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CHARACTERIZATION OF THE RED MUD RESULTED FROM THE ALUMINA BAYER PROCESS PRODUCTION FOR THE FUTURE USE IN GEOPOLYMERS SYNTHESIS

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ABSTRACT

This paper presents the results of analyses on the chemical, structural and morphological processing of bauxite red mud resulting from alkaline wet Bayer technology. The characterization of the material considered as waste from alumina production industry aims at obtaining geopolymeric materilas. The results obtained were compared to literature data and support further research for the synthesis of inorganic polymers (geopolymers) intended for the manufacture of construction materials, starting from red mud as base material.

KEYWORDS: red mud, geopolymers, property, building materials

1. Introduction

The solid and semi-solid industrial waste is generated in large quantities in many production processes, which involve real problems with treating and storage. Geopolymerization as a recycling or reuse of waste technique, has become attractive both because of the need to resolve environmental issues and sustainability and stability of the material while geopolymeric materilas are obtained. By geopolymerization, a rich source of aluminosilicate is activated in a strongly alkaline solution to yield a solid, compact polymer structure due to the typical network of three-dimensional arrangement of atoms [1]. Because the reactions that occur are running in parallel and can not clearly distinguish the mechanism of the geopolymerization, in literature, there have been proposed four stages, namely: the first stage corresponds to the dissolution of Al and Si atoms in aluminosilicate materials in strongly alkaline solution; the second stage is the formation of oligomers in the aqueous phase of Si-Si and/or Al-Si; the third stage is the stage of polycondensation of the oligomers and the formation of three-dimensional aluminosilicate grid and the fourth stage is the formation of a solid geopolymeric structure [2].

Inorganic polymers, and hence the geopolymers, have outstanding chemical and physical properties, a chemical composition similar to that of zeolite even though their structure is amorphous, not crystalline. Wastes that are used most often as a source of aluminosilicate to obtain geopolymers are: fly ash [3-5] clay resulting from the production of pig iron [6-8] demolition waste [9] metakaolin result by kaolin calcination [10-12] and red mud resulting from the production of alumina by the Bayer process [13-16]. In this regard, the paper presents the results of analyses on the chemical, structural and morphological characteristics of red mud resulted from bauxite processing, using the wet alkaline Bayer technology. The characterization of this material aims at obtaining subsequent realization of geopolymeric materials. The results were compared to data from the literature and support further research to obtain inorganic polymer types (geopolymers) intended for the manufacture of construction materials, starting from red mud as base material.

2. The red mud

Red mud (RM) is the most important industry waste product from the alumina production by the Bayer process bauxite ore. In this process it is used a sodium hydroxide concentrated solution to solubilize the aluminum from bauxite ore in the condition of pressure and high temperature (150-250 °C) depending on the nature of the ore, respectively, gibbsitic, diasporic or bohemitic [17]. After completing the steps in the process red mud will result in the main-product and by-product aluminum hydroxide. The by-product is highly alkaline (pH = 10.5-13), has a high content of water [18], and a big content of heavy metals which make its re-use to be limited. Figure 1 shows the global production of NO exceeding 120 million tonnes (MT) annually [17].

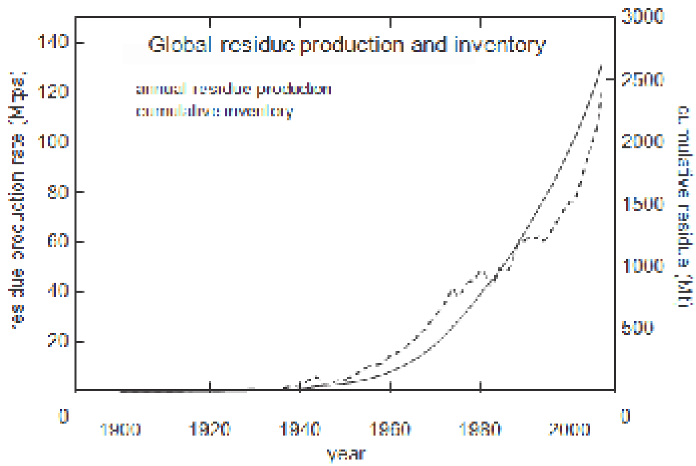

Fig. 1. *Global production and inventory production of red mud* [17]

As environmental legislation contains strict regulations regarding the disposal of untreated waste directly or unprocessed, and RM is subject to these regulations, storing it in any circumstances is prohibited [4]. Although there are many areas to use red sludge, recycling technology to meet environmental requirements and economic aspects has not yet been put into practice.

3. Experimental results

Red mud samples, uncalcined and calcined samples, were analyzed in terms of chemical composition using X-ray fluorescence spectrometry (XRF), a qualitative analysis was performed to determine the mineralogical composition and the phases of red mud by X-ray diffraction method (XRD), and determination of structure and elemental composition by electron microscope (SEM).

3.1. Materials and methods

In order to conduct the experiment it was used the red mud resulted from the Bayer alumina obtaining process, namely the dump from ALUM Tulcea. Freshly dried red mud grain was brought to 0.5 mm, after which a sample weight of 10 g was subjected to calcinationin a furnace type Lens Thermal Design, at a calcination temperature of 600°C with a heating rate of 10 °C/minute, an a hold time of 45 minutes. After calcination there was a weight loss of the sample subjected to calcination of about 23%.

3.2. XRF analysis

XRF analysis was performed with an analyzer type INOVIX Systems with a slot width of 1 cm^2. The measurements revealed the chemical composition of the item expressed as a percentage of red mud uncalcined and calcined respectively and are tabulated in Table 1 or Table 2. Following the results obtained for the sample calcined ash, it was observed a decreased percentage of iron and increased percentage of Al, Si, and Ti due to chemical reactions. The changes that occurred at that temperature increase is observed in the SEM images and by XRD analysis of these samples.

Table 1. *Elemental chemical composition of the uncalcined sample*

Element	Si	Al	Fe	Ti	Others elements	Total
Weigth (%)	7.20	8.58	78.43	5.33	0.46	100
Error (%)	0.19	0.48	0.86	0.35	0.03	--

Table 2. *Elemental chemical composition of the calcined sample*

Element	Si	Al	Fe	Ti	Loss of ignition	Total
Weigth (%)	11.01	12	69.99	6.3	0.70	100
Error (%)	0.23	0.56	0.88	0.42	0.01	---

3.3. XRD analysis

X-ray diffraction analysis (XRD) of the samples of fresh red mud and red mud calcined at calcination temperature of 600 °C were performed with DRON III analyzer, X-ray diffractometer, the endowment of the University of "Dunărea de Jos". This analyzer uses Co Ka radiation at a voltage of 30 kV, a current of 30 mA intensity 2θ and scans the wavelength of 1.78896 Å, with a range between 40° and 80°. By analyzing and characterizing the phases present in red mud many researchers [19-22] observed that the types of red mud differ and vary depending on the area, [23] how to extract alumina [24], on its age, on the warehouse [25]. Red mud is a industrial complex waste even though chemical analysis of the red mud mostly used in this study indicates the presence of calcium, silicon, iron and aluminum, and small amounts of titanium and sodium. Figure 2 shows the diffraction pattern of uncalcined red mud. The analysis of the diffraction pattern points out that the most important phases present in the uncalcined red mud are calcium carbonate as calcite ($CaCO_3$) and aragonite ($CaCO_3$), iron oxides, hematite (Fe_2O_3), otherwise observed in [26], respectively [27]. Sglavo *et. al* [19], considered that gibbsit, aluminum hydroxide ($Al(OH)_3$), aluminum oxide are decomposed at around 400 °C, crystallinity and stability are much less than the ones of aluminum oxide of corundum (α-Al_2O_3). It should be noted that, when the temperature rises up to 600 °C, aragonite peaks decrease and disappear completely at around 600 °C but calcium oxide can be detected in the samples treated at 500 and even 600 °C, suggesting that decomposition of aragonite in CaO is in the range 500-600 °C.

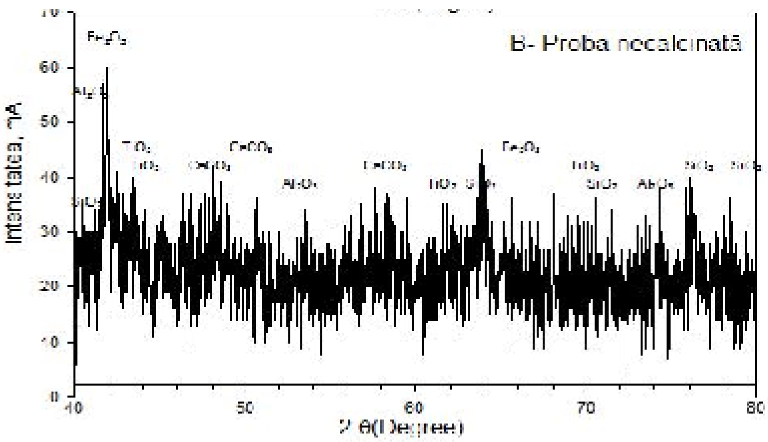

Fig. 2. *XRD spectrum diffractograms patterns of the uncalcined sample*

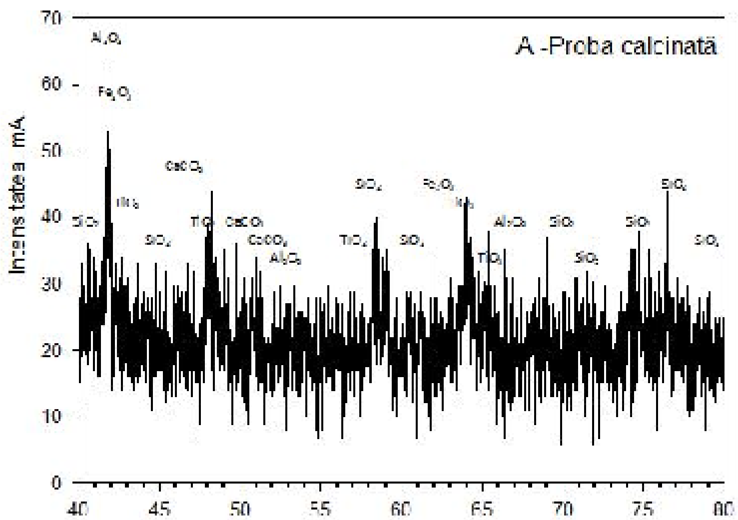

Fig. 3. *XRD spectrum diffractograms patterns of the calcined sample*

By comparing the observed spectra to both an increase in the intensity of peaks corresponding to oxides of aluminum, silicon, titanium, when calcined sample and a corresponding decrease in peak intensity of iron oxides, which is observed in X-ray fluorescence analysis, the mass of uncalcined sample elements is different compared to the calcined sample.

3.4. SEM analysis

SEM analysis of the structure of the scanning microscopy was conducted in the laboratories of UDJG, the type QUANTA analyzer 200, which is provided with an EDAX analyzer type.

These analyses were carried out on sample calcined at 600 °C and uncalcined sample to reveal structural changes that occur as a result of the heat treatment applied. In Figures 4 and 5 are shown SEM images of an uncalcined sample and calcined sample in Figures 6 and in Figure 7 are shown the images spectra of samples of red mud and elemental chemical composition of these samples, and in Figures 8 and 9 are given maps of the layout of the main chemical components of red mud uncalcined and calcined samples.

Through the comparison of the SEM image of the uncalcined and calcined red mud, SEM image at 600 °C, it is noted that the red mud particles at 600°C are low-crystalline or have amorphous form.

This indicates that the red mud calcined at 600°C is more reactive than the uncalcined one, and can provide a good cementitious property when used in combination to obtain a new binder, otherwise shown in other studies [28-30].

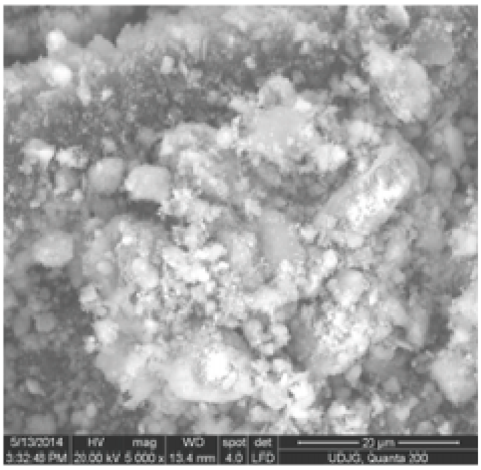

Fig.4. *SEM image of an uncalcinated sample*

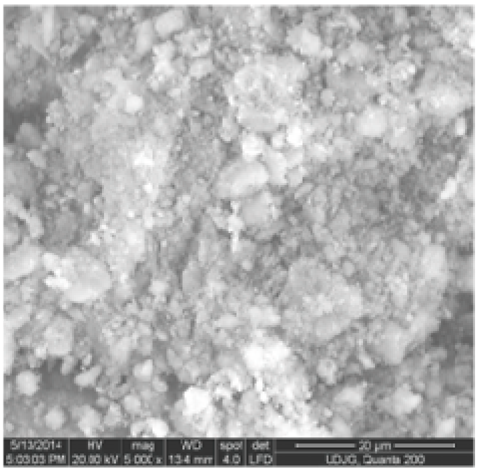

Fig. 5. *SEM image of a calcinated sample at 600 °C*

Table 3. *The elemental chemical composition of the uncalcinated sample, EDAX analysis*

Element	C	O	Na	Al	Si	Ca	Ti	Fe
Mass (%)	18.06	40.81	5.33	7.87	4.25	3.01	3.20	17.47
Atomic mass (%)	29	49.21	4.47	5.63	2.92	1.45	1.29	6.03

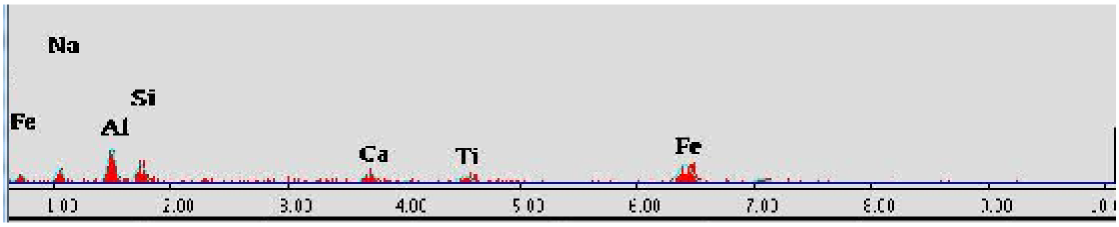

Fig. 6. *Uncalcined sample spectrum image*

Table 4. *Elemental chemical composition of the calcined sample by EDAX analysis*

Element	C	O	Na	Al	Si	Ca	Ti	Fe
Mass (%)	6.00	40.76	6.40	11.31	8.29	4.14	2.95	20.14
Atomic mass (%)	10.93	55.80	6.10	9.18	6.46	2.26	1.35	7.90

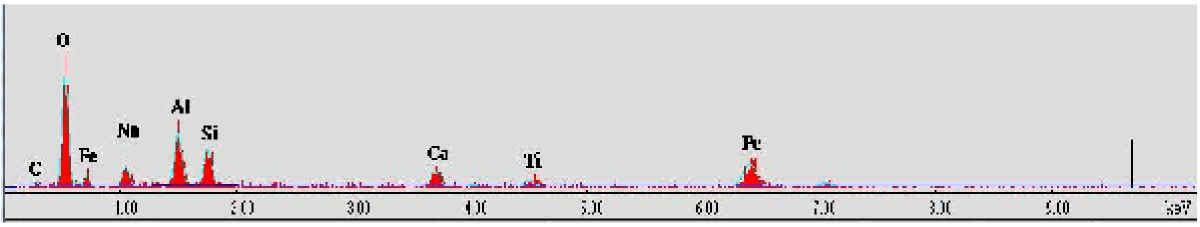

Fig. 7. *Calcined sample spectrum image*

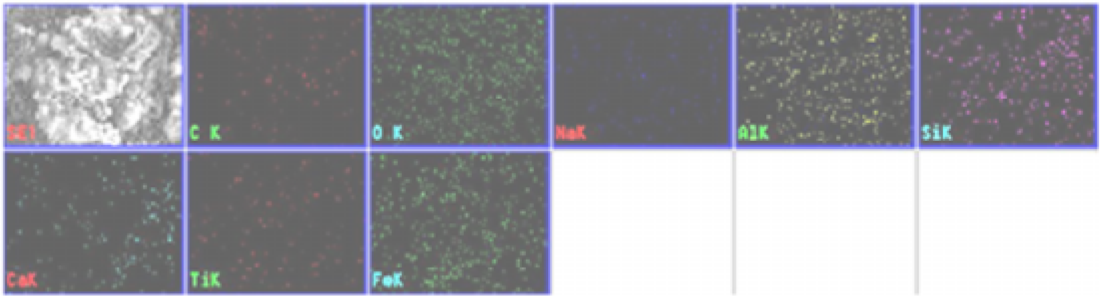

Fig. 8. *Distribution maps of the main chemical elements in the uncalcined sample*

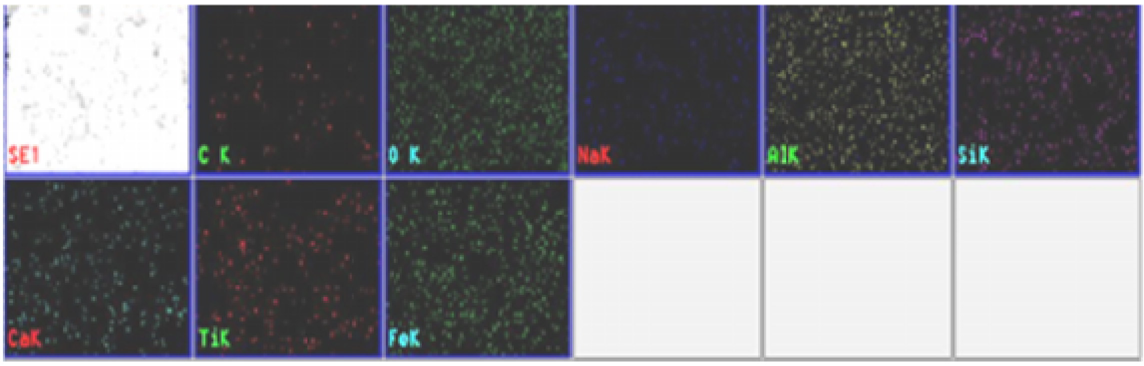

Fig. 9. *Distribution maps of the main chemical elements in the sample calcined at 600 °C*

From the analysis of scanned images by scanning electron microscopy it was observed that changes have occurred in the morphology and structure of the calcined sample, as evidenced by the overall appearance of the amorphous phase compared to the sample subjected to the calcination treatment phase is predominant crystalline phase. The explanation for these changes is that during the ignition chemically and physically bound water was removed and some metastable phase, for example silica, in the form of tridymite, has been converted into the stable phase, namely the lower cristobalite, which has been demonstrated by XRD analysis.

4. Conclusion

1. Geopolymers are materials produced by geosyntesis of an aluminosilicate material in a strongly alkaline solution and have developed several lines of operation. Literature has highlighted advantages of geopolymers synthesis, such as the fact that these materials are obtained at a low production cost, contributing to lower environmental pollution, and are long-lasting materials.

2. The results on the characterization of red mud from the point of view of the chemical composition, structure and morphology are comparable to some data from the literature on capitalization of red mud geopolymers in building materials.

3. XRF analyses, XRD and SEM performed on red mud pointed out the fact that after calcination, red mud uncalcined amorphous phases were transformed into crystalline phase that helps to form a material with geopolymeric properties, obtaining useful and superior construction materials.

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