

Hydrogen Metallurgy for a treatment of bauxite residues-First results on the EURO-TITAN Project

Vodonik u metalurgiji za tretiranju boksitnih ostataka- Prvi rezultati na EURO-TITAN projektu

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Abstract

Hydrogen is the most abundant element in the universe (75 % by mass) and the lightest element (density of 0.00082 g/cm³). Because of its presence in many different forms such as gaseous hydrogen, its plasma species, water, acid, alkaline, ammonia and hydrocarbons, has high application in different metallurgical unit operations. In this paper, reduction of metallic oxides by hydrogen will be studied. Especially hydrogen reduction of the aluminium residues such as red mud from the Bayer Process will be discussed as first step in production of metallurgical solid residue needed for the recovery of valuable metals such as titanium, rare earth elements and iron.

Keywords: *hydrogen, reduction, metallurgy, recycling, red mud*

Izvod

Vodonik je najzastupljeniji element u univerzumu (oko 75 %) i najlakši element sa gustinom od 0.00082 g/cm³. Zbog prisustva raznih oblika vodonika kao što su gasoviti vodonik, razni plazma oblici, voda, kiselina, baza, amonijak i ugljovodonici, on ima veliku primenu u raznim osnovnim metalurškim operacijama. U ovom radu, redukcija metalnih oksida vodonikom biće proučena. Naročito, vodonična redukcija ostataka iz metalurgije aluminijuma kao što je crveni mulj iz Bajerovog procesa će biti diskutovana kao prvi korak u proizvodnji metalurških čvrstih ostataka neophodnih za ekstrakciju metala kao što su titan, elementi retkih zemalja i železo.

Ključne reči: *vodonik, redukcija, metalurgija, recikliranje, crveni mulj*

Introduction

Hydrogen as a key element in energy transition replacing fossil fuels and their CO₂ emissions was used as a reducing agent instead of carbon [1]. Application of hydrogen in metallurgical operations has gained strong interest in hydrometallurgy and pyrometallurgy of non-ferrous metals [2]. As mentioned by Rodriguez et al. [3] control of hydrogen formation during hydrometallurgical processes such as electrocoagulation and winning electrolysis has a high significance for the metal recovery. Generating green hydrogen efficiently from water and renewable energy requires high-end technology and innovative solutions — like the Silyzer product family from Siemens Energy. Using Proton Exchange Membrane (PEM) electrolysis, the Silyzer is ideally suited for harnessing volatile energy generated from wind and solar [4].

The Bayer Process is the traditional industrial method to produce alumina from bauxite ore. The chemical quality of precipitated aluminum hydroxide, and consequently the final alumina product in the Bayer process directly depends of the level of impurities in a refinery's Bayer liquor. Under optimal reaction parameters (temperature and time) it is possible to remove iron, zinc and copper from Bayer liquor using precipitation agent such as calcium hydroxide with an efficiency of more than 90%, in such a way that the treated solution is still economically usable in the following stages of processing while obtaining different types of aluminum trihydrate [5].

In Europe, alumina refineries operate in Bosnia and Herzegovina (Alumina, Zvornik), France, Hungary, Germany, Greece, Ireland (AAL), Romania (ALUM), Spain and Ukraine, while significant BR deposits from refineries that have stopped their operations (legacy sites) exist in former Yugoslavia (Podgorica, Kidricevo, Mostar, Obrovac), Italy, France (RT), Germany, Hungary and other countries. The current BR production level in the EU is 6.8 million tonnes per year; while the cumulative stockpiled level is a staggering >250 million tonnes (dry matter). The mineralogical structure of bauxite residue, where nearly 80 % consists of three of these phases: cancrinite, sodalite and hematite, as shown in Table 1. [6]

Table 1: Typical mineralogical structure of the bauxite residue (in wt. -%)

Cancrinite [$\text{Na}_6\text{Ca}_{1.5}\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_{1.6}$]:	29.0-33.0
Sodalite [$\text{Na}_8(\text{Cl},\text{OH})_2\text{Al}_6\text{Si}_6\text{O}_{24}$]:	16.0-24.0
Hematite [Fe_2O_3]:	27.0-29.0
Boehmite [$\text{AlO}(\text{OH})$]:	5.0-6.0
Gibbsite [$\text{Al}(\text{OH})_3$]:	4.0-5.0
Anatase [TiO_2]:	5.0
Andradite [Ca-Fe-Al-Si oxides]:	4.0
Quartz [SiO_2]:	2.0

The bauxite residues contain scandium and gallium (approx. 50-150 ppm) and up to an order of magnitude higher for elements such as: vanadium and rare earths elements (0.05-0.5 %). MYTILINEOS, Greece since 1991 has been pioneering research on BR handling and reuse, focusing initially on massive low value applications such as use as a raw material for geopolymer bricks, cement clinker production, iron production, bricks and tile production, soil remediation (vegetation), extraction of rare earth elements and road substrate.

Due to the generation of large amounts of Bauxite Residue (red mud), an alternative method, called the Pedersen Process was considered in order to prevent the Bauxite Residue generation [7]. In the conventional Pedersen Process, iron in the bauxite is separated in the form of pig iron through a carbothermic smelting-reduction step which has a carbon dioxide emission similar to that during

conventional iron production. In order to eliminate the carbon dioxide emission of this step, the focus of their work was to reduce the iron oxides of bauxite ore by hydrogen gas prior to smelting and minimizing the use of solid carbon materials for the reduction. Calcination and reduction of bauxite ore by hydrogen was studied by thermogravimetry method supported by microstructural and phase analysis confirming that the reduction of hematite via magnetite to iron starts at temperatures below 560 °C with slow rate and is faster at higher temperatures. At higher temperatures, i.e., 860, 960, and 1060 °C, the formation of hercynite (FeAl_2O_4) retards the complete reduction to metallic iron.

The possibilities to recover rare earths from bauxite residues, which commonly contain only low concentrations of rare-earth elements, but are available in very large volumes and could provide significant amounts of rare earths to European countries are main research subject of the European funded projects (EURARE; REMOVAL, SCALE, REDMUD) in last ten years. The extraction rate of the rare-earth recovery from these industrial waste streams is a part of a comprehensive, zero-waste, “product-centric” valorisation scheme, in which applications are found for the residual fractions that are obtained after removal of not only the rare earths but also other critical metals such as scandium, vanadium and gallium and especially the base elements: aluminium, titanium and iron [8]. EURO-TITAN will study decarbonized technologies for Ti recovery from aluminium and titanium residues in the next 4 years, as shown at Fig.1.



Figure 1. Euro-Titan Research strategy

Unfortunately, the extraction of aluminium, iron and titanium from bauxite residue under acid leaching is limited due to insufficient amount of acidic solution from leaching caused by the polymerization of silica [9]. Kinetic studies have demonstrated that at constant temperatures, silica dissolution increases with increasing acid concentration, but it decreases when the temperature is increased and the acid concentration is reduced. This is due to the enhancement in the solubility of monomeric silicic acid formed during acidic leaching. The control mechanisms of silica dissolution have been described according to the shrinking core model by a chemical reaction stage, i.e. silica polymerization, followed by a diffusion stage, because of the silica gel adsorbed on the surface of the particles that limits the metal extraction. Alkan et al [10] studied a recovery of iron, titanium, aluminium, rare earth elements from bauxite residues preventing silica gel formation was performed using dry digestion process with sulphuric acid and hydrogen peroxide. The operational parameters were investigated and the addition of 2.5M hydrogen peroxide into 2.5M sulfuric acid was decided to be the best leaching condition to have favored quartz formation with a suppressed rhomboclase precipitation. Since the leaching reactions mainly controlled by diffusion, no significant increase in the efficiencies were observed after 30 minutes of leaching. While silica gel was not formed in

oxidative environment, high titanium extraction from bauxite residue was only achieved when hydrogen peroxide was introduced into the acidic solution.

The combined pyrometallurgical and hydrometallurgical treatment of bauxite residue for the recovery of valuable metals included firstly carbothermic reduction [11]. The reductive smelting of bauxite residue using coke as the reductant between 1500 and 1550°C and acidic to basic fluxes to lower the smelting temperature and the production of conditioned slag. Additional conditioning of the bauxite residue with basic oxygen furnace slag and bottom ash as fluxing agents in the smelting process was performed in order to recover the valuable metals with exclusive use of secondary resources as slag formers [12, 13].

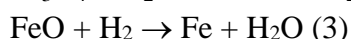
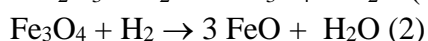
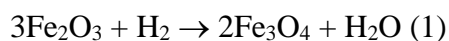
Jovicević-Klug et al. [14] proposed how this red mud can be turned into valuable and sustainable feedstock for ironmaking using fossil-free hydrogen-plasma-based reduction at higher temperatures in electric arc furnace (more than 1600°C), thus mitigating a part of the steel-related carbon dioxide emissions by making it available for the production of several hundred million tonnes of green steel. The process proceeds through rapid liquid-state reduction, chemical partitioning, as well as density-driven and viscosity-driven separation between metal and oxides.

The aim of this work is to offer first information about characterisation of bauxite residues from Alumina, Zvornik and study of hydrogen reduction at temperature below 1000°C. As mentioned this study is only first part in frame of the EURO-Titan Project (2024-2027) aiming to explain an importance of hydrogen metallurgy in production of green steel.

Thermochemical analysis of hydrogen reduction

Equilibrium calculations were done to identify relevant species and changes in chemical composition during hydrogen reduction at 900°C, as shown at Figure 2. Reduction by hydrogen, even with small ratios of H₂/red mud (kg/kg) lead to reduction of Fe₂O₃ to Fe and CoO and NiO to metallic forms. All these components can be easily recovered by magnetic separation.

Reduction of hematite by hydrogen proceeds in two or three steps, under and above 570 °C, respectively, via magnetite (Fe₃O₄) and wustite (FeO) according to the following equations:



Pineau et al. [15] found reduction of iron ores with hydrogen leads to compact iron layers that could slow their reduction rate. Additionally thermochemical analysis revealed the formation of Fe₂TiO₄ and FeAl₂O₄; what can lead to the formation of a passivation layer in reduction process. The formation of ferrite phases is expected for other elements such as calcium and sodium.

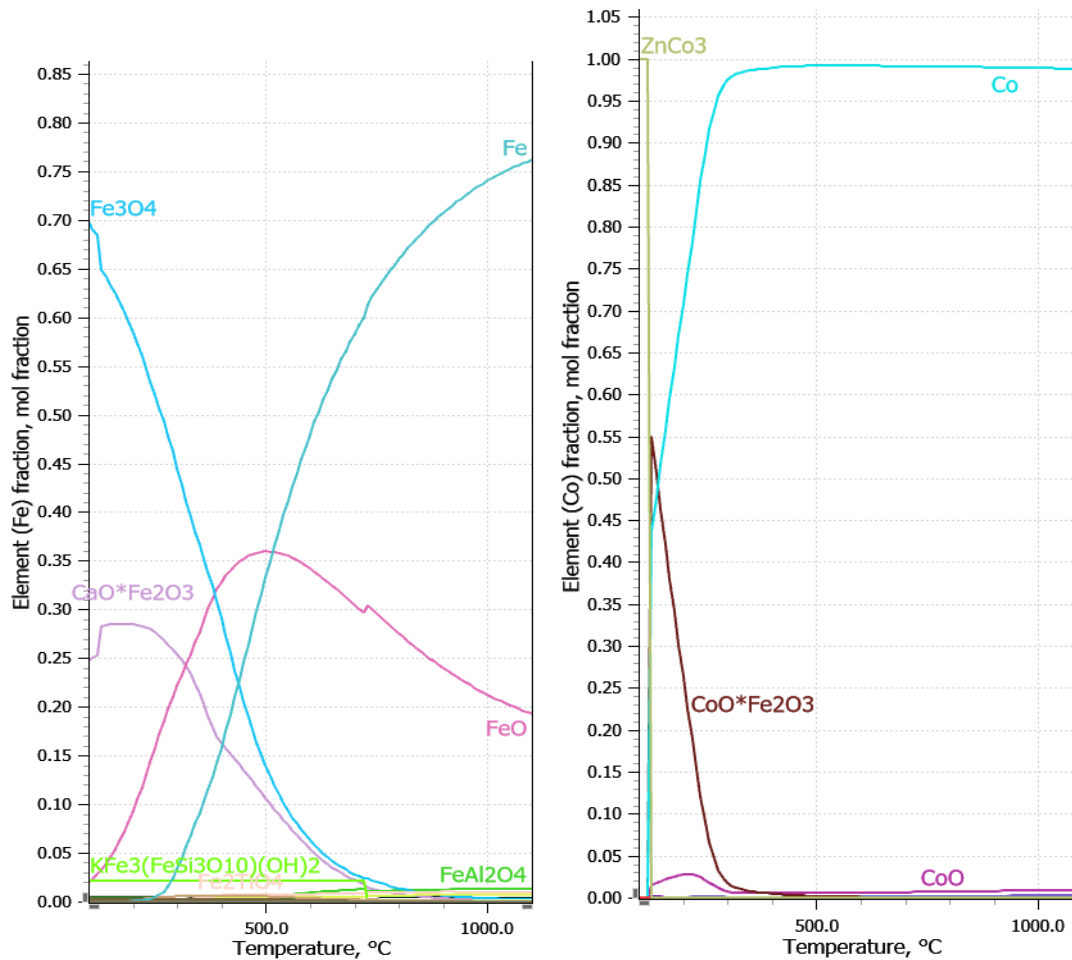


Figure 2. Thermochemical calculation of reduction of iron oxides and cobalt oxide at 900°C

Red Mud, Alumina, Zvornik

During the operation of the company Alumina, Zvornik about $19.4 \times 10^6 \text{ m}^3$ of red mud suspension was disposed of. Depending on the quality of the bauxite, the amount of completely dry red mud typically ranges from 0.8 to 2 tons of tailings per ton of alumina produced. Accordingly, the amount of red mud that is separated and disposed of at the landfill is about 1.0 - 1.2 tons per ton of Al_2O_3 produced, or approximately 400,000 t per year. The bauxite residue from Alumina was filtrated, washed and dried at 105 °C for 24 h. The chemical composition of red mud is presented in Table 2:

Table 2: Chemical composition of BR, Zvornik

Compounds	%	Compounds	%
Ignition loss at 1000°C	8,32	Ga ₂ O ₃	0,225
SiO ₂	10,52	CuO	0,007
Fe ₂ O ₃	49,29	K ₂ O	0,159
Na ₂ O	2,45	Tl ₂ O ₃	0,088
TiO ₂	4,59	MnO	0,145
CaO	8,23	MgO	0,627
Al ₂ O ₃	12,03	NiO	0,034
Ag ₂ O	0,001	PbO	0,019
BaO	0,014	P ₂ O ₅	0,930

Cr ₂ O ₃	0,133	ZnO	0,016
Sc ₂ O ₃	0,011	V ₂ O ₅	0,135
Co ₂ O ₃	0,012	SrO	0,075

As shown at Fig.3, XRD-analysis of red mud after found the following phases: hematite, perovskite, cancrinite, ilmenite, calcite, diaspore, gibbsite and hydrogarnet. Iron is present in hematite and ilmenite structure. Titanium is present in perovskite and ilmenite structure, while aluminum is present in structure of cancrinite, diaspore, boehmite, gibbsite and hydrogarnet.

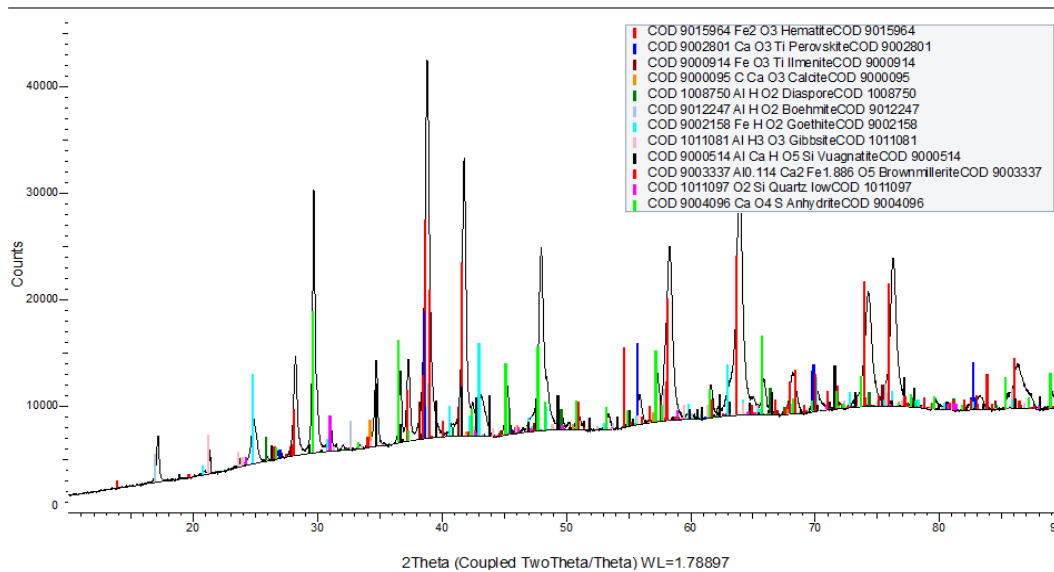


Figure 3. XRD Analysis of Red mud, Alumina, Zvornik

The XRD-analysis at Figure 3 has confirmed the presence hematite and other very stable oxides for hydrogen reduction.

Particle size distribution analysis of red mud found very fine particles, as shown at Figure 4. The obtained particle size have the following values ($x_{50,3} = 4.70 \mu\text{m}$ and $x_{90,3} = 5.98 \mu\text{m}$).

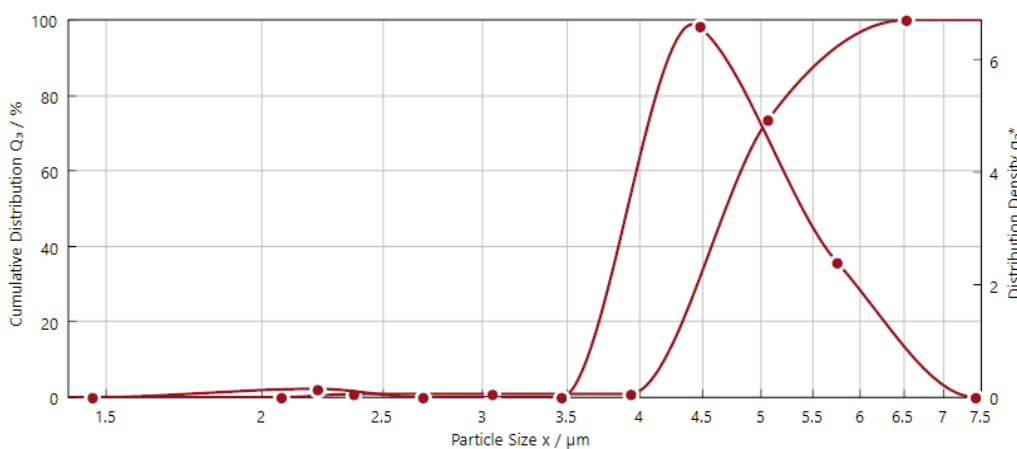


Figure 4: Particle size of red mud from Alumina Zvornika

Reduction with hydrogen

Reduction of 1.0 g red mud is performed in small tubular furnace at 700, 800, 900 and 1000 °C at 30 and 60 min using flow rate of 2 l/min of hydrogen and 1l/min of argon. Mass loss of initial sample amounted between 18 and 23 % (as shown in Table 3), what is accorded with an expected total theoretical value of reduction process regarding the mass loss of oxygen from iron oxide, cobalt oxide and nickel oxide through hydrogen reduction (max 15 %) and evaporation in neutral atmosphere (max. 9 %). The obtained particles after hydrogen reduction have magnetic properties, what is very important for the following separation process.

Table 3. Experimental results for hydrogen reduction (constant flow rate: 2l/min H₂, 1 l/min Ar)

Mass loss (%)	700°C	800°C	900°C	1000°C
30 min	18	20	21	23
60 min	21	23	23	-

SEM/EDS analysis of powders

The prepared powders obtained between 700°C and 1000°C have irregular, polygonal form with grain sizes more than 100 µm, as shown at Figure 5.a and 6.a.

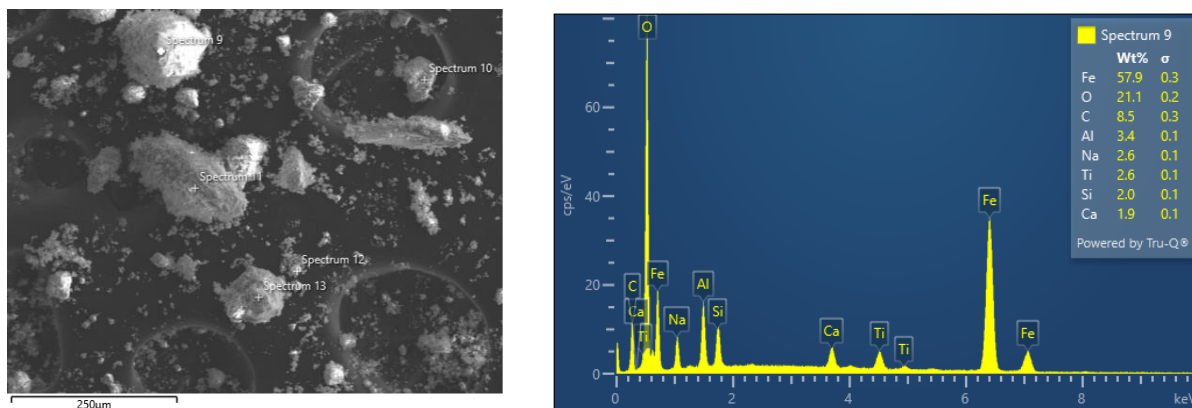


Figure 5.a. SEM analysis of powders obtained at 700°C Figure 5.b. EDS analysis of powders obtained at 700°C

An increase of temperature from 700°C to increases the content of iron and decrease the content of oxygen as shown at Figure 5a and 5b. The morphological study of the reduced samples of iron oxides by H₂ shows agglomeration of the reaction product at temperatures between 700 and 1000°C.

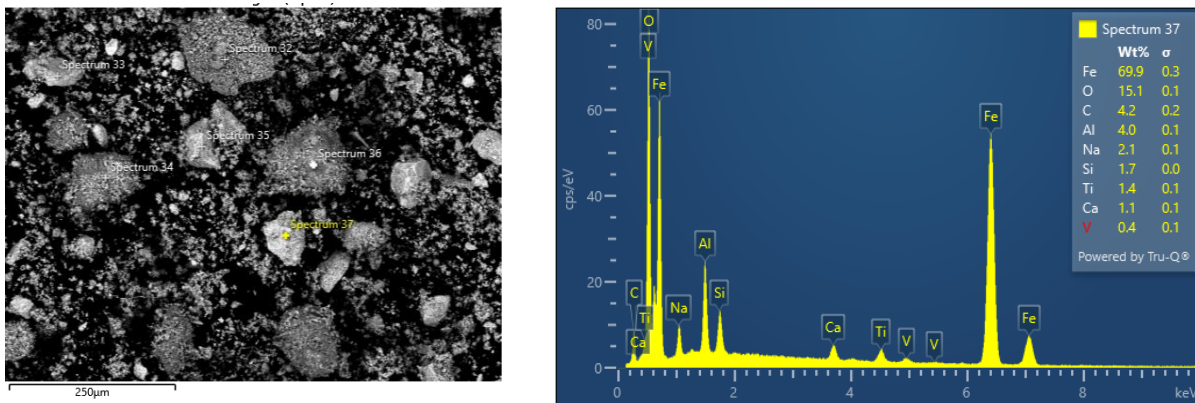


Figure 6.a. SEM analysis of powder obtained at 900°C by hydrogen reduction of red mud. Figure 6.b. EDS analysis of particles obtained at 900°C by hydrogen reduction of red mud.

An increase of temperature from 700°C to 1000°C increases the content of iron and decrease the content of oxygen as shown at Figure 5b and 6b.

The particle size distribution of reduced red mud revealed an increase of particle size during reduction ($x_{50,3} = 18,32 \mu\text{m}$ and $x_{90,3} = 308,97 \mu\text{m}$), as shown at Figure 7.

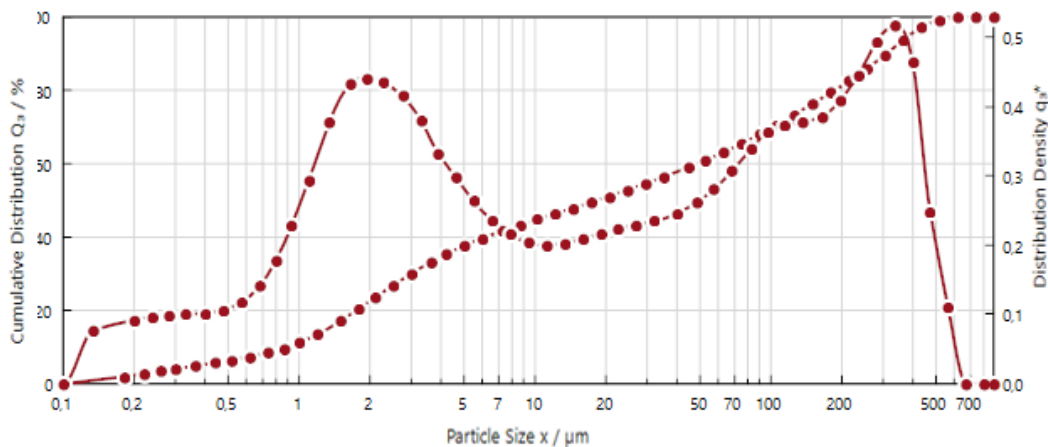


Figure 7. Particle size distribution of reduced red mud at 900°C

XRD analysis of reduced powder samples

The reduced red mud powder samples were analysed at room temperature by X-ray powder diffraction technique using the Ultima IV Rigaku diffractometer, equipped with $\text{CuK}\alpha_{1,2}$ radiation, using a generator voltage of 40 kV and a generator current of 40 mA. The range of $10\text{--}100^\circ 2\theta$ was used for all powder samples in a continuous scan mode with a scanning step size of 0.02° and at a scan rate of $1^\circ/\text{min}$, using D/TeX Ultra high - speed detector. Glass sample carrier for sample preparation was used. The PDXL2 (Ver. 2.8.4.0) software was used to evaluate the phase composition and identification [16]. All obtained powders were identified using the ICDD database [17].

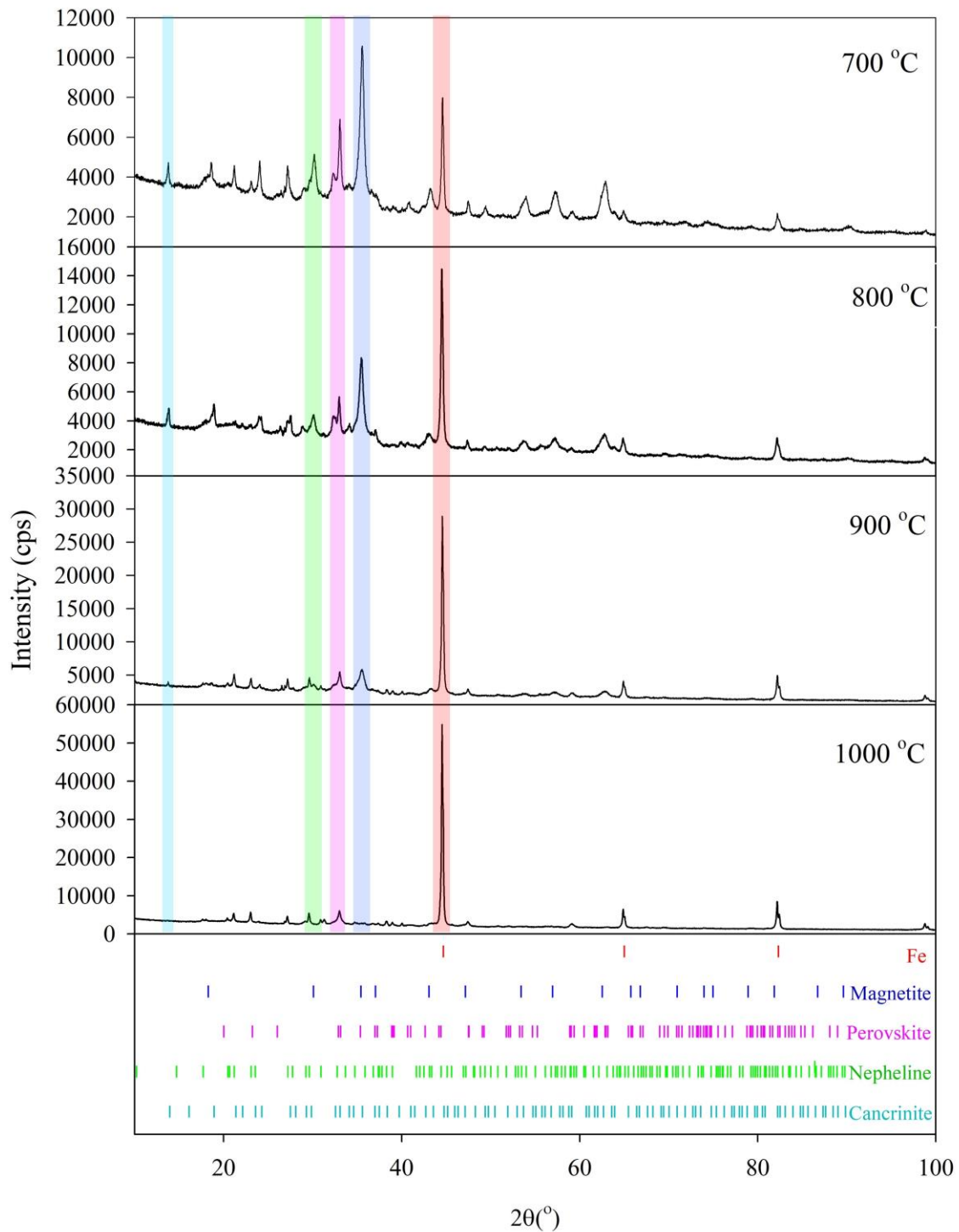


Figure 8. Diffractograms for the red mud reduced at 700, 800, 900 and 1000 °C. Identified minerals with positions of diffraction maxima are shown in lower part. The position of intensive diffraction maxima which do not overlap with other maxima of other minerals are shown in colored bands and used for comparison in mineral abundance.

Diffractograms for four red mud samples reduced in hydrogen atmosphere at 700, 800, 900 and 1000 °C are shown in Figure 8. The intensities of diffraction maxima are commented as the proxies

for the abundance of mineral phases present. The identified phases are: metallic iron, magnetite, perovskite, nepheline and cancrinite.

Metallic iron appears as the new phase not present in raw red mud which is characterised with sharp diffraction maxima reflecting the high cristallinity of iron. The intensities of iron diffraction peaks with respect to those of other phases progressively increase with the increase of reduction temperature indicating an increase of iron abundance. At 900 °C, and especially at 1000 °C, metallic iron dominates with respect to other phases.

Iron is partly accomodated in magnetite. Magnetite appears as the most abundant phase in sample reduced at 700 °C. The intensity of magnetite diffraction peaks as well as magnetite content progressive decrease with the increase of reduction temperature. The slight shift in position of diffraction maxima compared to pure Fe_3O_4 may be attributed to the presence of Al, Ti, Ca which is consistent with cetrain amount of those presumably alloying elements determined by EDS analysis.

The most stiking feature is a progressive increase in metallic iron content accompanied with the decrease in magnetite content with an increase of reduction temperature. Magnetite appears to be virtually absent in sample reduced at 1000 °C where only reduced elemental iron dominates.

Of other non-ferrous phases identified are perovskite and nepheline formed during reduction process and not identified in raw red mud as well as the residual cancrinite which is authigenic raw red mud mineral. Perovskite as the only Ti-bearing phase appears to be stable in examined range of temperatures (i.e. 700-1000 °C) inferred from XRD. Nepheline apperas as only newly formed silicate phase stable in examined range of temperatures as well. The striking feature is the observed trend in decrease in residual cancrinite content accompanied with the increase in nepheline content with increase of reduction temperature until complete disappearance of cancrinite at highest reduction temperature. This trend is interpreted as the cancrinite breakdown and transformation into nepheline.

Conclusion

Results of the reduction of iron oxides from red mud with hydrogen in the temperature range of 700–1000 °C leads to the following conclusions:

1. An increase of temperature from 700 °C to 1000 °C leads to reduction of Fe_2O_3 to Fe, but also partial transformation to Fe_3O_4 that is more stable at lower reduction temperatures. The most striking feature inferred from XRD is a progressive increase in metallic iron content accompanied with the decrease in magnetite content with an increase of reduction temperature whereas metallic iron is only identified iron phase at 1000 °C. Similarly, the decrease in residual cancrinite content accompanied with the increase in nepheline content with the increase of reduction temperature is another observed trend in silicate mineralogy.
2. The morphological study of the reduced red mud by hydrogen shows agglomeration of the reaction product at temperatures higher than 700 °C
3. The reduction process leads to increased particle size in comparison to used red mud

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