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PRIMARY AND SECONDARY MINING POSSIBILITIES OF CRITICAL ELEMENTS OF ELECTRONIC WASTE

ABSTRACT

Electrical equipment e.g. smartphones, notebooks represent one of the fastest-growing waste (WEEE) stream. These electrical devices contain a lot of rare earth elements, platinum group metals, noble metals and other precious metals. Critical raw materials can be recovered from electronic waste and recycled into the manufacturing process, thus significantly reducing dependence on primary sources, but the mining of these remain strategic importance. The biggest problem with the recovery of these elements is the relatively low concentration of these devices. In addition, their distribution is not uniform. Some units have a higher enrichment than others, so it is often better to treat the components on the circuit boards separately, thus increasing the efficiency and economy of recovery. The solution is sensor-based sorting and the development of these devices.

Keywords: WEEE, notebook, mining, recycling, separation, sensor-based sorting

1. INTRODUCTION

Technological development entails more and more electronic waste every year (Figure 1). These electronic devices contain significant amounts of rare earths, noble metals, platinum group metals, and other precious metals. The importance of the best-known elements, such as copper, aluminum, or precious metals, is often understood by all, but few know that other lesser-known elements are also essential in our modern technical life [7].

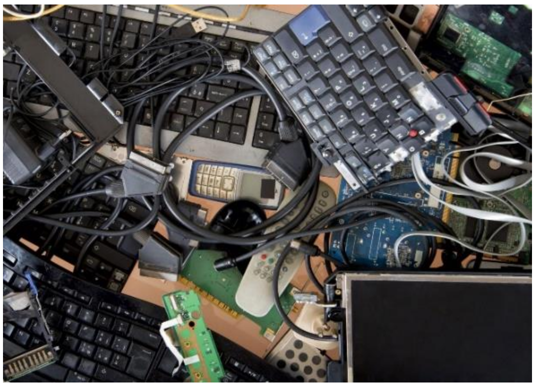


Figure 1. Electronic waste

Mining of these lesser-known rare elements, which are already strategically important today, is currently shared by few countries. Therefore, in its Communication SECC(2008)2741 [2], the European Union has set the direction for the need to relaunch the assessment of strategic mineral resources in EU countries. In 2017, the Raw Materials Group issued a related report [3]. The report has been developed in line with the expected industrial needs of EU countries by 2030. Ranked by possible sources of supply, it identifies 27 raw materials that could become a major need in the European economy and could be heavily imported. We have previously dealt with existing reserves of raw materials [7], and in this article, we describe the evolution of the availability of critical raw materials in electronic waste from primary sources through the example of a CCFL screen notebook.

The chips, transistors, and other units on the motherboard of notebooks, as well as the contact pins, all contain different chemical elements. Their combined treatment is problematic and they cannot be treated simultaneously in terms of metallurgical or chemical processes. Each circuit element has its own unique marking system to optimize manufacturing processes [10]. These marking signs can be used even after they have been turned into waste, depending solely on the image processing software and database system of the optical sorting systems. However, this equipment can be damaged during the recovery processes, due to which the identification of their shape, form, and marking is also problematic. When this type of separation process is no longer suitable in the optical range, other physical properties must be examined, either in the X-ray, infrared range or on the basis of their conductivity or magnetic permeability.

2. CRITICAL RAW MATERIALS IN NOTEBOOKS

Electrical equipment e.g. smartphones, notebooks represent one of the fastest-growing waste (WEEE) streams. These devices thus become important sources of secondary raw materials. From the devices that have become waste, the desired critical raw materials can be recovered and recycled into the production process. Thus, dependence on primary sources can be significantly reduced. Table 1 shows the amount of critical raw materials in notebooks with cold cathode fluorescent (CCFL) background illumination.

Table 1. Mean content of critical raw materials in notebooks (incl. LCD monitors with CCFL background illumination) [1]

Critical raw materials		Content per notebook [mg]	Occurrence in notebook
Cobalt (Co)	-	65000	Lithium-ion batteries (100%)
Neodymium (Nd)	Rare earths	2100	Spindle motors (37%), voice coil accelerators (34%), loudspeakers (30%)
Praseodymium (Pr)		270	Voice coil accelerators (53%), loudspeakers (47%)
Dysprosium (Dy)		60	Voice coil accelerators (100%)
Gadolinium (Gd)		0.01	Background illumination (100%)
Cerium (Ce)		0.08	Background illumination (100%)
Europium (Eu)		0.13	Background illumination (100%)
Lanthanum (La)		0.11	Background illumination (100%)
Terbium (Tb)		0.04	Background illumination (100%)
Yttrium (Y)		1.8	Background illumination (100%)
Tantalum (Ta)	-	1700	Capacitors on the motherboard (90%), capacitors on other PCBs (10%)
Indium (In)	-	40	Display and background illumination (100%)
Platinum (Pt)	Platinum group	4	Hard disk drive platters (100%)
Palladium (Pd)		40	Motherboard (64%), other PCBs (36%)

3. LEADING MINE PRODUCTIONS OF SOME IMPORTANT CRITICAL RAW MATERIALS IN CASE OF NOTEBOOKS

3.1. Cobalt

94% of the world's cobalt production comes from the extraction and production process of nickel (50%) and copper (44%). Only 6% of the world's cobalt production goes directly from cobalt extraction. Most of the primary resources are in Africa. The Democratic Republic of the Congo accounts for the bulk of production, compared to the production of other countries (Table 2). As a result of cobalt research, the world's cobalt reserve has been estimated at 6.9 million tonnes.

Table 2. The world's leading cobalt producing countries over the past decade [10]

	2010	2011	2012	2013	2014	2015	2016	2017	2018	Total
Congo	47400	60000	51000	54000	63000	63000	64000	73000	90000	565400
Zambia	5700	5400	4200	5200	5500	4600	3000	2900	-	36500
China	6500	6800	7000	7200	7200	7700	7700	3100	3100	56300
Russia	6200	6300	6300	6300	6300	6200	5500	5900	5900	54900
Australia	3850	3900	5880	6400	5980	6000	5500	5030	4700	47240
Cuba	3600	4000	4900	4200	3700	4300	4200	5000	4900	38800
Canada	4600	7100	6630	6920	6570	6900	4250	3870	3800	50640
New Caledonia	1000	3200	2620	3190	4040	3680	3390	2800	-	23920
Philippines	-	-	-	-	-	-	-	-	4600	4600
Madagascar	-	-	-	-	-	-	-	-	3500	3500

3.2. Rare earth metals

The world's rare earth metal reserves (excluding Scandium) are estimated at 120 million tonnes. Production has increased in recent years, much of it produced in China, and Australia and the US have increased their production (Table 3). It is projected that China will make full use of its rare earth production shortly, so several rare earth metal mining projects have been launched recently. There are also significant stocks in Brazil, Vietnam and Russia.

Table 3. The world's leading rare earths producing countries over the past decade [10]

	2010	2011	2012	2013	2014	2015	2016	2017	2018	Total
USA	-	-	800	5500	5400	5900	-	-	15000	32600
China	130000	105000	100000	95000	105000	105000	105000	105000	120000	970000
Brazil	550	250	140	330	-	880	2200	1700	1000	7050
India	2800	2800	2900	2900	3000	1700	1500	1800	1800	21200
Australia	-	2200	3200	2000	8000	12000	15000	19000	20000	81400
Russia	-	-	2400	2500	2500	2800	2800	2600	2600	18200
Thailand	-	-	-	800	2100	760	1600	1300	1000	7560
Vietnam	-	-	220	220	200	250	220	200	400	1710

3.3. Tantalum

Tantalum-containing minerals (tantalite - (Fe, Mn) (Ta, Nb) 2O6, wodginite - MnSnTa2O8, microlites - (Na, Ca) 2Ta2O6 (O, OH, F)) can be found almost anywhere, but they are very rare with higher concentrations of tantalum. The world's leading tantalum producers in recent years are the Democratic Republic of the Congo and Rwanda (Table 4).

Most of the stocks for this item are not reported by countries due to strategic considerations. The current supply of tantalum consists mainly of primary (mineral) sources (65% of tantalum-containing minerals, 13% of slags leftover from tin processing), but more than 20% of the supply is recycled from secondary raw materials.

Table 4. The world's leading tantalum producing countries over the past decade [10]

	2010	2011	2012	2013	2014	2015	2016	2017	2018	Total
Brazil	180	180	140	98	150	115	103	110	100	1176
China	-	-	-	60	60	60	94	110	120	504
Congo	-	95	100	200	200	350	370	760	710	2785
Ethiopia	-	76	95	8	-	-	63	65	70	377
Nigeria	-	50	63	60	-	-	192	153	150	668
Rwanda	110	93	150	600	600	410	350	441	500	3254
Mozambique	120	260	39	115	-	-	-	-	-	534
Burundi	-	13	33	20	-	-	-	-	-	66
Canada	-	-	50	5	-	-	-	-	-	55
Australia	-	-	-	-	-	-	-	83	90	173

3.4. Indium

Indium is widespread in the Earth's crust but is found in very small concentrations. Indium production is connected to the mining of lead-zinc ores. With the identification of new deposits, the amount of indium reserves is no longer as critical as before. The specific price of indium is very high so the size of stocks is not reported by countries. China and South Korea account for a significant share of production (Table 5.).

Table 5. The world's leading indium producing countries over the past decade [10]

	2010	2011	2012	2013	2014	2015	2016	2017	2018	Total
Belgium	30	30	30	30	25	20	20	20	20	225
Canada	67	75	62	65	65	70	71	67	70	612
China	340	380	405	415	460	350	300	287	300	3237
Japan	70	70	71	72	72	70	70	70	70	635
Rep. of Korea	70	70	165	150	150	195	210	225	230	1465
Russia	-	5	13	13	5	4	5	5	5	55
Peru	-	-	11	11	14	9	10	10	10	75
France	-	-	-	33	43	41	0	30	50	197

From the table above, it can be seen that the EU is also heavily dependent on imports for indium. Among the EU countries, Belgium and France are active in refining and producing indium.

3.5. Platinum-group metals

Elements of the platinum group (PGM) occur very rarely in small concentrations in the Earth's crust. The average naturally occurring concentrations of platinum and palladium are approximately 5 ppm, while those of rhodium, iridium and ruthenium are around 1 ppm. The elements of the naturally occurring platinum group always appear in conjunction with other elements. The most common metallic constituents in these associations are platinum and palladium. Nearly 92% of the platinum group's inventories are located in South Africa, so it is not surprising that South Africa is the world's leading producer of platinum (Table 6.) and, in addition to Russia, the largest producer of palladium (Table 7.). In connection with the elements of the platinum group, an association of other elements, such as nickel, copper and gold, is also characteristic. While stocks in South Africa, Zimbabwe and the US are mined solely for platinum group elements, the production of platinum group elements from stocks in Russia and Canada appears as a by-product of nickel mining.

Table 6. The world's leading platinum producing countries over the past decade [10]

	2010	2011	2012	2013	2014	2015	2016	2017	2018	Total
USA	3450	3700	3670	3720	3660	3670	3890	3980	4100	33840
Canada	3900	1230	7000	7000	8500	7600	12600	9500	9500	66830
Russia	25100	25000	24600	25500	23000	22000	23000	21800	21000	211000
South Africa	148000	145000	133000	131000	94000	139000	133000	143000	110000	1176000
Zimbabwe	8800	10600	11000	12400	5800	12600	14900	14000	14000	104100

Table 7. The world's leading palladium producing countries over the past decade [10]

	2010	2011	2012	2013	2014	2015	2016	2017	2018	Total
USA	11600	12400	12300	12600	12400	12500	13100	13600	14000	114500
Canada	6700	14000	12200	16500	20000	21000	21000	17000	17000	145400
Russia	84700	86000	82000	80000	83000	81000	79400	85200	85000	746300
South Africa	82200	82000	74000	75000	58400	83000	76300	86800	68000	685700
Zimbabwe	7000	8200	9000	9600	10100	10000	8200	12000	12000	86100

4. SENSOR-BASED SORTING TECHNOLOGIE

Depending on the type of electronic materials and devices, there are already the right separators for recovered these. Each type of separators uses not only the electromagnetic spectrum to identify materials, but also other physical parameters such as conductivity or magnetic permeability [8].

4.1. Near-Infrared (NIR) separator

The samples are illuminated by a constant light source and either detect a camera reflecting from the sample. The analog signal captured by the camera placed above the conveyor is proportional to the wavelength of the beam of light. The selection is provided with two air jet nozzles, so there are three products at the same time for the sorting device.

a) b)

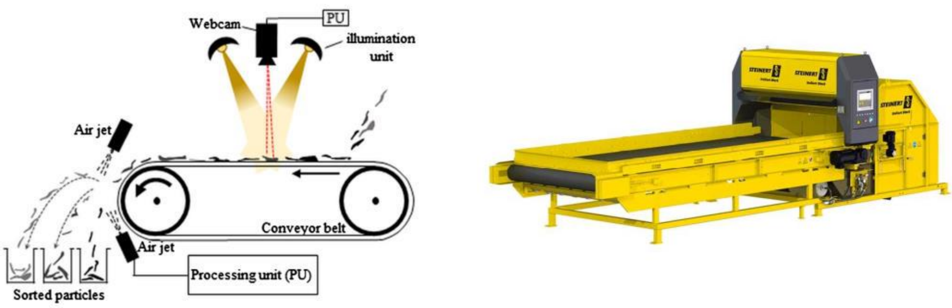
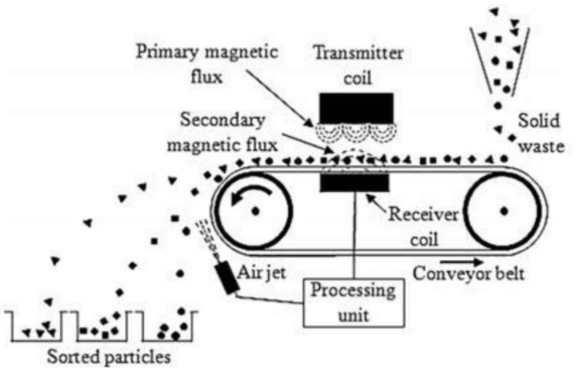


Figure 2. NIR separator a) operating concept [4]; b) Industrial size separator [9]

4.2. EMS Sensor-based separator

In this type of separator – like the eddy current separators – eddy current induced in the particles due to a transmitter coil, but this Lorentz force is weaker than the ordinary eddy current separators. In this case, when the transmitter coil induces the eddy current, the electromagnetic sensor (EMS) detects the electrical conductivity of the various nonmagnetic metals. After identification, the particles spilling out by an air jet from the nozzles.

a)



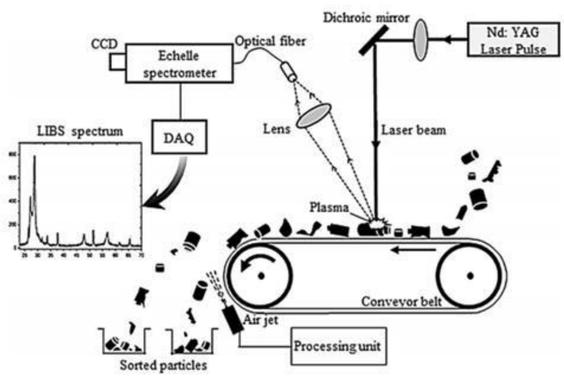
b)

Figure 3. Electromagnetic sensor-based separator a) operating concept [4]; b) The STEINERT EddyC MOVE separator [9]

4.3. Laser-induced breakdown spectroscopy

Laser-induced breakdown spectroscopy (LIBS) uses a high-energy laser beam. In 1990, the technology was developed at the Los Alamos National Laboratory, in collaboration with Metallgesellschaft, to identify metal waste. The LIBS system produces a large spectrometry of metal alloys, plastics and treated wood. Advanced atomic spectrometry technique based on optical emission monitoring of a microplasma generated by laser ablation. That is a very short-lived, time-varying temperature and composition source, it is necessary to synchronize with a laser at the time with the precision of μs fraction to operate the high-resolution spectrometer that can capture the entire UV and/or visible spectral range simultaneously.

a)



b)

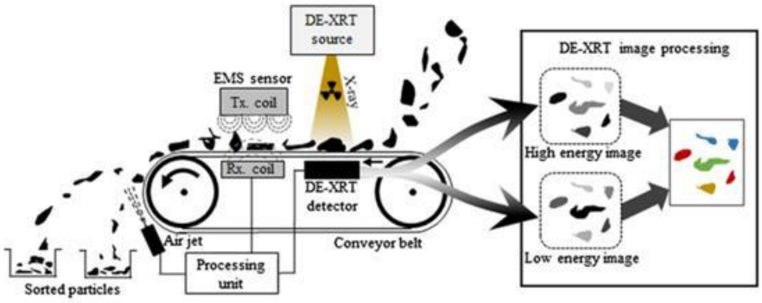
Figure 4. Laser-induced breakdown spectroscopy a) operating concept [4]; b) The STEINERT LSS LIBS [9]

4.4. X-ray separator

Two versions of X-ray separators are known. Thanks to the X-ray transmission system, image processing takes place quickly, in a few milliseconds. During operation, a high-intensity X-ray passes through the material, absorbing some of its energy, while the rest of the weakened X-ray is a tape detector. The atomic density can be determined from the information.

An X-ray fluorescence spectroscopy (XRF - X-ray fluorescence) ionizes the examined sample of electrons on a continuous spectrum X-ray. The kinetic energy of the leaving electron will be the difference between the photon and the electron binding energy.

a)



b)

Figure 4. X-ray separator a) operating concept [4];
b) The STEINERT XSS x-ray sorting system [9]

5. APPLICATION OF THE SIEMENS SIMATIC MV440 FOR ANALYZING ELECTRONIC WASTE

An instrument using optical principles also plays a significant role. The device available in our research is a Siemens Simatic MV440 shape recognition system that works with the internet. You can use the recognition camera cooperating with any browser installed on your computer through a preset IP address. The processing software running at the manufacturing company provides information about the scanned object. According to the information provided by Siemens, we can search for one-dimensional and two-dimensional code on the examined image, as well as the possibility to use different text and shape recognition (Figure 5).

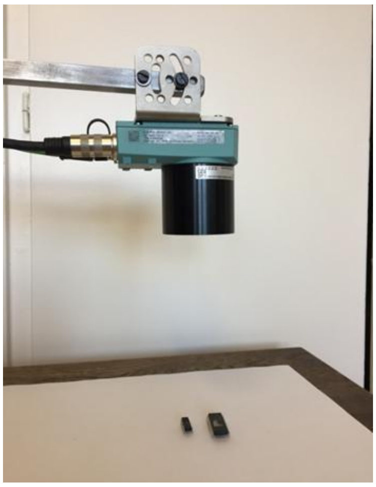


Figure 5. Siemens Simatic MV440 HR in operation

On the user interface, you can use the various menu items to upload the objects you want to recognize to the library. Once you have completed uploading libraries containing the objects you want to recognize, you can begin to read optically. There is no clear read speed for shape recognition, its size depends on:

- Number of shapes in the image
- The number of trained models
- Complexity of shape

The camera can reproduce the X-Y position of the recognized shapes to determine where the product is located on the examined surface. With continuous tape movement, fixed tape speed, and accurate time synchronization, you can determine the position of the item. The feasibility of the task depends to a large extent on the quantity and type of shapes (Figure 6).

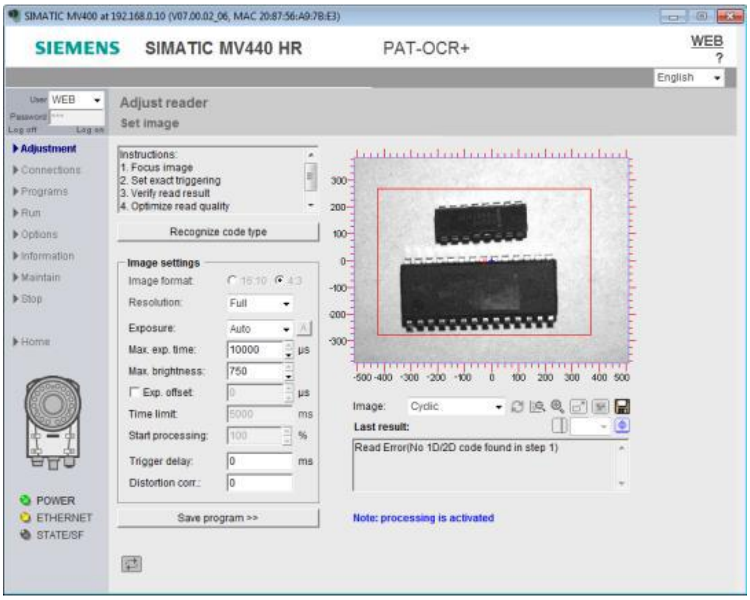


Figure 6. Siemens Simatic user interface

During the tests, we found that the camera can recognize shapes perfectly on black and white images. However, because of the black-and-white images, it is very important to pay attention to light conditions, because under changing light conditions the effectiveness of the recognition is rather weak. The camera we use does not have autofocus capability, which could be a disadvantage. Since selecting the objects that are defined for us is the main consideration, we get more sorting help. With the camera set with manual focus, the subject contours are sharply visible within a certain size range. These are the items we want to identify. Objects outside focus are not detected by the camera's imaging software. Thus, they may enter a separate stream of material during separation. When it comes to size ranges, it should be mentioned that the angle of view of the camera used for our experiments is small. This, the app. 25cm focal length of the camera's field of view approx. It limits the area to 100x100 mm. So with these optics, the system will max. 100mm wide material flow.

We need to talk about our experience that undermines the effectiveness of sorting in such a system. We have found that the system, even under constant light conditions, is mistaken. That is, the target object that passes through the checked surface is not always recognized. In the next part of the research, we want to look further into this direction. So, make a numerical rating of the recognition efficiency of different object types [11].

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REFERENCES

1. **Buchert, M., Manhart, A., Bleher, D., Plinger, D.:** Recycling critical raw materials from waste electronic equipment. Öko-Institut e.V., p. 88., Darmstadt, 2012
2. **European Commission:** The Raw Materials Initiative, 2018
3. **European Commission:** Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on the 2017 list of Critical Raw Materials for the EU, COM/2017/0490 final, 2017
4. **Gundupalli, S.P., Hait, S., Thakur, A.:** A review on automated sorting of source-separated municipal solid waste for recycling. Waste Management, Vol. 60, pp. 56–74, 2017
5. **Kritikus Elemek (CriticEl) projekt:** Alapkutatási program egy biztos és biztonságos jövőért - Projekt leírás, Miskolc, 2012
6. **Magyar, T., Faitli, J., Nagy, S., Virág, Z., Romenda R.:** Elhasznált nyomtatott áramköri lapok tantál kondenzátorainak újrahasznosítása/Recycling of Tantalum Capacitors from Waste Printed Circuit Board, XX. Bányászati, Kohászati és Földtani Konferencia, Gyulafehérvár, Románia, Erdélyi Magyar Műszaki Todományos Társaság (EMT), pp. 87-91., 2018
7. **Magyar, T., Virág, Z.,:** Elektronikai hulladékok kritikus elemeinek primer fellelhetősége, Műszaki Földtudományi Közlemények 86:(1) pp. 145-153., Miskolc, 2017
8. **Romenda, R., Virág, Z., Magyar, T.:** Mechanical processing methods of waste electronic and electrical equipment with special regards to NIR separation, UNIVERSITARIA SIMPRO 8 pp. 445-448. Paper: 3/11 , 4 p., 2018

9. **Steinert Gmbh.**: Magnetic Separation & Sensor-Based Sorting from a Single Source, Produktbroschuere sensorsortierung, 2018
10. **U.S. Geological Survey:** Mineral commodity summaries 2012-2019., Reston, Virginia, 2012-2019
11. **Ladányi, G., Tóth, A., Romenda, R., Virág, Z**.: Possibilities of an optical identification system used to identify secondary mining raw material extracted from e-waste, II. SUSTAINABLE RAW MATERIALS International Project Week and Scientific Conference, Conference Book, pp. 93-97., 2019