Strategic elements - Primary and secondary resources in Hungary

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ABSTRACT

The first decade of the 21st century has ended with a world-wide economic crisis. New economic powers and industries evolve which change the long-term demand for raw materials. The new materials were not covered by previous research, with insufficient information about their enrichment and extraction methods. The solution should come from scientists and engineers. The CRITICEL, an EU co-funded project in Hungary has the main objective of creating basic information about the domestic sources of these raw materials.

1. INTRODUCTION

The EU Commission has issued the first warning about the depleting raw material sources in 2008, declaring that meeting our needs in raw materials is critical for the economic growth and job security in the EU. An in-depth analysis of supplies and definition of a roadmap revealed the tasks to contain or reduce the related risks (EUAd-hoc Working group 2011). Of the 40 elements and minerals studied, the following have been defined as having a high supply risk in the EU:

Antimony	Indium
Beryllium	Magnesium
Cobalt	Niobium
Fluorite	Platinum group PGE
Gallium	Rare Earths REE
Germanium	Tantalum
Graphite	Tungsten

There are three main reasons why some of these materials, such as platinum and indium, are particularly critical: first, they have a significant economic importance for key sectors, second, the EU is faced with a high supply risks, associated with e.g. very high import dependence and a high level of concentration in particular countries, and third, there is currently a lack of substitutes.

To obtain funding for raw material oriented basic research was never easy in our country. The TAMOP - Operative Program for Social Renovation (co-financed by the EU and the Hungarian government) has offered an excellent opportunity to finance such works. The goal was finally reached by the team of the Earth Science Engineering Faculty of the University of Miskolc, to launch the CRITICEL project (www.kritikuselemek .uni-miskolc.hu) - Basic research program of primary and secondary sources of critical elements.

The paper describes the planned structure of the research, and presents case-studies of generated research programs from the field of both the primary and secondary raw materials. The CRITICEL project aims at delineating the potential sources of raw materials of strategic importance for further exploration and development, either as primary mineral raw materials or as recovered materials from secondary sources. Also an important objective is to find research partners who may join in proposals of similar projects for the Horizon 2020.

2. THE DETAILS OF THE CRITICAL PROJECT

The CRITICEL project is a two years research program to define the resource potential of the above listed critical elements. With an overall budget of 1.5MEuro the program's main goal is to reach significantly better understanding of these resources with potential continuation of exploration and research in the industrial segment. Although the main partner is the Miskolc University, a large number of cooperating partners support the program, from the Hungarian Geological and Geophysical Institute to industrial companies, like Wildhorse UCG, Geonardo. The external partners actively participate in one or more subprojects, R+D programs.

A specialty of the program is its integrating nature. Besides the two main groups: Earth scientists and process engineers other partners, like mining engineers, economists also participate in the research. The Earth science branch focuses its work mainly on primary mineral resources, either as main mineral or by-product of other ores. Their work extends from archive data reprocessing of remote sensing, geological, geophysical datasets to diagnostic sampling of new outcrops, archived drill-cores. They also assist in the phase-analysis, mineralogical tests of technological samples of secondary raw materials.

The process engineers search for and investigate secondary raw materials (like mine waste, technological and electronic waste, metallurgical waste) to detect, recover the critical elements, advising possible processing routes for further development. They also cooperate with the Earth scientists to provide first diagnostic processing information of the discovered enrichments of these elements in primary raw materials.

Apart from the obvious benefits in research, the project offers outstanding possibility to involve numerous young undergraduate and graduate students in the research teams and give them strong motivation in choosing geology and material processing career.

3. RESOURCES OF STRATEGIC MINERALS IN HUNGARY

Albeit Hungary is a net importer of energy minerals and mineral raw materials, with large dependence and supply risk in many key segments, the country has not done much on the field of reducing its dependence from remote raw material sources. Unsatisfactory rates of exploration and development have led to increasing gap between the exploration, development and the market demand of mineral raw materials in Hungary. The last booming period of the mineral explorations was in the 1970-1980 decades.

In these times Hungary was a centrally planned economy, and the mining and exploration was also fully state-controlled. Following this period, with the change to market-economy, no large-scale mineral explorations or mine developments have taken place, except for episodic exploration efforts of few junior companies. Only the petroleum and gas (later the geothermal) resources have drawn the attention of investors. Since 2011 there is an increasing trend to give more attention to the domestic mineral resources and fossil energy production both in medium and long term strategic planning map of known mineral occurrences of Hungary basically reflects most of the known major areas, where the above mentioned strategic minerals may be enriched either as main components or as potential by-product of other known mineral deposits. Our first work program in the project was aimed at delineating the status of information related to these occurrences. About 300 publications and exploration reports were reviewed and evaluated. Two of the strategic minerals ever mined as main commodities and two other elements as by-products. Four other ore types are known to occur in near-economic grade or tonnage, although none of them were explored until today. Six other elements have not yet been not found as enrichment in geological formations. Important data have been collected from the historic regional geological and geophysical mapping projects of the state geological and geophysical institutes, which have avoided the attention of the exploration companies so far. The best example of these regional data collection is the nationwide geochemical research program (Földváryné Vogl, 1970), which gave a full cross-section of geochemical distribution of a great number of elements, many of them is on our criticality list. Although the analytical techniques used are outdated by now, and the results should be treated with caution, yet the large number of data and the wide coverage over the whole set of geological formations provides the best starting point for our evaluation.

After the first phase of data collection, the potential target elements and areas were ranked according to probability of near-economic enrichment (Table 1). On this ground, four target elements have been selected as first priority: fluorite, germanium, PGE, REE. A number of others, like beryllium, graphite, tungsten were ranked as second priority and a limited budget was dedicated to carry out a small-scale sampling program, normally at one occurrence. Two elements - gallium and magnesium - were transferred to the processing technology research sub-program, since the core of the problem is to adapt suitable recovery technology from the known mineral raw materials. The other elements were ranked as third priority, generally requiring more detailed information to generate a further sampling project.

4. MINERAL RESOURCES OF GERMANIUM – AN EXAMPLE

Germanium is a scarce, but not an extremely rare element in the Earth's crust. It is increasingly used in the manufactured electronic devices, fibre-optic systems, infrared optics, solar cell applications and nanowires or as polymerization catalysts (Höll et al., 2007). An unusual property of germanium is to exhibit variable siderophile, litophile, chalcophile and organophile character in different geologic environments. Certain ores and coals can be strongly enriched in germanium as compared to some sulphide ores. Differentiated granite weathering may release germanium which is transported to the sedimentary basin. The Ge enrichment is effected by chemisorptive processes on relatively stable organocomplexes as lignin or humic acids producing humate complexes, chelates with lignin-derivates. Due to its organophile character it is frequently found in high concentration in different coals.

Table 1: Strategic minerals in Hungary according to archive information.

	1	2	3	4
Be			+	
C*			+	
Co				+
F	+			
Ga		+		
Ge			+	
In			+	
Mg		+		
Nb				+
PGE*			+	
REE*			+	
Sb			+	
Ta				+
W				+

Legend - 1: mined and recovered 2: recovered as byproduct, 3: identified, unexplored, 4: un-identified. *C, PGE, REE denotes graphite, platinum group elements, Rare Earth elements respectively.

The Eastern-Mecsek Mts (SW-Hungary) contains important hard coal deposits, with identified resources of about 1 billion tonnes. The Mecsek coal basin was deposited during the Early Jurassic (Hettnangian, Early-Sinemurian) in a half-graben sloping towards south, with coal seams becoming thicker towards the south (Nagy, 1969). Historic assays indicate high germanium content (average 15 ppm increasing to 110 ppm in the northern zone of the basin). The source of the germanium in the coal may be linked to the neighbouring granitic and metamorphic rocks.

Germanium is also accumulated in coal ashes. In the Mecsek coal ash the Ge content reaches 40-600 ppm maximum values. Therefore, coal ash is a potential economic source of Germanium. Previous technological records indicate that the germanium content was economically extracted from scrubber waters in several gas plants and power plants in Hungary during the 1950s.

There are ongoing tests to use the Mecsek coal for energy production by un-conventional technologies. One of these is the underground gasification of coal (UCG) which is an equivalent of the town-gas process. A subproject of the CRITICEL aims at testing coal seams designated for combustion using UCG with regard to potential germanium by-product recovery.

5. SECONDARY RAW MATERIALS OF CRITICAL ELEMENTS

There is possibility to extract strategically important raw materials from secondary raw materials even in Hungary joining to European Raw Material strategy. Waste streams with high concentration of certain important metals like electronic scrap are available for processing. There are some strategic chemical components, like gallium, indium, platinum group elements, which have got no routine economic recirculation technology yet. Also an important fact is that most easily recoverable secondary raw material streams come from production lines. The chemical composition of the manufactured products is relatively constant.

This is obviously not true for the waste materials taken from end users who make development of logistics, end of lifecycle friendly production methods and protocols to be enhanced. It is also important to note some of the high-tech industries use strategic metals in large amount. However, they can not be considered as secondary raw material source in short-term, since they are quite new, therefore their waste streams is forecasted only in 10-20 years time. That means research and development of technology for recycling and recovery of these materials has to start now.

Metallurgical processes are the most relevant for processing such waste streams. However they could be more effective and feasible if feed material of these processes is better pre-enriched by physical methods. One of the most promising development shows analogy to conventional froth flotation where surface tension is altered selectively on solid particles by changing the wettability of the particles during controlled circumstances. There are literature data about magnetic properties or electric conductivity of particles is possible to change using magnetic or metallic film layer covering part of the particle. This means that the key factor in separation of different particles from each other is selective coating of them by film layers with special properties can be used in mechanical separation.

In the field of mechanical processing, normal gravity concentration is not effective in small particle size regions below 0,1 mm, where pre-concentration of printed circuits is optimal. Also, very diverse and small difference in density between some of the target elements or parts of PCB containing it may make centrifugal gravity concentrators (like Knelson or Falcon concentrators) a good alternative. These are designed to process feed with grain size below even 0.063 mm. Although the main field of application is gold recovery from sands, other heavy minerals, like REE minerals could be also potentially enriched by these methods, for example in the heavy mineral concentrates obtained during glass-sand beneficiation.

Eddy current separators are widely used processing electrically conductive materials, but according to their today technologic status can process particles down to 3 to 5 mm. Further decreasing the particle size capability of the process and the separator could be a real breakthrough in solid particle processing techniques.

As a conclusion, it can be seen that basic research targeting critical elements from secondary sources in our project is mainly focusing to its technological aspects. These results and promising new technologies on the other hand could be useful also in primary ore processing with similar or same target materials on the list.

6. STRATEGIC ELEMENTS IN WASTES - EXAMPLES

Glass-sand production in Fehérvárcsurgó results heavy mineral rich fraction as a tailing. This tailing material contains ilmenite, zircon, rutile and other heavy minerals. There is also a chance to find REE bearing minerals, like monazite. Selective gravity separation of heavy minerals by Knelson concentrator is capable enrich heavy minerals effectively and process development is going to be set up for the optimal number of process stages to actually do that at high capacity.

Processors and computer chips are a special combination of metallic and ceramic materials, which can be processed only in highly ground state using metallurgic methods. Decreasing separation size limit of today's eddy current separators down to at least 0.5 mms would make pre-concentration of fine crushed material effective. After pre-concentration, only valuable, and lesser amount, of the computer parts have to be

Table 2: Rare Earth elements in luminescent powders of LCD devices (Buchert et al., 2012) – mg per piece.

	Note-books	Monitors	Television
Y	1.8	16	110
Eu	0.13	1.20	8.10
La	0.11	1.00	6.80
Ce	0.076	0.680	4.500
Tb	0.038	0.340	0.095
Gd	0.011	0.095	0.630

ground making grinding and whole processing operation more economic.

Printed circuit boards and all the other similar components contain different metallic elements (Table 2). Vacuum tubes consist of mainly Fe-Co-Ni alloys, copper, molybdenum, titanium tungsten, tantalum, the latter two elements being on the strategic list. On the electrodes platinum alloys are conducting electrons and there are also wolfram cathodes covered by film layers of osmium and ruthenium. Within the frame of the CriticEl project, new crushing-grinding method and equipment is going to be developed for selective separation of critical element bearing electronic components and printed circuits in one step.

7. FUTURE PLANS AND EXPECTED OUTCOMES

It is expected to achieve significant advance in the building of information database of critical elements from domestic sources, as both primary and secondary raw materials. A monograph series and parallel publications will cover partly the background information, partly the new research results.

In the primary resources segment these information should bring at least two new generated exploration projects, to identify critical elements as independent resource of mineral raw material (potentially the rare earths and platinum group elements). Similarly, in case of germanium, gallium, the geological information may help to review and improve the technological processes by which these elements may economically be recovered as valuable by-products from either the primary resources (bauxite, coal) or secondary resources (fly ash, stack gases, red mud).

In the secondary resource segment proven beneficiation technologies (gravity, magnetic, froth flotation, bio-processing methods) will be applied to different fractions of industrial waste streams, supported by applied mineralogy (detailed chemical and phase analysis), normally used on mineral resources. Special attention is paid to electronic wastes, different types of mine waste, and rejects materials of thermal power plants. A technological patent regarding processing of waste streams is expected to be submitted within the frame of the project.

A significant benefit of the project is the serious involvement of students and young research fellows (all levels, BSc, MSc, PhD, Post-Doc), in all of the programs included in the project. This involvement guarantees the sustainability of these research fields during the following decades.

The technological developments are under the continuous supervision of a Panel of Experts, organized from the most experienced professors of the university and representatives of relevant industrial research and development organizations. More than 15 cooperating industrial and research partners participate in the execution of the program. The final objective is to construct long-term high-quality research objectives and teams of researchers capable to continue the work - hopefully on a larger scale - during the follow-up period, either on national or on international level, for example in the frame of the Horizon 2020 cooperation.

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