SOME SEGMENTS OF THE PROJECT CRITICEL

Zoltán Pap¹, Tamás Magyar², Zoltán Molnár³, Katalin Bohács⁴
¹,²,³,⁴PhD student
¹,²,³,⁴University of Miskolc, Faculty of Earth Science & Engineering,
Institute of Raw Material Preparation and Environmental Processing

ABSTRACT

Within the frame of the TÁMOP-4.2.2.A-11/1/KONV-2012-0005 project, the Institute of Raw Material Preparation and Environmental Processing in cooperation with many other Institute of the University of Miskolc work on the exploration of the primary and secondary sources of raw critical materials in Hungary. This paper summarize some aspects of the work had been carried out, briefly presented the main steps of the project highlighted some of the main part.

Keywords: Rare Earth Elements, mineral processing, CriticEL project

INTRODUCTION

Recently, EU has required the assessment, exploration and evaluation of strategic importance mineral resources in its member states. Priority should be ensured to the trainings for raw material extraction and processing technologies. Raw Materials Group – which was organised under the European Commission – published a report that defined 14 types of raw material, which involves risk for the EU [1]. In 2012 the list had been reviewed and 6 more raw material has been added to the list. As a response to the EU critical raw material list a new fundamental research programme were started in Hungary called CriticEL. The scientific aim of this project was to look for potentially economic sources of some of the relevant critical raw materials can be found primary and secondary sources as well. In the frame of this project we were only focusing few critical elements, which have potential sources available in Hungary.

EXAMINATION OF THE PRIMARY SOURCES

First of all we tried to find possible primary raw material sources. Many geological survey has done at the past. According to previous data, gauge material of Fehérvárcsurgó sand glass site is rich in heavy minerals, mostly titanium bearing minerals like rutile and ilmenite. The average heavy mineral content of sand deposit is around 1% which is concentrated using gravity and magnetic concentrators and flotation during the purification process of market ready sand products with high SiO₂ content. The reason of testing this gangue material was that there were previous indications of monazite in the area which probably concentrating in the heavy fraction of the separation of quartz and heavy minerals [2].

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Samples were taken from the deposit site of glass sand tailings. According to international practice, mineral processing of Ti bearing heavy minerals and monazite can be done successfully using combination of gravity and magnetic concentration and also electrostatic separation. Magnetic and electrostatic separation efficiency can be enhanced using thermal treatment of the mineral particles. In case of rutile for example, preliminary thermal treatment of rutile at approx. 400 °C yield of rutile can be increased from around 70% to 90% during electrostatic separation. Rutile also becomes paramagnetic after treating at 500 °C, therefore rutile can be separate from zircon using magnetic separators. According to this knowledge a general scheme of separation of heavy minerals can be drawn of which can be seen in fig. 1 [2].

![Figure 1. General mineral processing concept for monazite containing Ti bearing heavy minerals [7]](image)

Lots of publication deals with this topic and many researchers are dealing with the development of the heavy mineral processing: [3], [4], [5], [6]. Based on all the collected information general mineral processing scheme (fig. 1) was tested on the samples taken at Fehérvárcsurgó. For the tests, laboratory scale equipment of Institute of Raw Material Preparation and Environmental Processing has been used (fig.2.).
According to the experimental data, proof of concept has been validated. Since appearance of monazite has been recognised only using optical microscopy further confirmation of results need to be carry out. Also, the applied technological scheme has been found to be successfully applied for separation of heavy minerals [7].

MECHANICAL PREPARATION OF CAPACITORS FROM WASTE PCBs

The increasing claim of reducing the size of electronic devices especially laptop computers and cellular phones has accelerated the demand for small volume but high-performance tantalum capacitors. The major constituent of tantalum capacitors is a porous structured anode made by metallic tantalum powder pressed into pelletized form. The anode represents approximately 50 wt% of tantalum capacitors [8]. Tantalum is categorised as a critical element by the EU, therefore intensive research is being carried out to find secondary raw material sources. If the electronic parts from used PCBs (printed circuit boards) are firstly dismantled and separated, higher purity secondary products can be recovered. In this section the results of the mechanical preparation of tantalum capacitors were briefly summarized. The Institute of Raw Materials Preparation and Environmental Processing of the University of Miskolc has developed a method to mechanically prepare of used tantalum capacitors, partly based on the literature [9][10][11]. The first process of the developed method is the oxidisation of the used and separated capacitors. Because of this thermal process the fireproof epoxy cover becomes powder like and the complete inner part remains unaltered. The thermally handled capacitors with powdered fireproof epoxy cover can be further processed by ultrasonic bath on a screen surface. By this way the practically total amount of the epoxy layer can be removed and the complete inner part of the capacitors remains unaltered. After drying, the complete inner part can be milled in a planetary mill and by sieving the negative and positive terminals and the residual fine particular part can be separated.
Figure 3.

The optical microscope picture of the examined SMD tantalum capacitor after thermal handling in a furnace (on the left side) and ultrasonic bath treatment (on the right side)

The separated terminals are high purity metallic products and the fine particulate residual part can be further processed by chemical methods.

FLY ASH AS RAW MATERIAL OF RARE EARTH ELEMENTS

Dai et al. [12] investigated fly ash for germanium. The coal (burned in power plant) originated this area where Ge source was also appeared. The concluded, that fly ashes consists not only Ge, but also other elements with following ratios: 4.66 wt% Ge, 2.12 wt% As, 1.56 wt% F, 1.22 wt% Sb, 0.56 wt% W, 0.56 wt% Zn, 0.55 wt% Pb, 0.13 wt% Sn, 0.12 wt% Ga, 0.056 wt% Bi, 0.04 wt% Be, 0.028 wt% Cs, 0.017 wt% Tl, and 0.016 wt% Hg.

Figure 4.

Processing of fly ash – enrichment to organic, magnetic, coarse and fine components [13]
Blisset et al. [13] investigated fly ashes from Poland and UK and developed a technology for processing of fly ash. They wrote the followings: Interest has grown in recent years in the concept of multi-component utilisation of CFA (C-type fly ash). Within this concept it is envisaged that CFA, an intrinsically heterogeneous product, can be separated into distinct components. Fig. 4 illustrates a processing scheme capable of separating a raw CFA feed into four components: (1) an organic concentrate, (2) a magnetic concentrate, (3) a coarse improved residual fly ash (IFA), and (4) a fine IFA. It can be calculated from Fig. 4 that relative to the feed CFA, the REO (Rare Earth Oxide) content is reduced by 47% and 21% in the magnetic concentrate and organic concentrate, respectively. Conversely, the REO content increases by 11% and 26% in the coarse and fine IFA, respectively. This result is in accordance with the size fraction analysis but it also suggests that a large proportion of the REE (Rare Earth Element) in CFA is present in the non-magnetic inorganic material. Recent research has shown, using Ce as a proxy for all the lanthanides that REE elements reside homogeneously within the glass phase. This has implications for REE extraction as it requires that the leaching agents must contact the entire particle. A possible explanation for why REE appears in more concentrated form on the smaller size fractions, larger size fractions of CFA tend to have a higher carbon content.

In Hungary the fly ash of Pécs contains in highest amount of trace elements like Be, Ga, Ge, Nb, Ta, Th, Zr, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y és Co in 12.9, 30.4, 1.74, 146, 9.58, 41.5, 743, 294, 348, 40.5, 134, 18.1, 17.8, 2.58, 13.5, 2.72, 7.89, 1.19, 7.49, 1.11, 69.6 and 195 ppm [14].

**IMMOBILIZATION OF WASTES**

After the extraction of rare earth elements from primary and secondary raw materials it needs to immobilize them due to its mobilized toxic contents. One possible way are geopolymers to encapsulate these materials. Geopolymers are inorganic polymers which can produce by the reaction between alumino silicate oxides and alkali silicates in alkaline media. This reaction yielding a three dimensional polymeric structure which consist of Si-O-Al bonds. In the frame of CRITICEL project, geopolymer specimens was made from fresh lignite type fly ash. A geopolymer paste and producing process is developing which suitable for waste immobilization [15]. Hydraulic conductivity of geopolymer specimens were investigated. Plasma Display Panel, LCD glass, EAF dust, residue of leaching of batteries, and perlite fine fraction were added to fly ash. These materials are physically encapsulated.

**CONCLUSIONS**

The aim of this paper is to present some main part of the project CriticEL. The first stage was to find possible primary raw material sources. Based on the research, it was concluded that the Fehérvárcsurgó sand glass site is rich in heavy minerals, mostly
titanium bearing minerals like rutile and ilmenite. A technological scheme has been developed for the successful separation of heavy minerals. At the second stage, the possible secondary raw material sources were investigated to recover some critical elements from them (e.g. e-waste). The results of the mechanical preparation of tantalum capacitors were briefly summarized as an introduction.

The third section of this paper deals with the fly ash as raw material source of rare earth elements. According to literature it was found that a large proportion of the rare earth elements in C-type fly ash is present in the non-magnetic inorganic material. Last but not least the results of immobilisation of residual waste materials were discussed to decrease its hazardous environmental potential. Namely, one possible way can be the encapsulation of these materials in geopolymers.

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REFERENCES


