) ₃	4.79; 2.02; 2.26	Rutile-TiO ₂	3.25; 1.69; 2.49
Boehmite -AlOOH	6.11; 3.16; 2.35	Quartz-SiO ₂	3.34; 4.26; 1.82
Diaspore -AlOOH	3.99; 2.31; 2.13	Calcite- CaCO ₃	3.03; 1.87; 3.85
Goethite-FeOOH	4.18; 2.45; 2.69	Dolomite -MgCaCO ₃	2.88; 2.18; 1.80
Hematite-Fe ₂ O ₃	2.69; 1.69; 3.68; 2.51	Muscovite-KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	9.97; 3.33; 4.98; 2.54
Kaolinite-Al ₂ Si ₂ O ₅ (OH) ₄	7.16; 3.56; 4.41	Lithiophorite-(Al,Li)MnO ₂ (OH) ₂	4.69; 9.38; 2.38

3. RESULTS AND DISCUSSION

This paper presents the results of the investigation of chemical and mineralogical characteristics of bauxite from four different deposits: Brazil, Milići, Čitluk and Kosovo (Table 2). The investigations were carried out from the aspect of determining the possibility of their application as a raw material in the production of alumina which later produces aluminium by the process of electrolysis. Among the investigated samples there are certain differences regarding chemical and mineralogical properties. The content of Al₂O₃ varies from 49.23 to 57.38 %, whereas that of SiO₂ is 1.47 to 5.69%. According to these values, the silicon module which serves to define the quality of bauxite ranges from 9.36 to 33.49. Based on the values of these three key parameters, these bauxites have good quality with high silicon module and high content of aluminium oxide.

The loss of ignition is known to depend on the mineralogical composition of bauxite. With the

bauxites investigated this value ranges from 8.89 to 28.20% which indicates that they have different mineralogical compositions. Based on the high value of loss of ignition, it can be concluded that aluminium oxide is hydrated with three molecules of water in the Brazil bauxite, and one molecule of water in bauxites Milići and Kosovo, where it is necessary to take into consideration the results of x-ray and differential-thermal analysis in order to determine the type of monohydrate-boehmite or diaspore. The loss of ignition with the Čitluk bauxite is within these values, therefore it can be expected that both monohydrate and trihydrate are present in the bauxite. According to the results of the chemical analysis, the Čitluk bauxite is characterized by somewhat higher content of titanium dioxide. A higher content of ZnO is noted in the Čitluk bauxite, whereas the Brazil bauxite does not contain this component being a typical tropical bauxite. Iron is a very important component in bauxites and represents the basic component of the gangue. Depending on its mineralogical form, it acts differently and can limit the

dothermal changes caused by dehydration of boehmite and kaolinite, was recorded at the temperature of 564 °C. In this region, crystal water from boehmite present in the sample, the „deficient boehmite“ which is formed by dehydration of gibbsite and kaolinite, is separated. These effects are overlapped on the DTA curve into one extended and weak peak and are difficult to separate. Although this change is somewhat more easily discernible on the DTG curve, the loss of mass cannot be determined which belongs to individual reactions. However, the results

shown are sufficient to be a complement to the XRD analysis results (Figure 5).

According to the surface of the characteristic endothermic peaks and based on the results of the XRD analysis, the Čitluk bauxite contains more boehmite than the gibbsite phase. Using the DTA curve it is difficult to establish the presence of goethite, though the change on the DTG curve at 387 °C and the loss of mass (TG) could correspond to goethite. Dehydration peak of gibbsite was observed at 322 °C, and endothermic peak at 541 °C is the result of dehydration of boehmite and kaolinite (Figure 6).

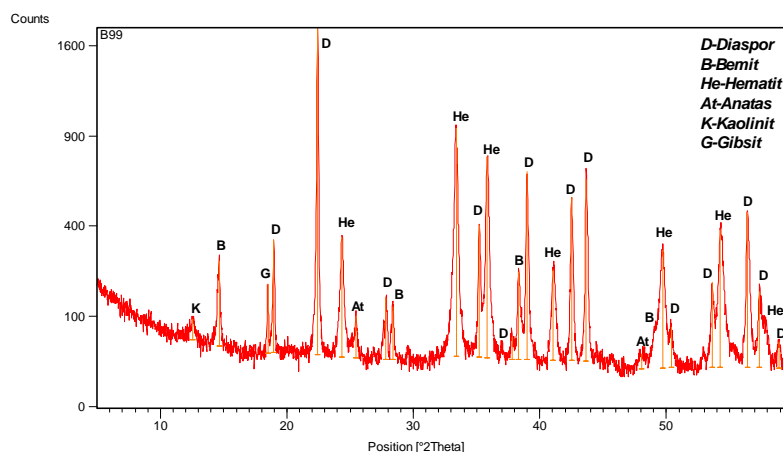


Figure 4. Diffractogram of the Kosovo bauxite sample

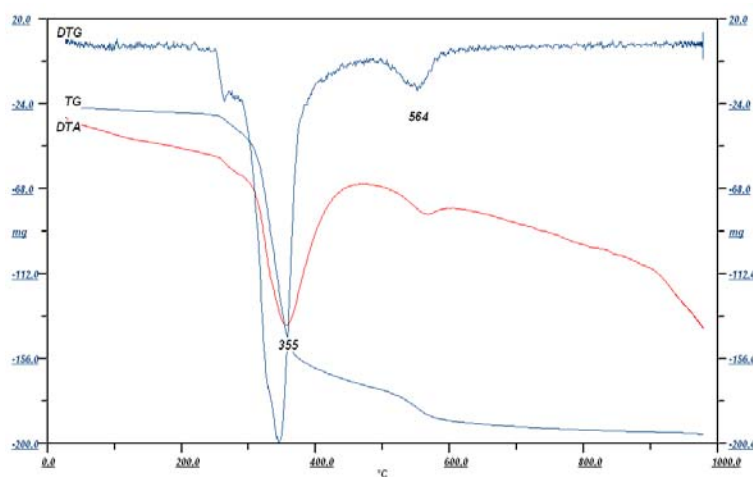


Figure 5. Thermogram of the Brazil bauxite sample

From the aspect of thermal analysis, the Milići bauxite is of boehmite type which is confirmed by the reaction of dehydration of boehmite in a characteristic temperature range at the temperature of 549 °C. According to the diffractogram of the investigated sample, all the SiO₂ is in the form of kaolinite, which is obvious based on the characteristic peak at the temperature of 586 °C. This peak is covered by dehydration of boehmite, so that it is much

drawn out on the DTA curve; however, it can be more easily discerned if the DTG curve is taken into consideration. The DTA curve of the Kosovo bauxite shows only one endothermic peak at 538 °C, which corresponds to the reactions of dehydration and removal of the structural water of diaspore, boehmite and kaolinite. Due to a low content of boehmite and kaolinite compared to diaspore, these effects overlap with dehydration effect of diaspore

(Figure 8). Based on the results of electron microscopy with microprobe analysis it is obvious that aluminium minerals occur in bauxite with dispersed impurities of iron silicon and titanium minerals (Figure 9–12). The microprobe analysis shows that

elementary composition of certain points is not homogeneous. When it comes to the Brazil bauxite, certain compact structure of hydrargilite particles is observed with impurities of iron, silicon and titanium minerals (Figure 9).

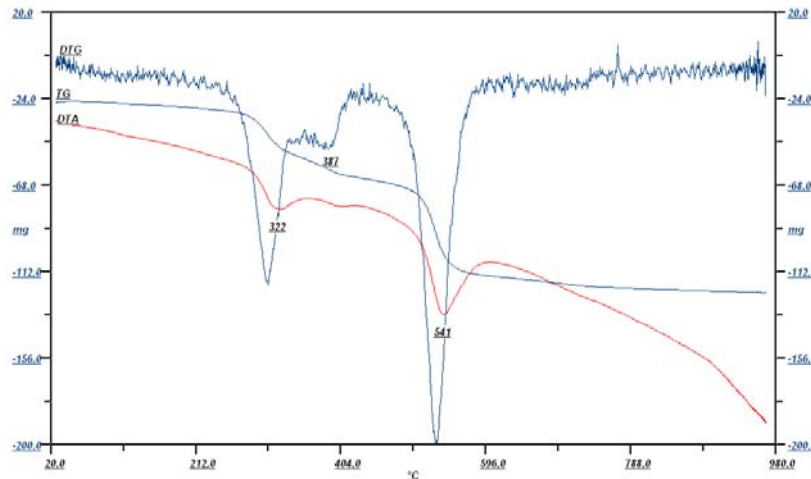


Figure 6. Thermogram of the Čitluk bauxite sample

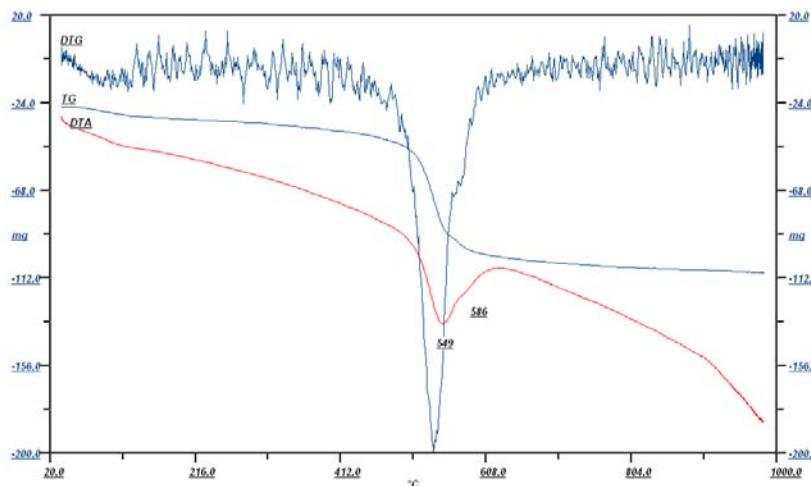


Figure 7. Thermogram of the Milići bauxite sample

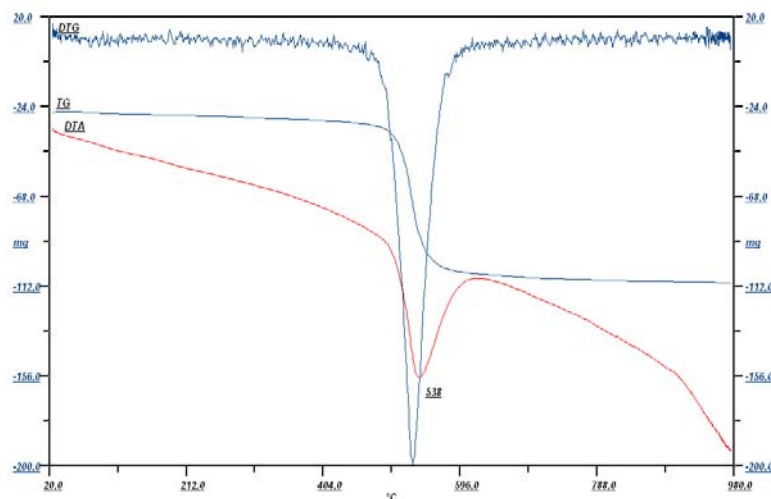


Figure 8. Thermogram of the Kosovo bauxite sample

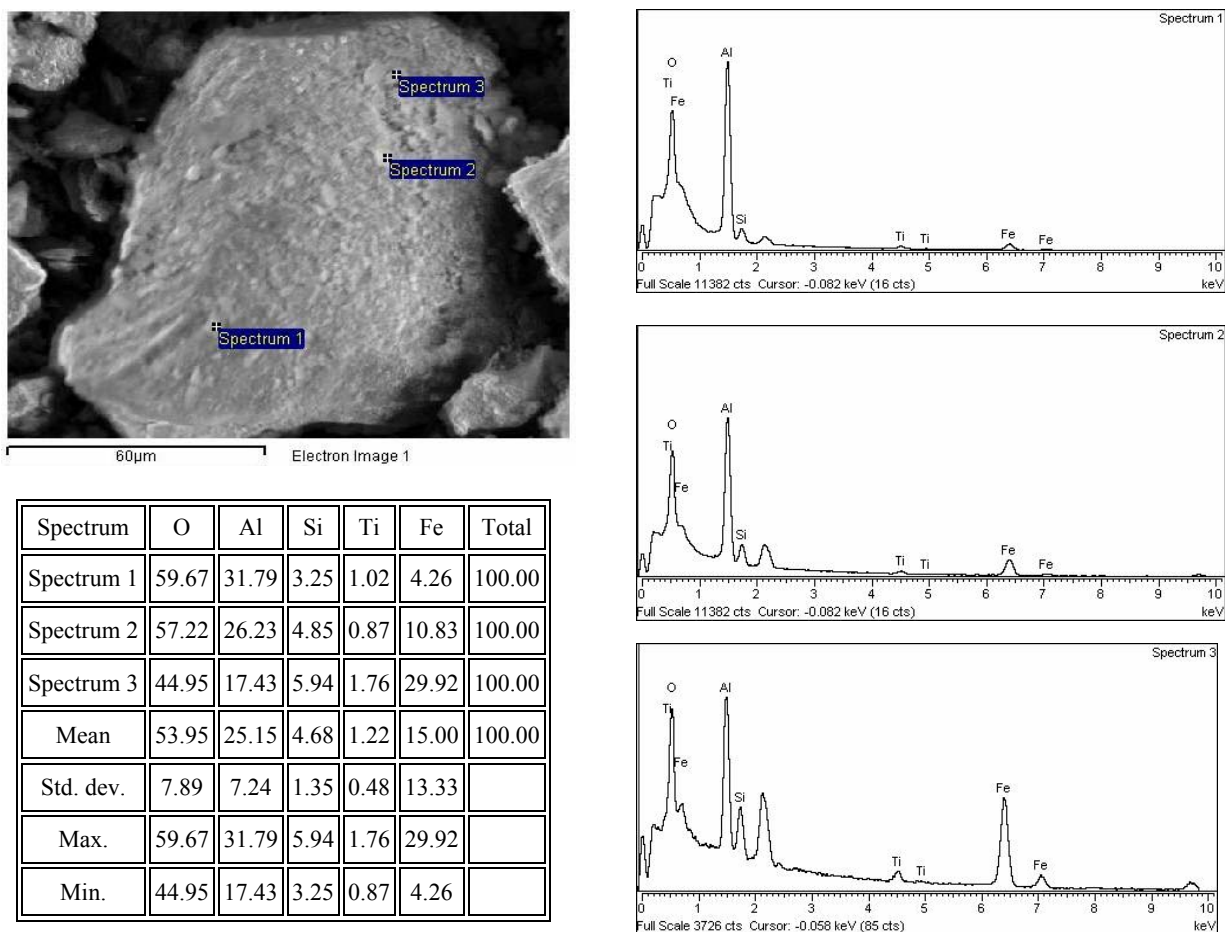


Figure 9. EDX for the Brazil bauxite sample-three points of one particle

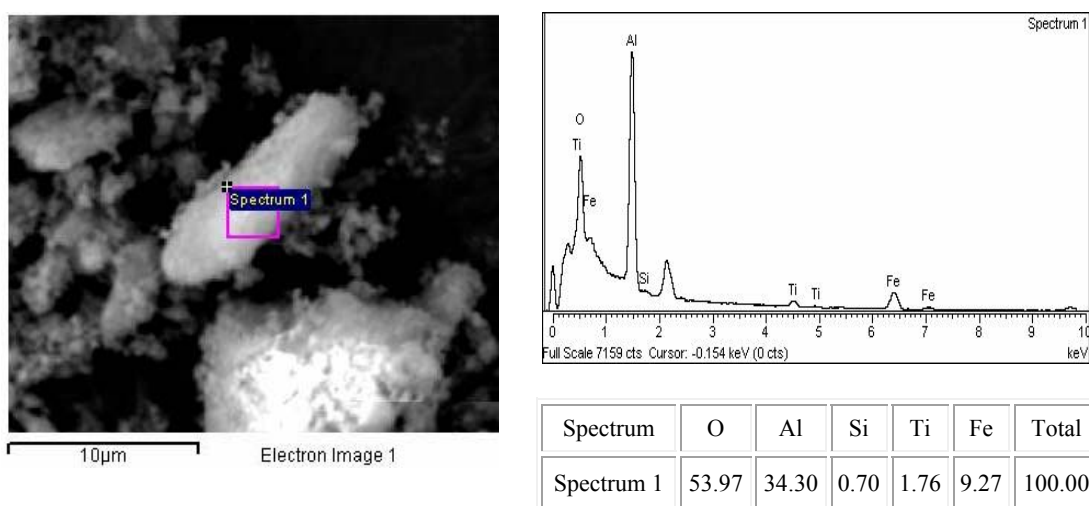


Figure 10. Electron microscopy snapshot (SEM) with EDX for the Čitluk bauxite sample

These impurities of other minerals are also present on polyhedron boehmite particles in the Milići bauxite, the most common one being hematite (Figure 11). Results of the electron microscopy of the Kosovo bauxite show diaspore particles of irregular shape,

with inlays of minerals of other elements, especially those of hematite. However, based on EDX analysis of several points, in certain regions there are clearly discernible round hematite particles with impurities of other elements, which is expected considering a high

content of Fe_2O_3 in bauxite. The results of these investigations that we presented are another proof of the complex composition of bauxite and they confirm the

data found in literature stating that minerals in bauxite are intertwined rather than occurring separately (Figure 12).

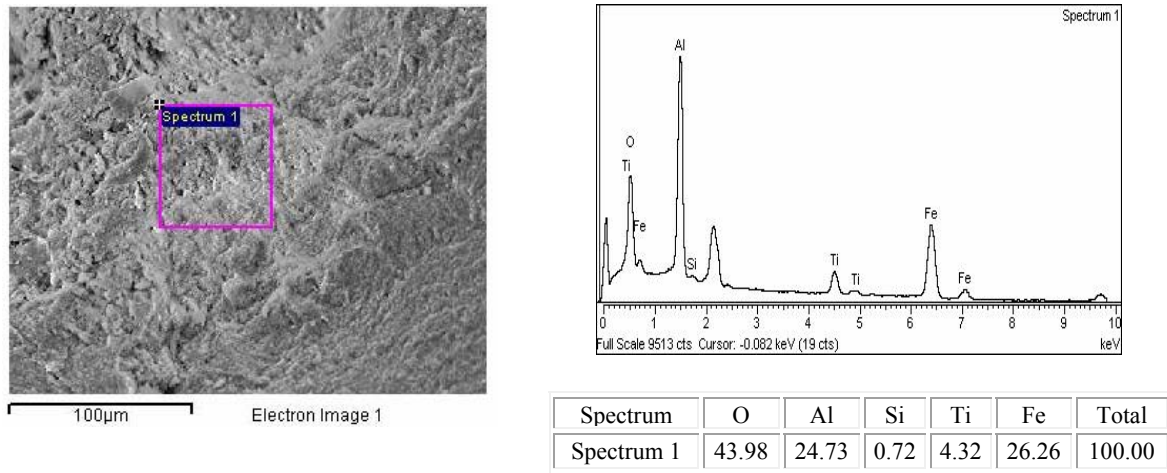


Figure 11. Electron microscopy snapshot (SEM) with EDX for the Milići bauxite sample - boehmite type

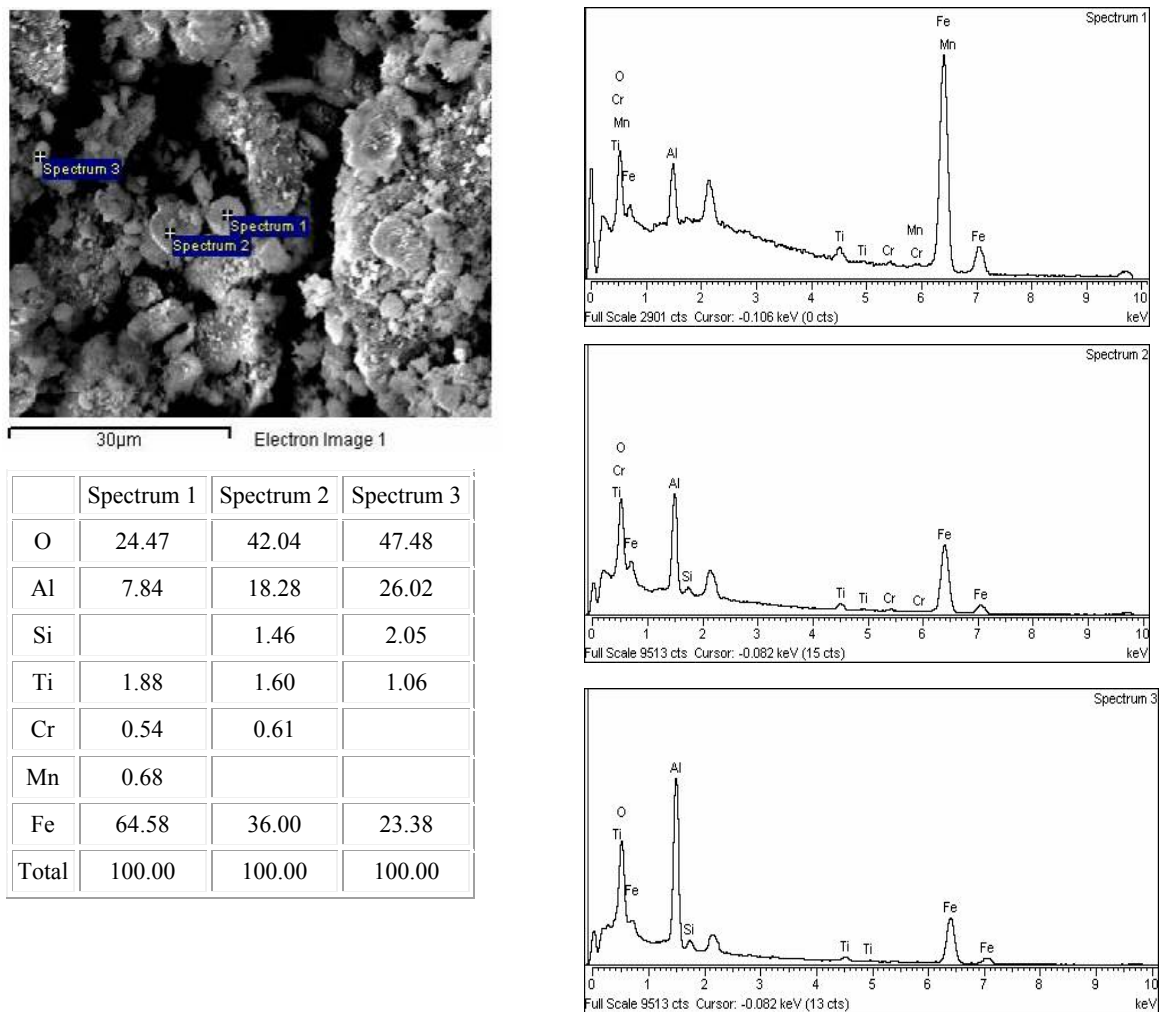


Figure 12. Electron microscopy snapshot (SEM) with EDX for the Kosovo bauxite sample – diaspore type

4. CONCLUSIONS

According to the results of all the investigations that were carried out (XRD, DTA, TG, DTG, AAS, UV-VIS, SEM with EDX analysis) it has been determined that the bauxites have the following characteristics:

– The main components in the investigated bauxites are the following: Al_2O_3 , Fe_2O_3 , SiO_2 , TiO_2 and CaO , whereas the following occur as micro components: P_2O_5 , V_2O_5 , ZnO , MnO , Cr_2O_3 , organic substances, etc.

– The Brazil bauxite is typical hydrargilite bauxite with Al_2O_3 mass fraction of 53.11% η_{Si} -10.17 silicon module. It is high quality bauxite, the mineralogical composition of which contains the following phases: hydrargilite, nordstrandite, boehmite, goethite, hematite, kaolinite and anatase.

– The Čitluk bauxite belongs to the mixed type with 57.38% Al_2O_3 , 3.99% SiO_2 and η_{Si} -14.38 silicon module. It is high quality bauxite, but a considerable quantity of Fe_2O_3 is in the form of goethite which could have a negative effect on certain stages of processing. Qualitative mineralogical composition contains the following phases: boehmite, gibbsite, hematite, goethite, kaolinite, anatase, rutile, and calcite.

– The Milići bauxite is typical boehmite bauxite, with Al_2O_3 mass fraction of 53.27%, SiO_2 of 5.69% and silicon module of η_{Si} -9.36, with the following mineral forms present: boehmite, hematite, kaolinite, rutile, anatase and traces of calcite.

– The Kosovo bauxite is typical diaspore bauxite, with a very high silicon module (33.49), and a higher content of hematite (37.25%). The phase composition of the sample contains the following mineralogical forms: diaspore, boehmite, hematite, kaolinite, anatase, calcite, and possibly a small amount of gibbsite and rutile. Since diaspore has the most stable structure of all aluminium minerals, processing of this bauxite according to Bayer process requires a higher temperature and energy consumption, so the presence of other types of bauxite is not desirable.

– Based on the results of electron microscopy with EDX analysis it is obvious that aluminium minerals in bauxite occur with dispersed impurities of iron, silicon and titanium minerals. The microprobe analysis shows that elementary composition of certain points is not homogeneous.

– Chemical and mineralogical composition of the selected bauxites is complex and varies widely depending on geographical background and the manner of formation. From the aspect of their application in the production of alumina, the investigated bauxites are of high quality; however, the final decision requires a technological characterization in the form of the Bayer process simulation.

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ХЕМИЈСКО-МИНЕРАЛОШКА КАРАКТЕРИЗАЦИЈА БОКСИТА РАЗЛИЧИТИХ ЛЕЖИШТА

Сажетак: Са становишта хемијског и минералшког састава боксити су комплексне вишекомпонентне сировине. У раду је извршена карактеризација боксита неколико различитих лежишта: Бразил, Милићи, Читлук и Косово. Хемијске карактеристике одређене су комбинацијом више аналитичких метода: гравиметрија, потенциометријска титрација, атомска апсорпциона спектроскопија (AAS) и UV-VIS спектрофотометрија. За утврђивање минералшког састава коришћене су рендгенска структурна анализа (XRD) и методе термичке анализе (DTA, TG, DTG). Допуну хемијској и структурној карактеризацији пружају резултати скенирајуће електронске микроскопије (SEM) са EDX анализом. Добијене информације искоришћене су за оцјену квалитета испитиваних боксита са аспекта њихове примјене у производњи глинице.

Кључне ријечи: боксит, карактеризација боксита, x-гау дифракција, термичка анализа, AA спектрофотометрија, UV-VIS спектрофотометрија.

