"Gheorghe Asachi" Technical University of Iasi, Romania

DETERMINATION OF THE RARE EARTH METALS IN THE RED MUD FOR POSSIBLE UTILIZATION

Tatjána Juzsakova[1]*, Ákos Rédey[1], Le Phuoc Cuong[2], Zsófia Kovács[1], Tamás Fráter[1], Alexandra Csavdari[3], István Ráduly[4], János Lauer[1], József Németh[1], Viktor Sebestyén[1]

[1]*Institute of Environmental Engineering, Faculty of Engineering, University of Pannonia, 10 Egyetem St., Veszprém, 8200, Hungary*
[2]*The University of Danang, University of Science and Technology, 54 Nguyen Luong Bang St., Lien Chieu, Danang, Vietnam*
[3]*Department of Chemical Engineering, Babes Bolyai University, 30 Fântânele St., Cluj-Napoca, 400294 Romania*
[4]*Faculty of Economics and Business Management, Babes-Bolyai University, Sfantu Gheorghe, 520036 Romania*

Abstract

Huge amount of red mud has been disposed for the past several decades and it is still generating all over the world. Red mud is a waste of the bauxite processing industry obtained during the alkaline extraction of alumina from bauxite ore. The red mud is a potential raw material containing several valuable components including iron, titanium and rare earth metals. The aim of the research was to develop an appropriate acid digestion technique for the red mud in order to determine the amount of rare earth metals (Nd, Sc, Ce, Gd, Sm, La, Y, Pr, Eu, Dy, Ho) in the red mud by ICP analysis. Sand bath acid digestion and microwave acid digestion techniques were applied. Based on the outcome of the ICP analyses conclusions were drawn on the determination of the individual REE elements regarding the optimum conditions (type of acid digestion, acids applied) of the acid digestion. The highest value for the total amount of REEs (923 ppm) in the red mud was obtained after microwave digestion in $3HCl:1HNO_3$ acid mixture. The precise determination of the metal composition of the red mud is the first step in the development of utilization process for the red mud.

Key words: microwave acid digestion, red mud, rare earth metal elements, sand bath acid digestion

1. Introduction

Aluminum industry and alumina production in Hungary goes back to the middle of the last century. At that time several bauxite processing plants had been constructed and operated at Mosonmagyaróvár, Ajka and Almásfüzitő. Since the year 2000 only one plant of MAL Hungarian Aluminum Production and Trade Company Limited by Shares at Ajka city has been operating using Bayer technology. Due to economic reasons in June 2014 the production of aluminum hydroxide was terminated at MAL Co. Ltd. (HGV, 2014). The red mud is a residue of the bauxite processing industry obtained during the alkaline extraction of alumina from bauxite ore (Yuzhakova et al., 2014). The Bayer process for producing alumina includes leaching of bauxite ores with a solution of sodium hydroxide (NaOH) to extract alumina minerals contained therein as a solution of sodium aluminate ($NaAl(OH)_4$). At the same time, as much as one third to one half of the total weight of the ore used is discharged as a residual red mud (Fulford et al., 1991).

Aluminum production in Hungary has generated around 50 Mt of red mud which was stored at disposal sites and has not been utilized. The red mud

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* Author to whom all correspondence should be addressed: e-mail: yuzhakova@almos.uni-pannon.hu; Phone: +36 88624403; Fax: +36 88624553

contains the following main elements: iron(III) oxide (Fe_2O_3) 12-48 wt%, calcium oxide (CaO) 2-42 wt%, aluminum(III) oxide (Al_2O_3) 12-26 wt%, silica (SiO_2) 8-43 wt%, titania (TiO_2) 4-18 wt% and sodium oxide (Na_2O) 2-11 wt% (Fulford et al., 1991; MAL Ltd, 2010; Pascual et al., 2009). The differences between these different values of red mud are due to the type of bauxite used and to the Bayer process technological parameters such as digestion temperature and pressure, amount of caustic soda added, etc. (Pascual et al., 2009). The red mud also contains small, however, valuable quantities of vanadium (V) 0.1 wt%, zirconium (Zr) 0.1 wt%, niobium (Nb) 100 ppm and rare-earth elements (REE) 0.1-0.3 wt% such as cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), dysprosium (Dy), holmium (Ho), erbium (Er), yttrium (Y), scandium (Sc), and lanthanum (La) (Fulford et al., 1991; Lakatos et al., 1978; Ochsenkühn-Petropulu et al., 2002). Therefore the red mud can be considered as a secondary raw material because of its valuable metal content. The total amount of REEs estimated in the Hungarian red mud is about 1500-2500 ppm (0.15-0.25 wt%) (Lakatos et al., 1978; Szépvölgyi and Kótai, 2012). The published data on the REE content in the Hungarian red mud are summarized in Table 1.

Table 1. REE content of bauxites, Hungarian red mud and manganese deposit in Hungary

REE element (ppm)	Bauxite[a]	Red Mud[a]	Red Mud[b]	Red Mud[c]	Úrkút deposit[d]
Sc	30	55	120	128	6
Y	66	120	121	195	-
La	133	240	299	372	60
Ce	265	450	188	1254	172
Pr	10	10	-	172	-
Nd	74	190	-	397	42
Sm	10	23	127	44	15
Yb	-	-	-	-	5
Gd	-	<0.003	-	-	-

Note: a - (Lakatos et al., 1978); b- (Szépvölgyi and Kótai, 2011); c- (Herbst et al., 2011); d- (Grasselly and Pantó, 1988)

In addition to REE values given in Table 1 the presence of Eu, Dy, Ho, Er in red mud was reported in the literature (Fulford et al., 1991). No quantitative data are available for the previously mentioned four REE elements in the deposited red mud in Hungary. As it can be seen in Table 1 that REEs are present in more concentrated form in the red mud in comparison with the respective figures of the original bauxite ore (Lakatos et al., 1978) or in the manganese deposit of Úrkút (Bakony mountains, Hungary) (Grasselly and Pantó, 1988). Therefore it can be concluded that the potential source of the REEs could be the red mud in Hungary.

Determination of the composition of rare earth metals in this work was carried out on samples taken from the slurry reservoirs at Ajka. The red mud disposal facilities in Ajka contain 35 Mt (with 70% dry matter content) of red mud. There are another minor disposal sites at Almásfüzitő and Mosonmagyaróvár

in Hungary, where totally 25 Mt of red mud is accumulated and most of the sites have been cultivated. The closed reservoirs at Mosonmagyaróvár were covered by clay and top soil on which special acacia shrubs were planted. One of reservoirs at Almásfüzitő is partly covered with the fly ash from the Dorog hazardous waste incinerator plant (Jávor and Hargitai, 2011), leading to modification of chemical composition and physico-chemical properties of the red mud. It is a challenge for the scientists and experts to devise technologies and processes in order to recover the valuable components/elements from the red mud. It should be noted that the red mud is considered to be hazardous waste material if the pH value of the red mud is high (higher than 11).

Up to now there is no economical and efficient utilization technology for the red mud industrial waste which could meet the safety and environmental regulations and requirements and at the same time it would be economically viable. In October 2010 an extremely serious environmental catastrophe - spill of the red mud sludge from storage reservoir - occurred in Hungary (Utasi et al., 2014). This disaster focused the attention of the scientists on the possibility of processing and utilization of the red mud and on decreasing the amount of red mud taken for disposal.

There are basically two main lines for the processing and utilization of the red mud. The first one is its use for construction material manufacturing. The second possibility includes the separation of different components and transformation of those into valuable products. The first step before the possible utilization of the red mud is the determination of the precise amounts of the elements in the red mud and neutralization of its caustic feature. This is followed by the utilization of the red mud e. g. for metal recovery and the use the valuable components e.g. as catalyst in environmentally friendly technologies. The rare earth components of the red mud could be used in electronic industry, the scandium can be used in solid oxide fuel cells (SOFC's), and aluminum alloys (Al-Sc alloys) (Duyvesteyn and Putnam, 2014).

The inductively coupled plasma optical emission spectrometry (ICP-OES) is a widely used technique for the determination of rare earth elements in low concentrations (Ochsenkühn-Petropulu et al., 2002). Before the analysis the solid samples should be dissolved/digested. For this purpose acid digestion is commonly used. Acid digestion/ or extraction can be performed in two ways: conventional - sand bath acid digestion (Melaku et al., 2005) and microwave acid digestion (Ghosh et al, 2011; USEPA, 2010).

The sample preparation with microwave energy radiation is one of the most efficient and convenient procedure. The method has several advantages: the extraction time is significantly lower, the solvent usage can be decreased and the efficiency can be improved with magnetic stirring (Martin at al., 2008). Acids or mixtures of acids, like HCl, HNO_3, H_2O_2, HF, H_2SO_4 are often used for digestion procedure. HF is applied for example to dissolve aluminosilicates. HCl and HNO_3 are very powerful in

dissolution of carbonates (Kulkarni et al, 2007; Martin at al., 2008). Martin at al. (2008) showed that for determination of total trace elements (Cd, Co, Cr, Cu, Mn, Pd and Zn) in concentration range of 3-400 ppm, the mixture of HCl-HNO_3 can be used. Elements such as Al, Ba,V, Ca, Cr, Fe, Mg, Mn, Mo, Ni, Na, Zn can be dissolved from sediments, sludges, soils with using nitric acid or alternatively with using nitric acid and hydrochloric acids (aqua regia) (USEPA, 2010). According to literature the dissolution of REEs from red mud can be achieved by dilute acid solution, with HNO_3 acid (Ochsenkühn-Petropulu et al., 1995, 1996, 2002), with HCl acid (Borra et al., 2015), with H_2SO_4 acid (Abhilash et al., 2014) or sulfur dioxide dissolved in water (Fulford et al., 1991). For the complete acid dissolution of the red mud aqua regia, HF, H_3BO_3 and H_2SO_4 were used (Ochsenkühn-Petropulu et al., 2002).

The objective of the research was to determine the rare earth metal element components of the Hungarian red mud and to compare the efficiency of the microwave digestion with that of the classical acid digestion. The solutions obtained during the digestion were analyzed with ICP-EOS method to determine the rare earth metal components in red mud (Nd, Sc, Ce, Gd, Sm, La, Y, Pr, Eu, Dy, Ho). The impacts of the digestion conditions and acid mixture applied on the efficiency of the metal recovery were studied as well.

2. Experimental

2.1. Sample preparation

The red mud sample used for the experiments was taken from the red mud disposal facility of Ajka, Hungary in 2012. Several filtered red mud samples formed on the drum filters during the dry technological process were taken and collected together in total amount of about 30 kg. From this amount 1 kg of red mud was provided for the experiment which is considered to be a representative sample for the determination of red mud elemental composition. The red mud sample was put into an oven and was kept at 105°C for overnight. The moisture content of the sample was 30%. The red mud was dissolved by using two methods: sand bath acidic digestion method and microwave acidic digestion method.

2.2. Microwave acid digestion

The amount of the red mud sample, volume of acid reagents (HNO_3, $1HNO_3$:$3HCl$) and reaction temperature were determined according to the recommendation of EPA Method 3051A for microwave assisted acid digestion of sediments, sludges, soils and oils (USEPA, 2010). In addition to this - mixture of acids were used for dissolution $3HNO_3$:$1HCl$, $3HNO_3$:$1H_2O_2$, $1HNO_3$:$1HCl$:$1H_2SO_4$ (1:1:1) with the purpose of comparison of the dissolution efficiencies with using different acids (Table 2).

The most widely used digestion technique is the microwave digestion carried out in closed vessel. Anton Paar Multiwave 3000 type device was used with microwave energy of 1700 W. The dried sample was weighted to the nearest 0.2500 g into a two fluorocarbon polymer microwave vessels (HF100), followed by addition of concentrated acid/s (nitric acid, hydrochloric acid, sulfuric acid) and hydrogen peroxide according to Table 2. Total amount of acid/s used was 12±0.1mL. The vessel was sealed and heated in the microwave unit equipped with pressure (max. working pressure of 40 bar) and temperature (max. working temperature of 220°C) controllers. The temperature was ramped to 175°C within 30 min followed by a contact time of 30 min. Then the vessels were cooled, vented and opened. After cooling, the vessel content was filtered with G4 porous glass filter (3-13µm) and diluted to volume of 25 mL and the samples were analyzed by the ICP-OES method. After each digestion run the filtered residue of the red mud was collected, dried and weighted. The amounts of the red mud residues (related to the original sample before dissolution) are given in Table 2.

2.3. Sand bath acid digestion method

The amount of red mud sample, the volume of acid reagents (Table 2) and digestion temperature for the sand bath digestion procedure were similar as used for microwave acid digestion in order to compare the efficiencies of the two methods. Approximately 0.5 g red mud was taken for the digestion and acids were added with using automatic pipette to red mud. The total amount of acid/s used for each experiment was 12±0.1mL. The digested red mud was placed onto sand bath and was kept for three hours at temperature 175°C. The boiling acid was condensed with spiral condenser. The red mud residue was separated from the solution with G4 porous glass filter (3-13µm). After each digestion step the filtered residue of red mud was collected, dried and weighted. The amounts of the red mud residues (in comparison with the same sample before dissolution) are given in Table 2.

2.4. Reagents

The following reagents were used in analytical grade: 65% nitric acid (HNO_3) and 85% sulfuric acid (H_2SO_4) from Molnar Chemical Ltd, Hungary 37% hydrochloric acid (HCl) from VWR Prolabo Co., Hungary and 30% hydrogen peroxide (H_2O_2) from Spectrum 3D, Hungary, were used. For the dilutions of the samples for ICP analysis distilled water was used. Table 2 contains the composition of the acid mixtures used for the experiments with sample indications.

2.5. ICP-OES analysis

The solutions obtained after the sand bath digestion and microwave digestion were taken for ICP analysis.

Table 2. Composition of acid mixtures used for the digestion and red mud residue after the digestion procedure

Acids		Acids				Red mud residue, %
	Ratio	HNO₃	HCl	H₂O₂	H₂SO₄	
Digestion on sand bath		Volume, mL				
HNO₃	1	12	-	-	-	47.8
3HNO₃: 1HCl	3:1	9	3	-	-	20.8
1HNO₃:3HCl [b]	1:3	3	9	-	-	**20.2** [a]
3HNO₃:1H₂O₂	3:1	9	-	3	-	44.4
1HNO₃:1HCl:1H₂SO₄	1:1:1	4	4	-	4	58.9
Microwave digestion						
HNO₃	1	12	-	-	-	27.8
3HNO₃:1HCl	3:1	9	3	-	-	26.5
1HNO₃:3HCl	1:3	3	9	-	-	22.6
3HNO₃:1H₂O₂	3:1	9	-	3	-	**16.4** [a]

Note: a - Number highlighted in bold shows the lowest amount of red mud residue measured; b –Aqua regia; c – Example of calculation:

$$\text{red mud residue} = \frac{m_2}{m_1} \cdot 100\% = \frac{0.1019}{0.5037} \cdot 100\% = 20.2\%$$

where: m_1 - mass of red mud sample before digestion, g; m_2 – red mud residue obtained after digestion process, g.

Elemental analysis was performed using inductively coupled plasma optical emission spectrometry (ICP-OES, hereinafter referred to as ICP) with Perkin–Elmer Optima 2000DV instrument (Perkin Elmer Inc., Wellesley, USA). The ICP was calibrated with using standards for each of the 11 rare earth metals.

Scandium, yttrium, lanthanum, praseodymium, neodymium, samarium, europium, dysprosium, holmium, gadolinium, cerium standard solutions in concentration of 1000 mg/l were provided for ICP analysis by Scharlab Ltd, Hungary. Standards were diluted to produce four calibration solutions for the investigated elements (0, 1, 2, 4 mg/L for Sc, Gd, Sm, La, Y, Eu, Dy, Ho, Pr elements and 0, 2, 4 and 8 mg/L for Nd and Ce elements). The wavelengths of the identification lines were as follows: Sc 361.383 nm; Gd 376.839 nm; Sm 359.260 nm; La 398.852 nm; Y 371.029 nm; Eu 381.967 nm; Dy 353.170 nm; Ho 345.600 nm; Pr 422.293 nm; Nd 430.358 nm; Ce 418.660 nm. The limit of detection (LOD = 3xSD/b) and the limit of quantification (LOQ = 10xSD/b) were calculated as the analyte concentration which corresponds to three times (LOD) and ten times (LOQ) of the standard deviation (SD) of fifteen (n=15) independent measurements of the blank, divided by the slope (b) of the calibration curve (Marin et al., 2008). The detection limit was higher than 0.001mg/L. The LOQ values mainly ranged from 1 to 200 μg/L depending on elements investigated (e.g. LOQ for Sc 1μg/L; Sm 136 μg/L; Y 7.2 μg/L; Dy 22 μg/L; Ho 93 μg/L). The analysis was carried out for three parallel samples for each digestion method applied and the relative standard deviations (RSD) for investigated rare earth metals was less than 5%.

2.6. X-ray diffraction techniques

The crystalline structure of well-grounded powders was examined by X-ray diffraction techniques (XRD). XRD patterns were recorded at room temperature by using a Phillips PW 1710 diffractometer (CuKα radiation source, λ=0.15406 Å). The samples were measured in continues scan mode with 0.02° *2θ* / s scanning speed.

2.7. Scanning Electron Microscope (SEM) study

The morphology of the dried red mud has been studied using a Philips XL30 SEM system having EDAX Genesis EPMA system. Accelerating voltage of 20 kV was used. SEM-EDX technique is widely used for determination of elemental composition of solid materials such as minerals (Shoumkova and Stoyanova, 2017) The magnifications 50 (M:50x) and 100 (M:100x) allowed to obtain the images in a 500 and 200 μm scale respectively. The red mud powder was fixed on a holder by double sided carbon adhesive tape. The sample was examined in lower vacuum water mode e.g. under the vacuum 1.2 mBar and without Au-coating of the specimen in order to improve detection limit of low concentration elements. Then the surface of the particle was photographed and simultaneously quantitative and qualitative electron probe microanalyses were performed. Electron beams were very finely focused. Therefore, elemental analysis of very small area on specimen surface was done in so-called "spot" mode. In this case the diameter of the microprobe beam was about 20 nm. The spot mode analysis was carried out for 4 points of the specimen (Fig. 3 points A, B, C, D). An average concentration of elements on specified area was determined using larger surface area scanning mode, so-called "area" mode. In this case the scanned surface was about 0.25 mm² (Fig. 3 area mode).

3. Results and discussions

3.1. Structural and morphological characterization of the red mud

In general the red mud contains several minerals including sodalite, cancrinite, hydrated Ca-

silacates, tri-calcium aluminates, hydrocalumites, calcite/aragonite, sodium carbonates (Grafe et al., 2009). Fig. 1 shows the XRD pattern of the original dried red mud powder used. As it can be seen in Fig.1, the main peaks of bohmite (AlOOH), rutile (TiO_2), hematite (Fe_2O_3), calcite ($CaCO_3$), hydrogarnet ($Ca_3AlFe(SiO_4)(OH_8)$), perovskite ($CaTiO_3$), cancrinite ($Na_6CaAl_6Si_6(CO_3)O_{24}2H_2O$), gibbsite ($Al(OH)_3$) crystalline structures were obtained for Ajka red mud sample. No crystalline lines for minerals containing REEs in the red mud were observed due to their low concentrations (ppm) and/or amorphous form which cannot be detected by XRD.

Hematite is present in all bauxite residues which provides its red color. Boehmite, gibbsite and anatase, rutile (both TiO_2) are the other minerals commonly present in bauxite residues (Lakos et al., 1978; Lockwood et al., 2014). Cancrinite with high probability is formed at elevated temperatures during the digestion of boehmite type bauxites. Perovskite and calcite are common in bauxite residue due to the addition of lime during the Bayer process (Grafe et al., 2009).

The amount of red mud residue was compared with the amount of the original sample before digestion / dissolution procedure and the results are summarized in Table 2. The best dissolution of the red mud was achieved in aqua regia for digestion on sand bath, and in combination of acids ($3HNO_3:1H_2O_2$) for microwave digestion where the values of red mud residues were 20.2 and 16.4 % respectively. The XRD pattern of the red mud after dissolution procedure in aqua regia is shown in Fig. 2. With this method the highest amount of total REEs was 923 ppm (0.09 wt%). Only rutile and anatise phases were detected after digestion of red mud in aqua regia (Fig. 2). It is in agreement with literature data where for dissolution of TiO_2 where HF acid was used (Ohno et al., 2001) or in combination with other acids.

The micrographs show that red mud is fine powder having variety particles sizes, mainly with particles less than 10 µm. Larger particles were also detected and those stem from agglomeration of smaller particles. The peaks of main components such as Fe, Al, Ca, Na, Si, Ti are observed on EDS spectrum (Fig. 3) which are agreement with XRD results and literature data (Pascual et al., 2009).

The elemental composition of small area of the specimen and chemical analysis of individual A, B, C, D points (Fig. 3) are summarized in Table 3. Selected points A, B, C and D showed higher concentrations of Fe, Al and Ca than in the investigated larger area of the specimen. The "area" mode provides information on the average elemental composition of the red mud sample. No separate peaks of REEs were resolved during the study with high probability due to overlapping of the energy bands of the main elements being present in high concentration.

E.g. La characteristic X-ray energy band at 4.65 keV is covered by Ti X-ray signal, and Ce band at 4.839 keV is covered by V X-ray signal. As it was mentioned above the REEs are present in ppm concentrations (in 10000 time less than main components) and this lower concentrations were impossible to be detected by SEM equipment used. Similar notes were made by Borra et al. (2015).
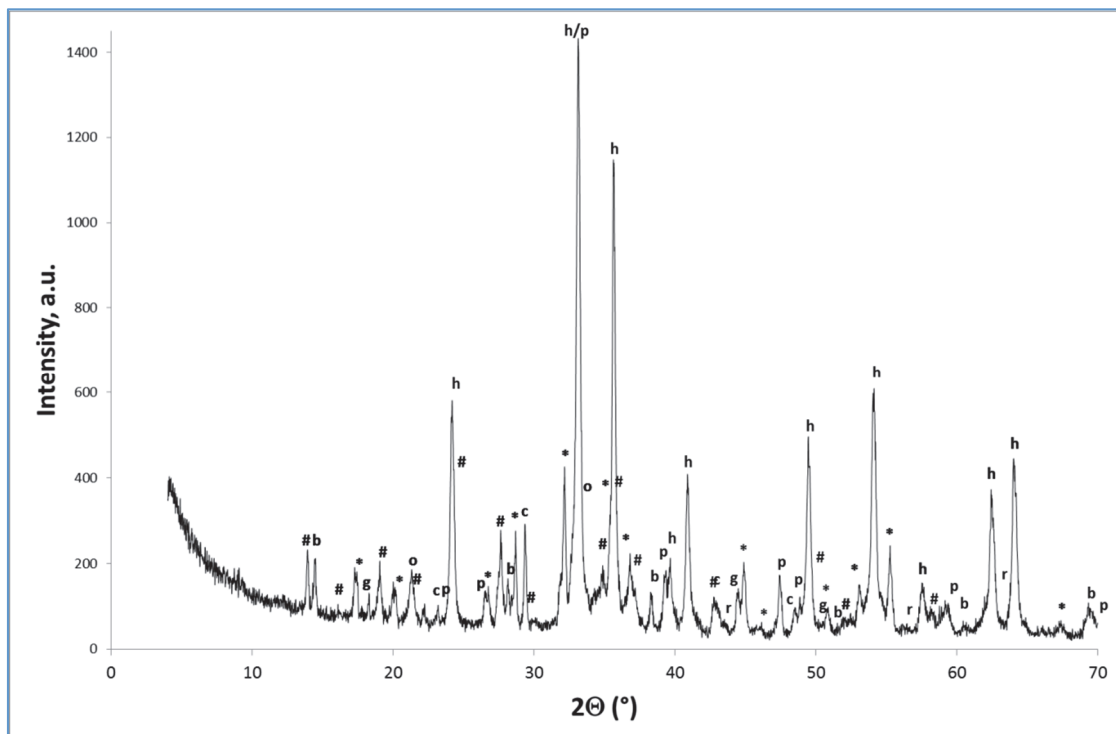

Fig. 1. XRD pattern of the original Ajka dried red mud, where b - bohmite; r - rutile; h - hematite; c – calcite; *- hydrogarnet; p - perovskite; # - cancrinite; g - gibbsite are crystalline phases
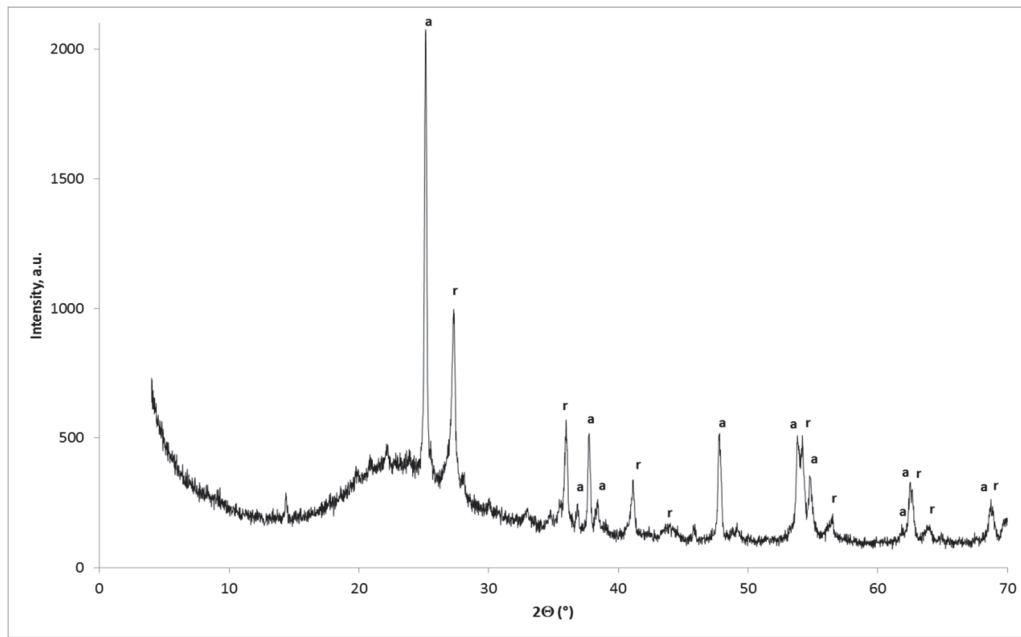
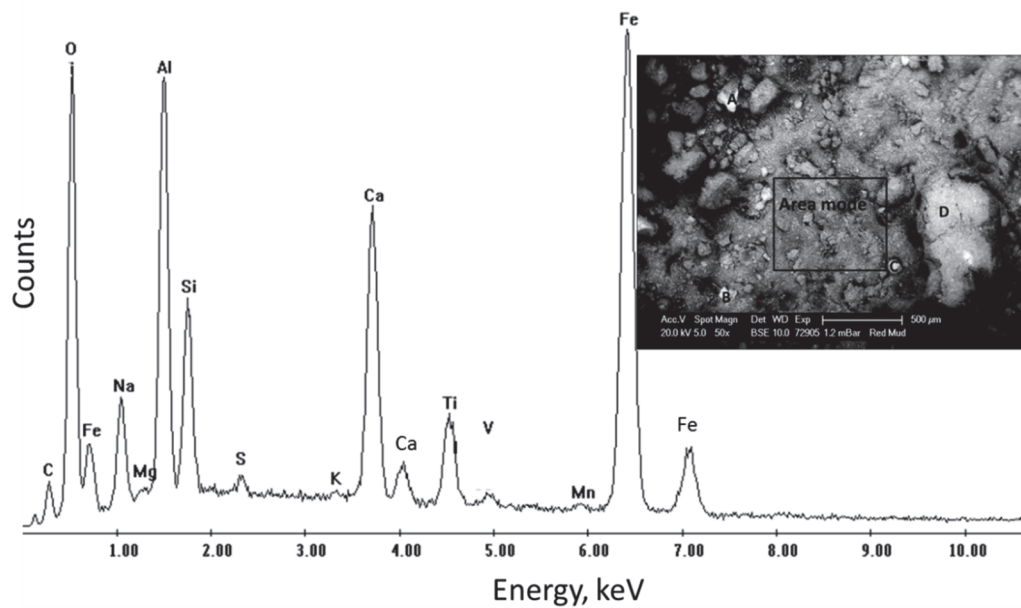**Fig. 2.** XRD pattern of the digested Ajka red mud in aqua regia, where r - rutile phase and q – anatase phase

Fig. 3. SEM micrograph of dried untreated red mud and EDS spectrum recorded in "area" mode
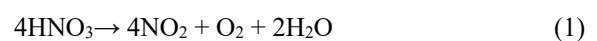
Table 3. Elemental composition of red mud determined by SEM, wt.%

Elements	*Fe*	*Al*	*Ca*	*Na*	*Si*	*Ti*	*Mg*	*Mn*	*S*	*K*	*V*	*Cr*
area	47.53	17.96	11.02	8.41	7.88	4.67	0.84	0.62	0.56	0.35	0.17	-
spot A	61.13	16.83	5.71	5.14	4.06	3.90	0.80	0.62	0.37	0.23	0.46	0.74
spot B	64.11	11.82	6.34	6.87	5.17	3.60	0.80	0.48	0.48	-	-	0.32
spot C	66.94	11.69	5.82	6.50	4.42	2.62	0.75	0.55	0.39	-	-	0.32
spot D	43.41	19.84	12.36	8.55	8.72	4.48	1.09	0.40	0.64	0.32	-	0.20

3.2. Microwave digestion

Comparison of temperature and pressure profiles during the microwave digestion process for using $1HNO_3:3HCl$ acids with or without red mud sample is shown in Fig. 3. The highest pressure (17 bar) in the microwave vessels was recorded in case of acid solution without red mud. Due to heat effect the decomposition of acids occurred in closed vessels according to the following equations (Eqs. 1-2):

$$4HNO_3 \rightarrow 4NO_2 + O_2 + 2H_2O \qquad (1)$$

$$2HCl \rightarrow Cl_2 + H_2 \qquad\qquad (2)$$

The gases formed increased the pressure in closed vessels from the atmospheric pressure to 17 bar. When the red mud is added to the solution pressure drop to about 11 bar occurred indicating that the acids react and generate soluble components thus less amount of gas phase is formed (Fig. 4).

3.3. REE concentration contents of the red mud

The solutions obtained after the sand bath digestion and microwave digestion were taken for ICP analysis. The results on dissolving the rare earth metals with applying two digestion techniques are summarized in Table 4. The decrease in the mass of the red mud after digestion indicates the dissolution of its elemental content: the low value of the red mud residues indicates that more elements were transformed into ionic form during sand bath / microwave digestions (Tables 2 and 4). The treatment of the red mud with mixture ($1HNO_3$:$1HCl$:$1H_2SO_4$) was carried out with only using sand bath method since using three acids simultaneously did not improve the solid sample dissolution.

The total amount of REEs (ppm) of red mud was higher in solutions obtained after microwave digestion in combination of different acids (except for the dissolution in HNO_3). The highest value of REEs (923 ppm) was detected for the dissolution of the red mud in aqua regia (Table 4).
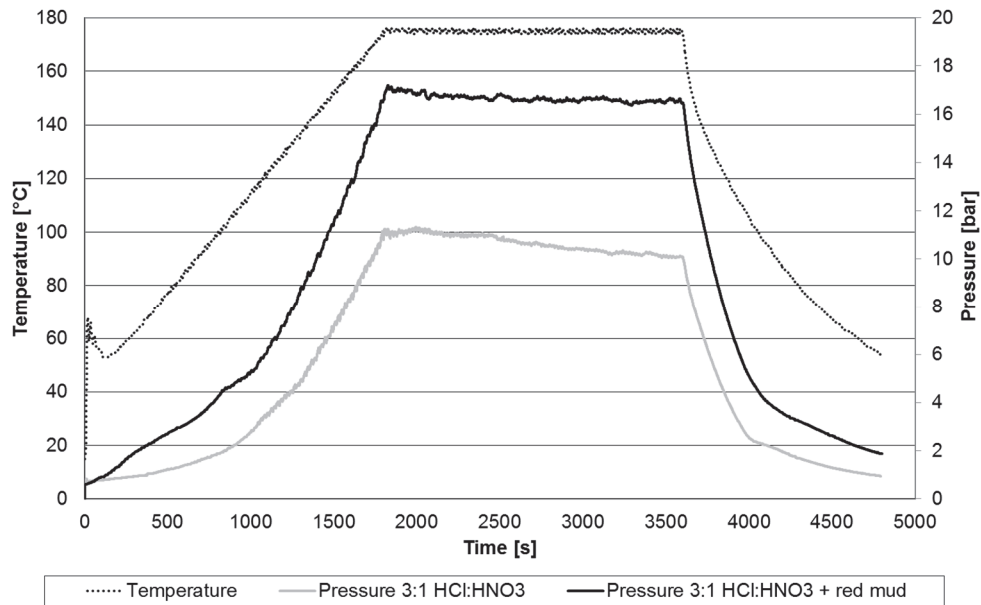

Fig. 4. Temperature and pressure profiles during microwave digestion process for using $1HNO_3$:$3HCl$ mixture with and without red mud sample

Table 4. The rare earth element contents of the red mud obtained from the sand bath and microwave digestions with using acids

Acid composition	Sc	Gd	Sm	La	Y	Eu	Dy	Ho	Pr	Nd	Ce	REE
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	total ppm
Sand bath digestion												
HNO_3	29.7	5.8	31.1	125.3	83.0	0.2	14.3	2.7	67.0	77.1	283.4	719.6
$3HNO_3$:$1HCl$	43.2	0.0[b]	33.7	105.2	60.6	0.0	14.5	3.3	56.3	63.4	269.8	650.0
$1HNO_3$:$3HCl$ king's water	53.0	0.0	35.8	118.5	67.1	0.0	**18.0**	**5.1**	46.1	80.6	**383.4**	807.6
$3HNO_3$:$1H_2O_2$	36.4	0.0	28.4	113.7	**84.3**[c]	0.0	15.1	3.4	49.7	69.2	293.1	693.3
$1HNO_3$:$1HCl$:$1H_2SO_4$	45.1	0.0	14.5	64.1	20.5	0.0	7.5	2.9	17.9	27.9	177.9	378.3
Microwave digestion												
HNO_3	41.4	0.0	**46.2**	97.1	72.9	0.0	17.1	2.4	27.7	49.6	311.5	665.9
$3HNO_3$:$1HCl$	50.1	0.0	36.6	156.6	63.3	0.9	15.6	2.3	109.3	86.6	319.0	840.3
$1HNO_3$:$3HCl$ king's water	**53.6**	0.0	38.7	**163.9**	80.7	0.0	16.8	2.8	115.8	91.9	358.7	**922.9**
$3HNO_3$:$1H_2O_2$	49.8	0.0	36.5	159.7	79.1	**1.1**	16.4	2.6	**115.9**	**92.9**	321.4	875.4
Average amount of REEs [a]	53.3	5.8	37.3	141.2	73.9	0.7	17.4	4.0	81.0	86.3	371.1	

Note: [a] *– Average amount of elements determined after digestions of the red mud in aqua regia by sand bath and microwave methods (except for Gd and Eu);* [b] *- Detection limit < 0.001mg/L;* [c] *- Number highlighted in bold indicates the highest element concentration measured*

However, this value is lower than reported in the literature, where for REE elements 1500-2500 ppm figure is given (Szépvölgyi and Kótai, 2011). The difference observed probably can be due to different procedure / acids applied for the determination of the elements. The improvement of the dissolution of REEs can be done by leaching of the red mud with dilute nitric acid which leads to selective and efficient recovery of REEs (Ochsenkühn-Petropulu et al., 2002). As it can be seen the amount of REE elements detected (Table 4) and reported in literature (Table 1) in the red mud is higher than in bauxite ore or manganese mineral deposit in Hungary. This makes the bauxite residue a valuable source of REEs.

The digestion method and the used acid mixture and its composition influence the dissolution of the 11 rare earth metals from the red mud.

The amount of gadolinium (6 ppm) was obtained in case of nitric acid digestion; the highest amounts of cerium (max. 383 ppm) and holmium (max. 5 ppm) were obtained in aqua regia digestion applying sand bath acid technique.

The highest amounts were measured in case of samarium (max. 46 ppm) with nitric acid digestion; in case of lanthanum (max. 164 ppm) with aqua regia digestion; in cases of europium (max. 1 ppm), praseodymium (max. 116 ppm) and neodymium (max. 93 ppm) with nitric acid and hydrogen-peroxide mixture digestion applying microwave acid digestion.

The detected amount of scandium after dissolution of the red mud sample in aqua regia was similar to that of the sample obtained on sand bath (53 ppm) and using microwave (54 ppm) digestion method. The amount of dysprosium (18 ppm) following nitric acid and hydrochloric acid digestion on sand bath was similar to the result obtained after digestion with nitric acid in microwave (17 ppm). The amount of yttrium (84 ppm) in red mud using sand bath with nitric acid and hydrogen peroxide digestion was similar to the results obtained after nitric acid-hydrochloric acid digestion in microwave (81 ppm). As it is mentioned above the addition of sulfuric acid to nitric acid and hydrochloric acid did not improve the dissolution of the rare earth metals studied. It can be assumed that the sulfuric acid reacts with red mud and forms insoluble sulfate compounds.

4. Conclusions

Structural data of red mud before the digestion procedure showed the presence of main mineral components such as bohmite, rutile, hematite, calcite, hydrogarnet, perovskite, cancrinite and gibbsite. SEM-EDX analyses gave information on the morphology and on the major elemental (as high as Fe, Al, Na, Ca, Na, Si, Ti) and minor elemental (less than 1 wt.%: Mg, Mn, S, K, V, Cr) composition of the red mud. REEs of low concentrations (at ppm level) were not detected by SEM-EDX.

The different digestion parameters such as concentration and volume of acids / oxidizing agents (e.g.: nitric acid, hydrochloric acid and hydrogen peroxide) and microwave oven parameters (e.g. digestion time, temperature and pressure) can be changed in order to achieve the complete dissolution/extraction of the rare earth metals from red mud prior to ICP analysis.

REE elements such as Eu, Dy, Ho were detected in red mud. These three elements were not reported in the Ajka red mud. It was observed that the dissolution of the studied 11 rare earth metals is different in acid mixtures. Adding of sulfuric acid to the acid mixture did not improve the digestion efficiency. The average concentrations (ppm) of the rare earth metals determined by ICP elemental analysis were studied. The red mud of Ajka contains the following elements in decreasing order according to their average content: Ce(371) > La(141) > Nd(86) > Pr(81) > Y(74) > Sc(53) > Sm(37) > Gd(6) > Ho(4) > Eu(1). The Ajka red mud contains cerium and lanthanum in the highest amount in agreement with the literature. On the basis of the experiments carried out it can be concluded that the digestion with microwave device is faster and meets the work safety regulations.

The microwave extraction method can be recommended for the determination of the rare earth metal composition of the red mud since it is more effective than sand bath method regarding the total dissolution of REEs. The exact elemental composition of the red mud is necessary for the elaboration of a processing technology of the red mud with the objective of the complex utilization of the bauxite residue. In this way the risks related with the storage of the red mud could be mitigated and the red mud as a potential secondary raw material could be considered for further utilization.

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