Utilization of Manganese clay industrial by-product

IN BUILDING MATERIAL INDUSTRY

A. SHAHROHKI[1], Z. SAS[1], F. FÁBIÁN[1], J. JÓNÁS[1], G. LE QUÉRÉ[2], T. VIGH[3], J. SOMLAI[1], T. KOVÁCS[1]

[1]UNIVERSITY OF PANNONIA, HUNGARY
[2]ECOLE DES MINES DE NANTES, FRANCE
[3]MANGANESE MINING AND PROCESSING LTD, HUNGARY

EU-NORM2
2014

JUNE 17 – 19, 2014, HOTEL DAP, PRAGUE, CZECH REPUBLIC

Introduction

Building materials (BM) in general

Role of building materials in human health, radiological aspect

Raw and add materials

New synthetic BM

Reuse of industrial by-products (BP)

- Potential starting material

Recycling could reduce the environmental impact

AIMS

Overall radiological survey of NORM origin by-products

Favorable compounds → NORM by-products as raw or add material in „clay-based" BM industry

- Red mud
- Coal slag
- Manganese clay
- Oil sludge

Mixing with clay matrix

Survey of potential Hungarian clays used in building material production

Unified classification protocol in PE-RRI

Reuse possibility of NORMs in BM production

Decorative color as add material or raw material in case of brick production

Closest building material factory capacity: 200 million brick/year → 600 000 t/year

- Distance of Manganese clay reservoirs: 22 km
- 20% Manganese clay: 120 000 t/year
- Total Mn-clay = 2 800 000 t → 23 year

- Distance of red mud reservoirs: 7 km!
- 20 % red mud: 120 000 t/year
- Total Red mud = 50 000 000 t → ~400 year

Manganese clay

- Originated as a result of manganese mining and processing of oxide type Manganese ore
- The ore was separated from the clay with excelsior (washed)
- ~2.8 Mt of manganese clay have deposited
- Favorable matrix features
- Ion exchanger capacity

Manganese clay

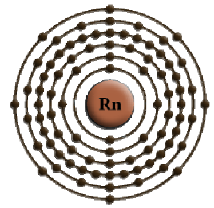
Chemical components [%]			
SiO_2	29-33	BaO	0.05-0.1
TiO_2	0.3-0.4	CaO	3-7
Al_2O_3	6-10	MgO	2-4
Fe_2O_3	22-26	K_2O	2-3
MnO_2	13-19	Na_2O	0.2-0.3
MnO_2	2-3	P_2O_5	0.4-0.5

Radionuclide content

Natural radioisotope content

Manganese (oxide, carbonate) ore, → Natural origin radioisotopes (U-238 (Ra-226): 20-200 Bq/kg, Th-232: 40-400 Bq/kg, 600-900 Bq/kg)

Radiological aspect of natural isotopes in case of BMs



Gamma-dose	→	Internal	→	Radon exhalation
Th-232, K-40, Ra-226		structure		Rn-222 (and its daughters)
External exposure		porosity		Internal exposure

Classification

Gamma-dose (Ra-226, Th-232, K-40)

- I-index

$$I = \frac{C_{Ra-226}}{300} + \frac{C_{Th-232}}{200} + \frac{C_{K-40}}{3000}$$

Material	Dose criterion (mSv y^{-1})
	1.0
Used in bulk amounts (concrete, brick, etc.)	I ≤ 1.0
Superficial or with restricted use (tile, etc.)	I ≤ 6.0

Radon exhalation

- Problematic task

Radon exhalation greatly depends on the structure of the materials

The investigation of possibilities to reduce exhalation capacity are very important

- Radon radon level → 300 Bq/m^3

Leaching of radionuclides

Leaching tests are required

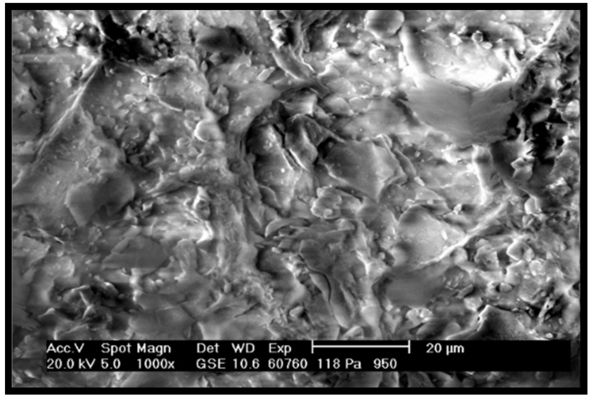
Classification protocol in PE-RRI

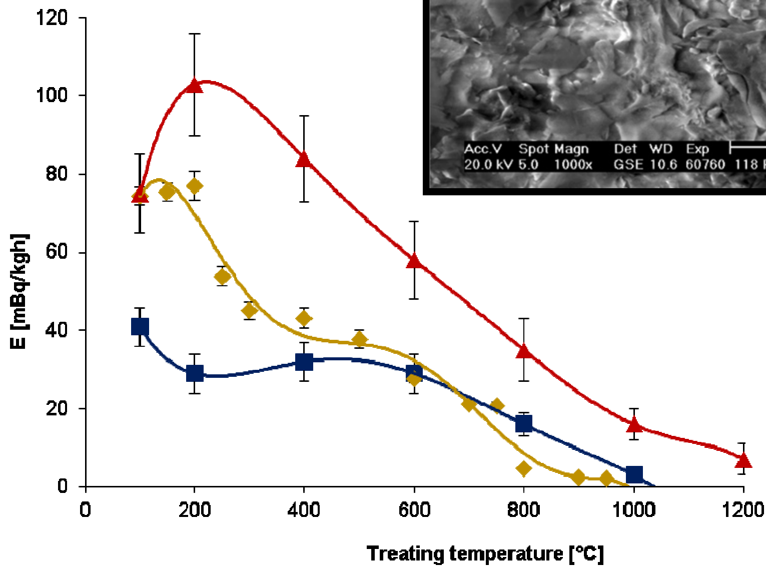
Determination of radionuclide content
- By-product sampling
- Gamma spectrometry, alpha spectrometry
- Classification (I-index)

Radon emanation exhalation influencing effects
- Heat-treatment
- Moisture content
- Sample thickness

Internal structure features
- Porosity
- Superficial morphology

Leaching behavior tests
- CEN/TS 15364:2006 Characterization of waste
  - Acid and base neutralization capacity test





Measurements and methods

SAMPLE COLLECTION

Clay samples

- Clay samples were taken from Tüskevár (Hungary)

Manganese clay

- 20 sample from Manganese clay reservoir (Úrkút)
- 0 – 40 cm depth

GAMMA SPECTROMETRY

- Drying, milling, storage in Marinelli vessels
- Instrument: ORTEC GMX40-76 HPGe detector with efficiency of 42 %
- Data collection: Tennelec PCA-MR 8196 MCA
- Measurement time: 80 000s

Determination of radon emanation and exhalation influencing parameters

Spherical and stick shape (d = 4 – 5 mm) clay-mixed samples (20% Manganese clay)

Effect of heat-treatment

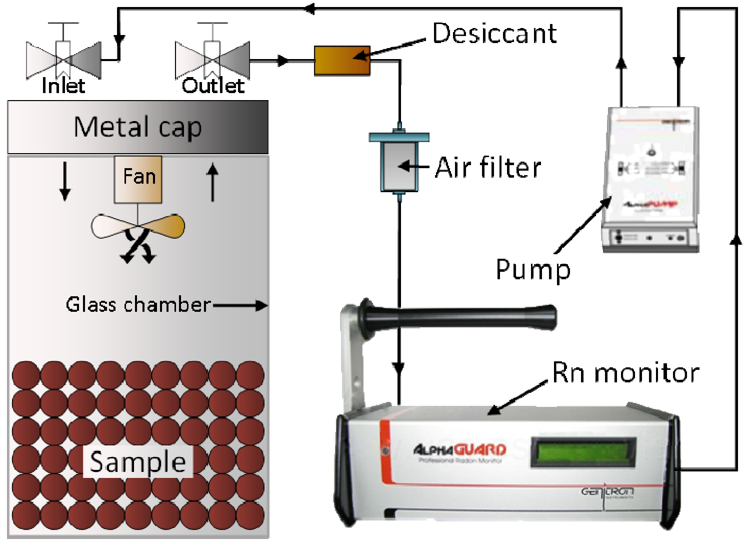
- Preheated kiln
- 4 h heat-treatment 100 – 750 °C

Exhalation measurement

- Optimal measurement conditions (Thickness → free exhalation state)
- Effect of heat-treatment

Internal structure measurements

- Specific surface, porosity (focused on micro and mezo pores)
- Pore diameter



Leaching tests

EN/TS 15364:2006 (ANC/BNC tests)

- For waste categorization
- Acid and base neutralizing capacity at 8 points between pH 4-12
- Liquid/solid ratio, concentrations, pH, redox potential, complex forming capacity and the aging of the waste can be measured

Provide information about the long term behavior of the waste

MSZ-21470-50

Hungarian regulation for toxic elements, heavy metals and chrome(IV) in soil

4 one-step extractions

- distilled water – water soluble
- Lakanen-Erviö solution – available for plants
- HNO_3+H_2O_2 – total digestion
- HNO_3+HCl – total digestion

Leaching tests

Tessier-extraction

For metals

5 step sequential extraction

Gives information about the speciation

Ion-exchangable	1 M $MgCl_2$ at pH 7 for 1 h at room temperature with constant stirring
Bound to carbonates	NaOAc set to pH 5 with acetic acid at room temperature for 5 h with constant stirring
Bound to Fe- and Mn-oxides	0.04 M NH_2OH*HCl in 25% acetic acid for 6 h at 93 ^{0}C
Bound to organic matter	0.02 M HNO3 and 30% H2O2 set to pH2 with HNO3 for 4 h with occasional stirring, then 3,2 M NH4OAc in 20% HNO3, dilute with distilled water and 30 minute of vigorous stirring
Residual	Microwave digestion

Mesurements of leachate

Na, K, Ca Mg, Heavy metals, rare earth:

-ICP, ICP-MS

NORM nuclides:

- Ra isotopes (226, 224, 228) **alpha spectrometry + Rn emanation method**
- U isotopes (234, 235, 238) **ICP-MS and/or alpha spectrometry**
- Po-210, Pb-210 **alpha spectrometry, LSC**

Results – Gamma spectrometry

27 clay samples							
	Activity Concentration [Bq/kg]						I-index
	Ra-226	±	Th-232	±	K-40	±	
AVG	37	7	40	9	803	37	0.59
Min	16	3	31	7	534	16	0.40
Max	105	17	49	11	1127	105	0.81

20 Manganese clay samples							
	Activity Concentration [Bq/kg]						I-index
	Ra-226	±	Th-232	±	K-40	±	
AVG	41	4	40	4	585	20	0.53
Min	23	3	25	2	369	15	0.37
Max	63	6	53	5	757	16	0.65

Low I-indexes → can be mixed according to choices

Z. Sas, J. Somlai, J. Jonas, G. Szeiler, T. Kovacs, Cs. Gyongyosi, T. Sydo: Radiological Survey of Hungarian Clays; **Radon Emanation and Exhalation Influential Effect of Sample and Internal Structure Conditions**, ROMANIAN JOURNAL OF PHYSICS 58:Number supplement (2013)
Z. Sas, J. Somlai, G. Szeiler, T. Kovacs: **Radon emanation and exhalation characteristic of heat-treated clay samples**, RADIATION PROTECTION DOSIMETRY 152:(1-3) pp. 51-54. (2012)

Results - Optimal measurement conditions

Free exhalation state

- If thickness << Diffusion length
- emanated radon ≈ exhaled

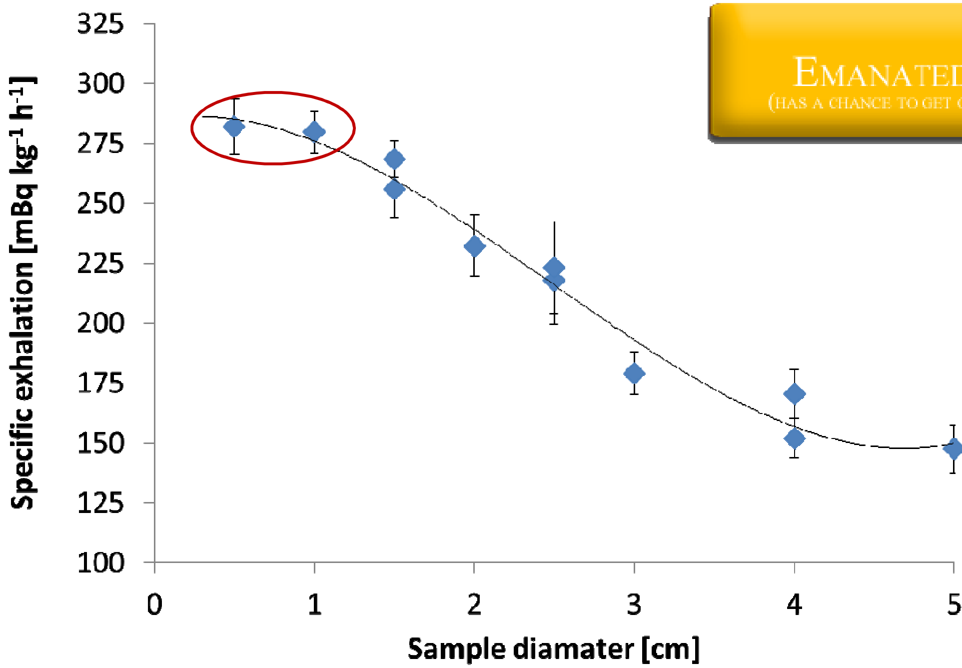
EXHALED
(DECAY WITHIN MATERIAL)

||

EMANATED
(HAS A CHANCE TO GET OUT)

Free exhalation depends on:

- Ra-226 content
- Emanation coefficient
- Amount of the sample

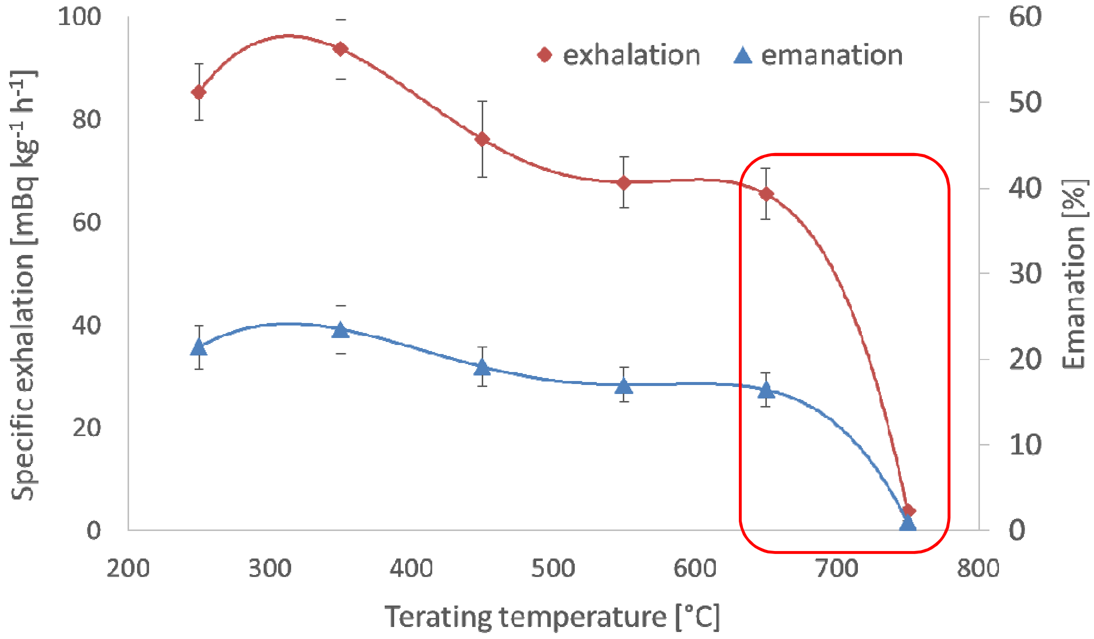


Z. Sas, J. Somlai, J. Jonas, G. Szeiler, T. Kovacs, Cs. Gyongyosi, T. Sydo: Radiological Survey of Hungarian Clays; **Radon Emanation and Exhalation Influential Effect of Sample and Internal Structure Conditions**, ROMANIAN JOURNAL OF PHYSICS 58:Number supplement (2013)
Z. Sas, J. Somlai, G. Szeiler, T. Kovacs: **Radon emanation and exhalation characteristic of heat-treated clay samples**, RADIATION PROTECTION DOSIMETRY 152:(1-3) pp. 51-54. (2012)

Results – Effects of heat-treatment

Radon exhaling capacity

- The radon exhalation depends on applied heat
- In case of 750 °C only 5 % of the initial
- Significant porosity changes
- Radon emanation is in direct proportion to radon exhalation under free exhalation state



Effective way to reduce exhalation capacity

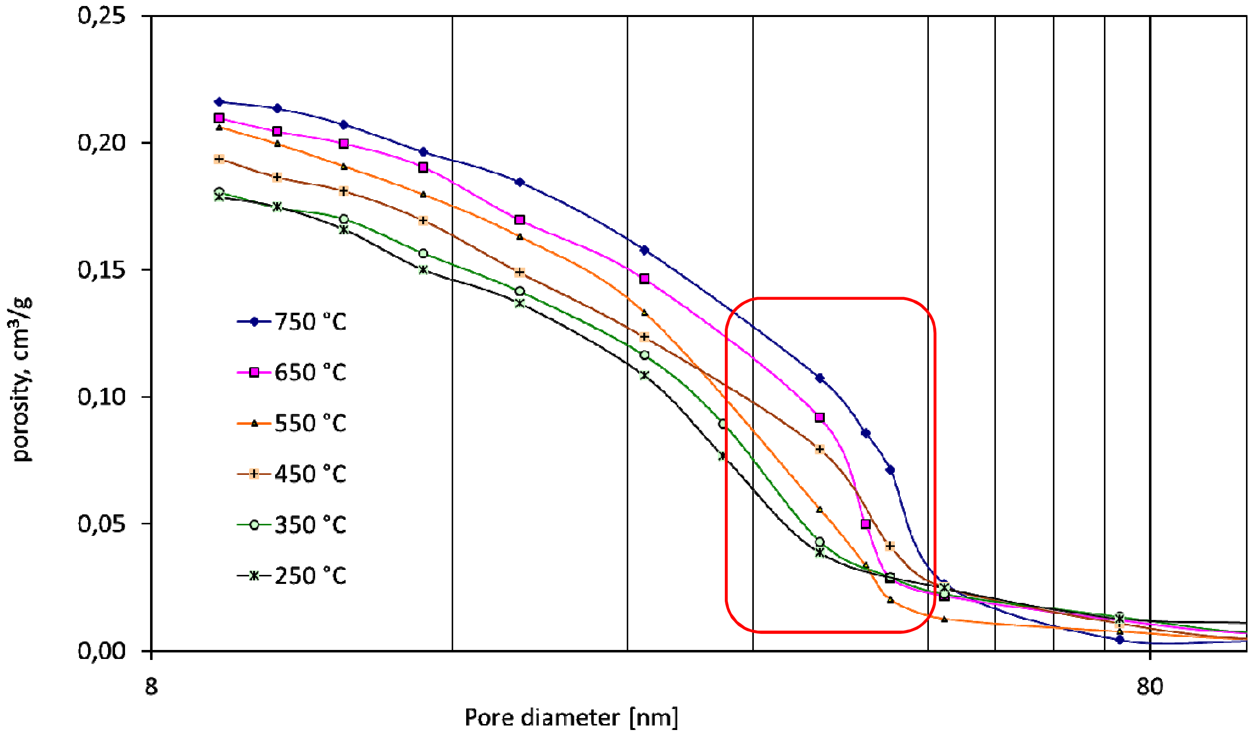
Z. Sas, J. Somlai, J. Jonas, G. Szeiler, T. Kovacs, Cs. Gyongyosi, T. Sydo: Radiological Survey of Hungarian Clays; **Radon Emanation and Exhalation Influential Effect of Sample and Internal Structure Conditions**, ROMANIAN JOURNAL OF PHYSICS 58:Number supplement (2013)

Z. Sas, J. Somlai, G. Szeiler, T. Kovacs: **Radon emanation and exhalation characteristic of heat-treated clay samples**, RADIATION PROTECTION DOSIMETRY 152:(1-3) pp. 51-54. (2012)

Results – Internal structure features

Porosity changes

- Remarkable porosity changes
- Mezopores closed
- Between 20 to 60nm pore diameter
- Great effect on the emanation
- On exhalation capacity as well



Z. Sas, J. Somlai, J. Jonas, G. Szeiler, T. Kovacs, Cs. Gyongyosi, T. Sydo: Radiological Survey of Hungarian Clays; **Radon Emanation and Exhalation Influential Effect of Sample and Internal Structure Conditions**, ROMANIAN JOURNAL OF PHYSICS 58:Number supplement (2013)
Z. Sas, J. Somlai, G. Szeiler, T. Kovacs: **Radon emanation and exhalation characteristic of heat-treated clay samples**, RADIATION PROTECTION DOSIMETRY 152:(1-3) pp. 51-54. (2012)

Results – Leaching test

- CEN/TS 15364:2006 Characterization of waste
- MSZ-21470-50: Hungarian regulation for toxic elements, heavy metals and chrome(IV) in soil
- Tessier-extraction: 5 step sequential extraction

Measurements in progress…

Results – Leaching test

Chemical components

Element	700 °C	850 °C	Element	700 °C	850 °C
	mg/ kg (dry)			mg/ kg (dry)	
Ca	704±23	680±11	**Cd**	<0.12	<0.12
Mg	34±4	15±3	**Cu**	0.34±0. 02	0.33±0. 02
Na	183±13	151±9	**Zn**	1.51±0. 2	2.11±0. 2
Cd	215±21	118±11	**Sb**	<0.01	<0.01
total Cr	<0.30	<0.30	**Ba**	0.63±0. 02	2.05±0. 2
Pb	<0.25	<0.25	**Se**	<0.012	<0.012
Hg	0.014±	<0.005	**Mo**	<0.05	<0.05
Ni	<0.25	<0.25	**Fe**	22±2	21±2
As	<0.009	0.016±0. 06	**Mn**	18±1	15±1

NORM nuclides

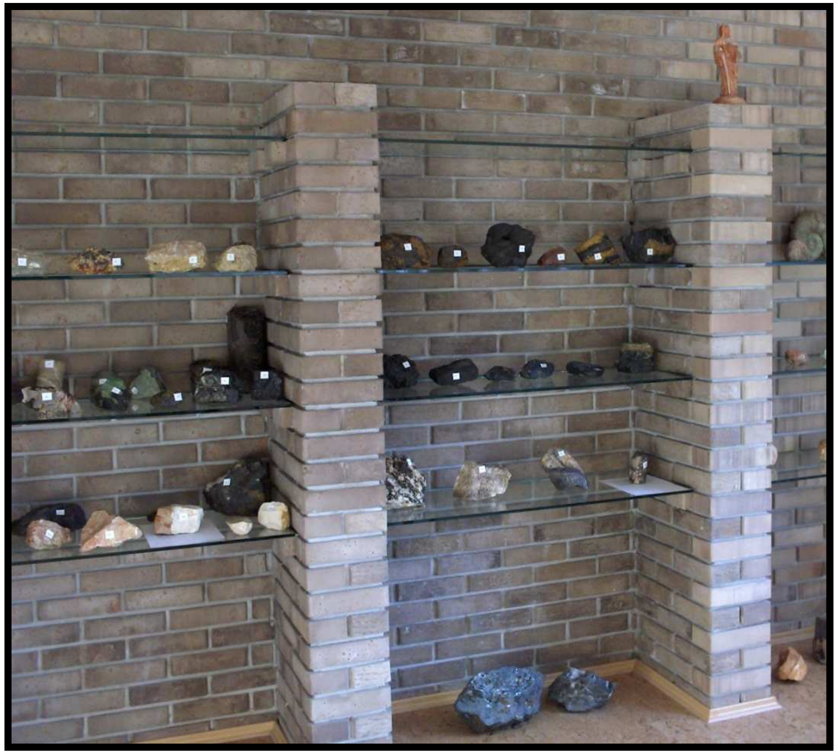
Element	700 °C	850 °C
	mBq/ g (dry)	
Ra-226	<1.5	<1.5
Th 232	<5	<5
Po/Pb 210	11±	11±
U-238	7±3	8±4

Reuse of Manganese clay

Based on the results: any mixing ratio is accepted over 750 C burning temp

Outside application

Inside application



Measurements in progress…

Preparation of samples:

- burning 1050 C
- self-glazing, coating is not necessary

Leaching method:

- by strong alcohol (pálinka)
- ambient prameters (pH, C etc)
- exctraction time (over 1 month)

Measurement method:

- organoleptic tests (by myself)

Thank you for your attention!
Děkuji vám za pozornost!
Köszönöm a figyelmet!