RIS-RESTORE

Transformation of the Hematite Ultramicroparticles from Red Mud into Other Forms of Iron Oxides

Dajana Cvijić, Sunčica Sukur, Biljana Đurić, Dragana Dragojlović, Predrag Ilić and Suzana Gotovac Atlagić

This activity has received funding from the European Institute of Innovation and Technology (EIT), a body of the European Union, under the Horizon 2020, the EU Framework Programme for Research and Innovation

Corfu 2022 conference

This presentation is part of the dissemination for the project:

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Evaluation of Red Mud Tailings in the ESEE region

This activity has received funding from the European Institute of Innovation and Technology (EIT), a body of the European Union, under the Horizon 2020, the EU Framework Programme for Research and Innovation

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Why doesn’t Europe dig anymore?

- Large problem with raw materials sustainabilityy
- High dependance on the Asian supply
- Recycle rates differing in different regions of Europe
- Prefering environmental protection over mining investments has its cost

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Bosnia is digging as never before!
In the heart of mining investments

- Sase (zinc)
- Milići, Jajce, Srebrenica (bauxite)
- Omarska, Ljubija (iron)
- Carmeus (lime)
- Bentoproduct (bentonite)
- Lukavac (cement)
- Srebrenica (copper coming soon)
- Vareš (barite, copper) ...

It is not only the classical mining that we should do! The tailings hold a large potential too!

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- What was wasted a century ago is now a valuable resource

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Our approach to raw materials for nanotechnology

ESTORE

1. Sampling the waste sludge from Bosnian mines (case study shown here: iron mine Omarska)
2. AcidiC digestion for removal of organic matter and rendering the metals soluble (oxydation)
3. Synthesis of the nanomaterials from the digested sludge

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Usual ingredents for nanosynthesis

Various P.A. Grade chemicals obtained from scrap metals (oxides, hydroxides, nitrates, sulfates ...) combined with surfactants, oils etc

!!! Lots of energy used only for ingredients production !!!

Basic process on the lab scale

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1.

2.

3.

4.

5.

1. Sludge separation
2. Gentle acid digestion (slow)
3. Oxidation finished
4. Water dissolution
5. Filtration: pure ionic metal solution

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Synthesis of the nanomaterials

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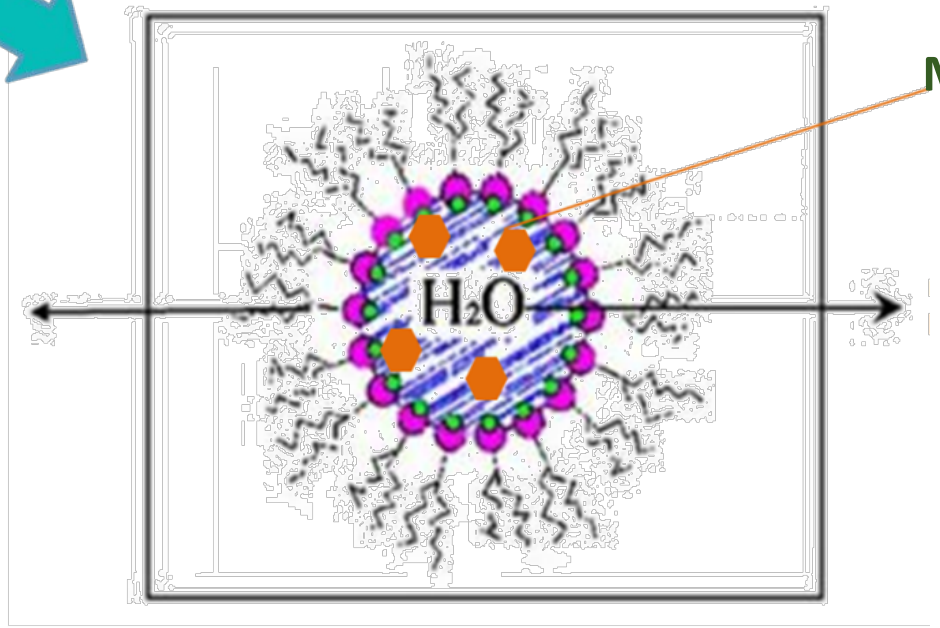
NaOH

Metal ions

Surfactant micelle



Nanoreactor

Collection of the nanomaterials obtained from iron mine sludge

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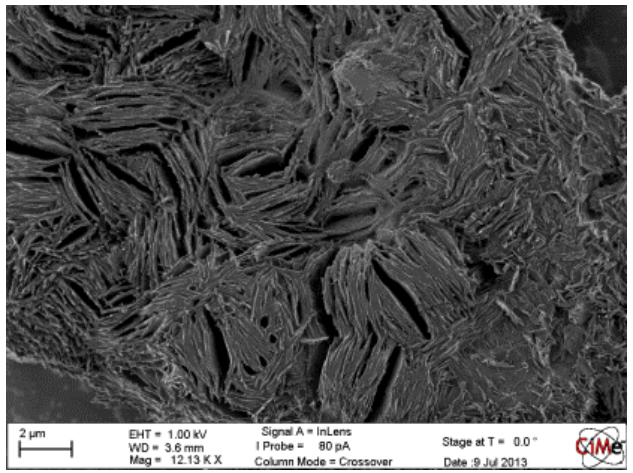
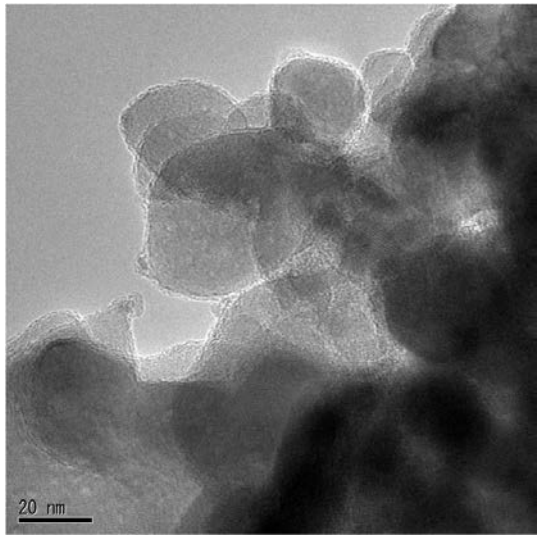
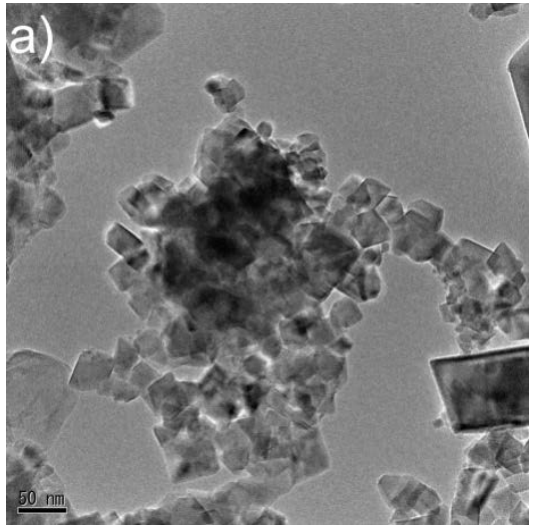


Highly porous iron oxide



Highly crystalline hematite with carbon shell



Highly crystalline cubic maghemite

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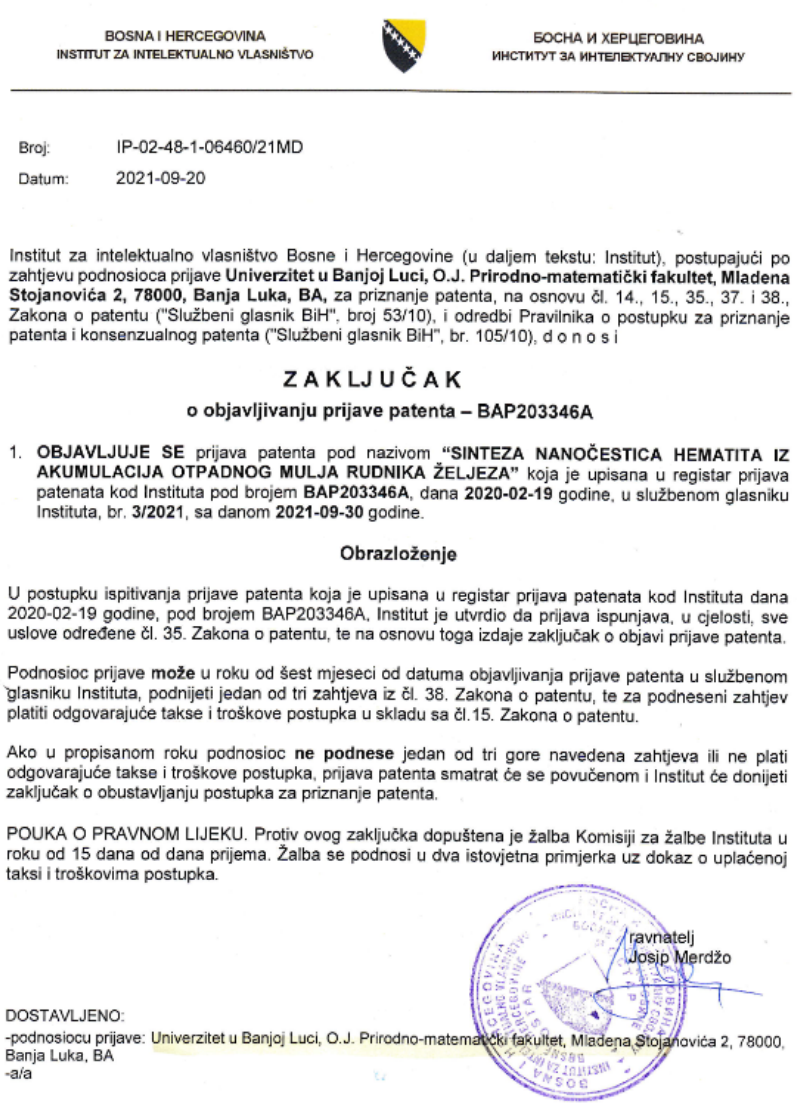
State of this invention:

Patent obtained in Sept 2021

We are offering to Arcelor Mital company the patent rights in exchange for employing our students



BOSNA I HERCEGOVINA
INSTITUT ZA INTELEKTUALNO VLASNIŠTVO

БОСНА И ХЕРЦЕГОВИНА
ИНСТИТУТ ЗА ИНТЕЛЕКТУАЛНУ СВОЈИНУ

Broj: IP-02-48-1-06460/21MD
Datum: 2021-09-20

Institut za intelektualno vlasništvo Bosne i Hercegovine (u daljem tekstu: Institut), postupajući po zahtjevu podnosioca prijave **Univerzitet u Banjoj Luci, O.J. Prirodno-matematički fakultet, Mladena Stojanovića 2, 78000, Banja Luka, BA,** za priznanje patenta, na osnovu čl. 14., 15., 35., 37. i 38., Zakona o patentu ("Službeni glasnik BiH", broj 53/10), i odredbi Pravilnika o postupku za priznanje patenta i konsenzualnog patenta ("Službeni glasnik BiH", br. 105/10), d o n o s i

Z A K L J U Č A K

o objavljivanju prijave patenta – BAP203346A

1. **OBJAVLJUJE SE** prijava patenta pod nazivom **"SINTEZA NANOČESTICA HEMATITA IZ AKUMULACIJA OTPADNOG MULJA RUDNIKA ŽELJEZA"** koja je upisana u registar prijava patenata kod Instituta pod brojem **BAP203346A**, dana **2020-02-19** godine, u službenom glasniku Instituta, br. **3/2021**, sa danom **2021-09-30** godine.

Obrazloženje

U postupku ispitivanja prijave patenta koja je upisana u registar prijava patenata kod Instituta dana 2020-02-19 godine, pod brojem BAP203346A, Institut je utvrdio da prijava ispunjava, u cjelosti, sve uslove određene čl. 35. Zakona o patentu, te na osnovu toga izdaje zaključak o objavi prijave patenta.

Podnosioc prijave **može** u roku od šest mjeseci od datuma objavljivanja prijave patenta u službenom glasniku Instituta, podnijeti jedan od tri zahtjeva iz čl. 38. Zakona o patentu, te za podneseni zahtjev platiti odgovarajuće takse i troškove postupka u skladu sa čl.15. Zakona o patentu.

Ako u propisanom roku podnosioc **ne podnese** jedan od tri gore navedena zahtjeva ili ne plati odgovarajuće takse i troškove postupka, prijava patenta smatrat će se povučenom i Institut će donijeti zaključak o obustavljanju postupka za priznanje patenta.

POUKA O PRAVNOM LIJEKU. Protiv ovog zaključka dopuštena je žalba Komisiji za žalbe Instituta u roku od 15 dana od dana prijema. Žalba se podnosi u dva istovjetna primjerka uz dokaz o uplaćenoj taksi i troškovima postupka.

ravnatelj
Josip Merdžo

DOSTAVLJENO:
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Hypothesis: is it possible to do something similar with the sludge from bauxite processing („red mud“)?

European red mud: where can we find it?

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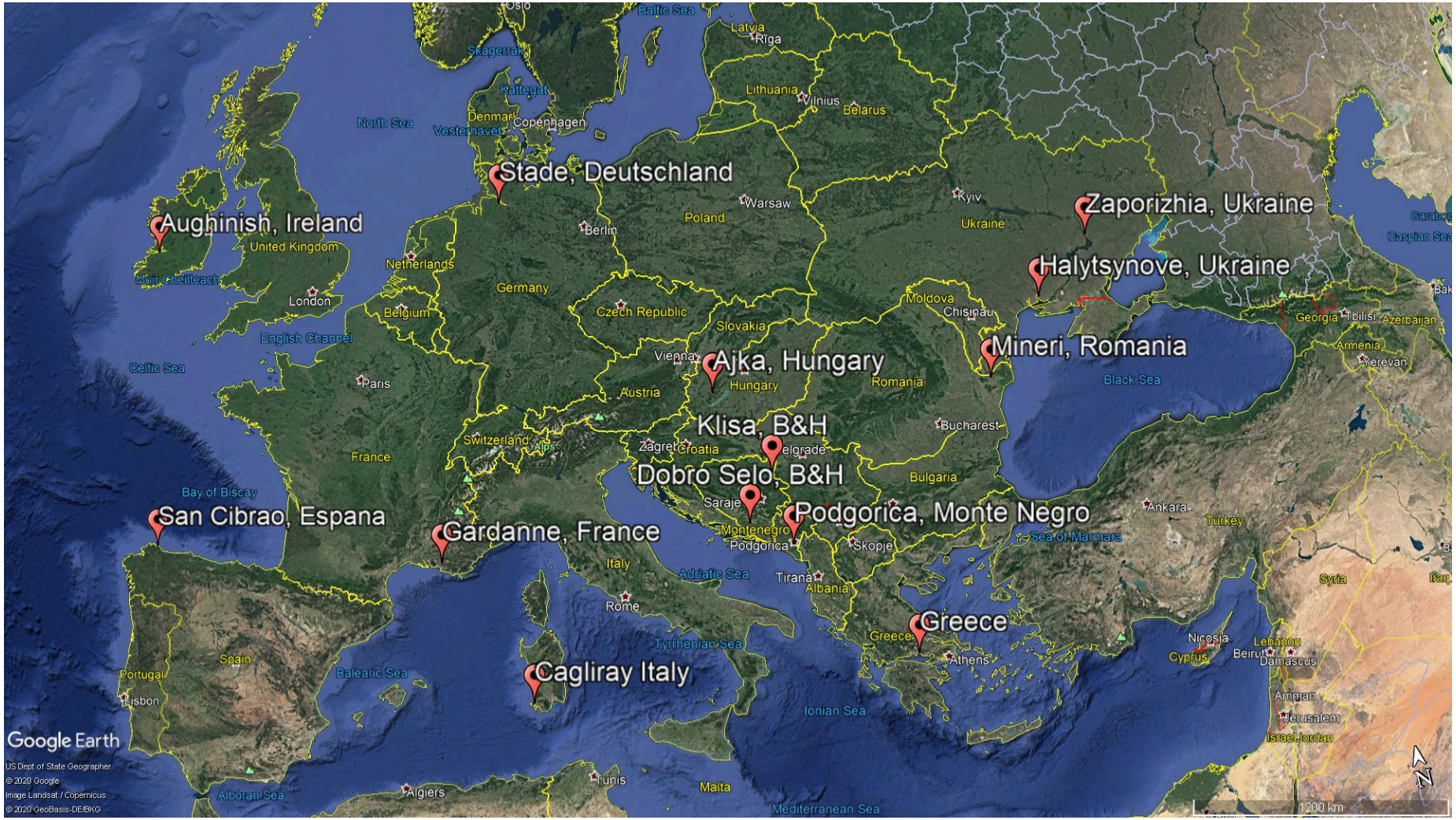

https://etn.redmud.org/where-is-all-of-the-red-mud/

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European red mud: some dissposal data

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Refinery	Disposal Period	Disposal Method	Rate (kt/year) *	BRDA Surface (ha)
Stade	1973	Lagooning	1500	150
Gardanne	1893–2012	Sea discharge	690	
	2012–2014	Sea discharge/Dry stacking	n.d.	29.4
San Ciprian	1981–2014	Dry stacking	2175	84
Aughinish	1983	Dry stacking	3000	121
Aluminium of Greece	1966–2012	Sea discharge/ Dry stacking	1200	19
	2012–2014	Dry stacking	749**	
Eurallumina	1977–2009	Lagooning	1200	120

*Calculated as 1.5 times of the production rate of alumina
**Mytilineos Holdings Sustainability report 2014

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https://etn.redmud.org/where-is-all-of-the-red-mud/

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Why the Bosnian red mud?

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We have plenty of bauxite and two major accumulation sites (tailings)

Location: Dobro Selo (5M t)

South of the country

Location: Đulići-Zvornik (>19M t)

East of the country

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Even if not using the acidic leaching: ultramicroparticles are already there!

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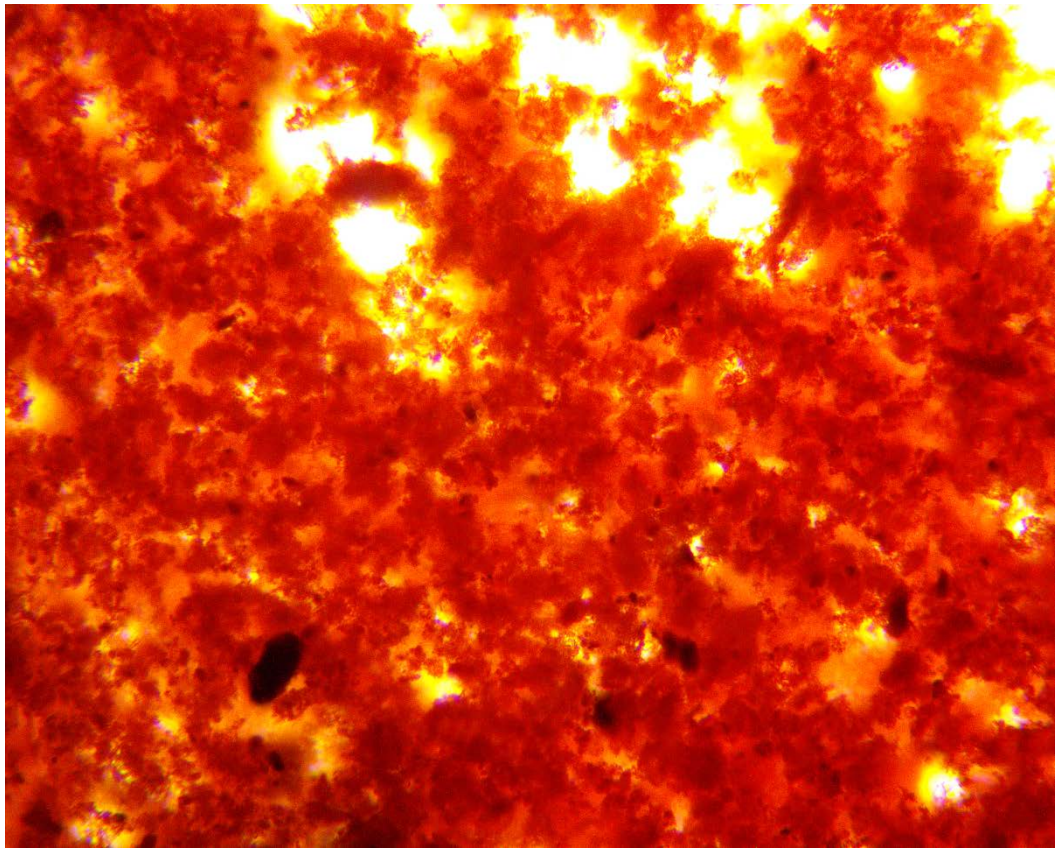

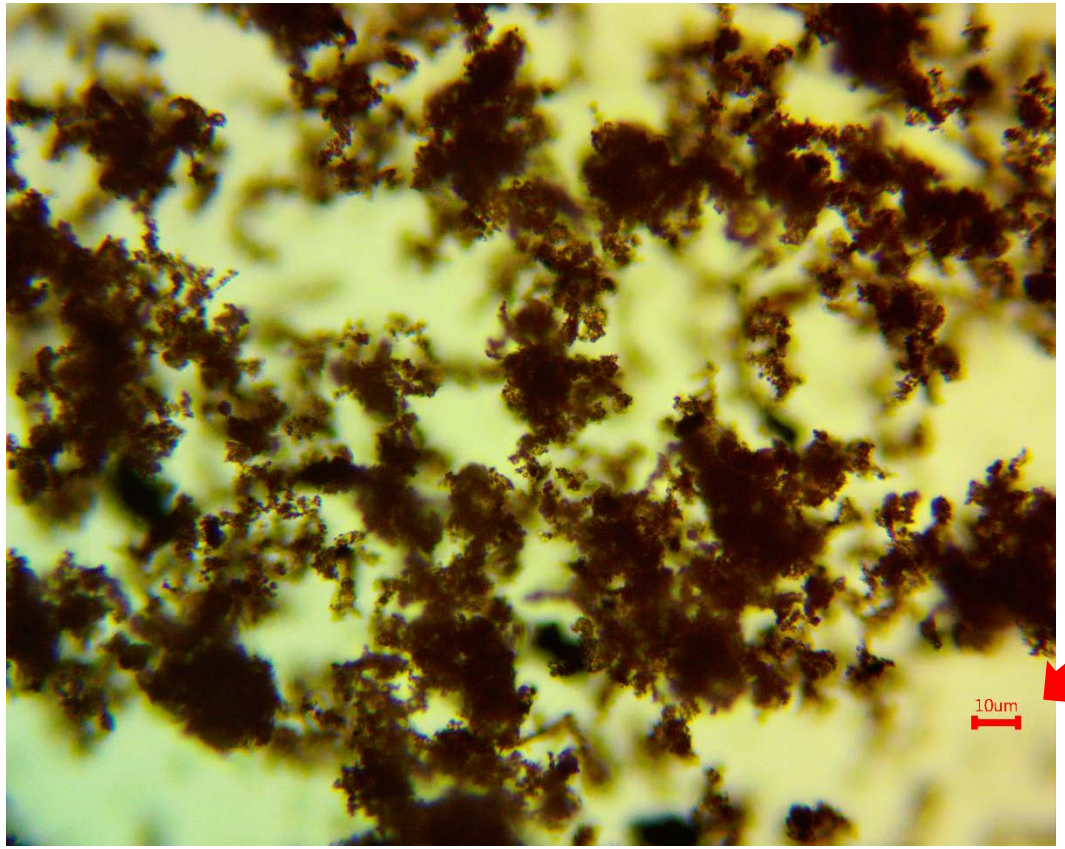

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Chemical analysis of Alumina red mud by 2021. months is given in the table:

	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	CaO (%)	Na_2O_v (%)	Na_2O_u (%)	LOI (%)	ZnO (%)
January	11,19	13,51	45,04	4,94	7,68	4,21	4,46	7,11	0,0195
February	9,97	12,94	48,94	5,38	7,76	5,11	5,24	6,69	0,0188
March	11,21	13,91	47,31	5,35	7,47	5,88	5,99	6,41	0,0192
April	10,87	12,88	44,62	3,82	7,87	5,20	5,44	9,06	0,0179
May	9,85	13,40	49,79	5,38	5,72	5,81	6,27	6,27	0,0202
Average value	10,62	13,32	47,14	4,74	7,3	5,24	5,48	7,11	0,0191

The pH of the filtrate of the mud is about 12,5. Filtrate also contains certain amounts of all macro and semi components from bauxite/red mud (Al, Fe, Ti, Ca, Zn..)

Some of the micro components in the filtrate and red mud:

	Cd mg/l	Co mg/l	Cu mg/l	Ga mg/l	K mg/l	Li mg/l	Mg mg/l	Mn mg/l	Ni mg/l	Pb mg/l	Zn mg/l
Filtrate of red mud	**0,112**	**< 0.006**	**0,069**	**1,928**	**> 48.179**	**0,058**	**0,003**	**0,009**	**< 0.010**	**0,979**	**< 0.001**
Red mud	%	%	%	%	%	%	%	%	%	%	%
	0,067	**0,0095**	**< 0.002**	**0,117**	**0,06**	**0,006**	**0,153**	**0,075**	**0,018**	**0,037**	**0,011**

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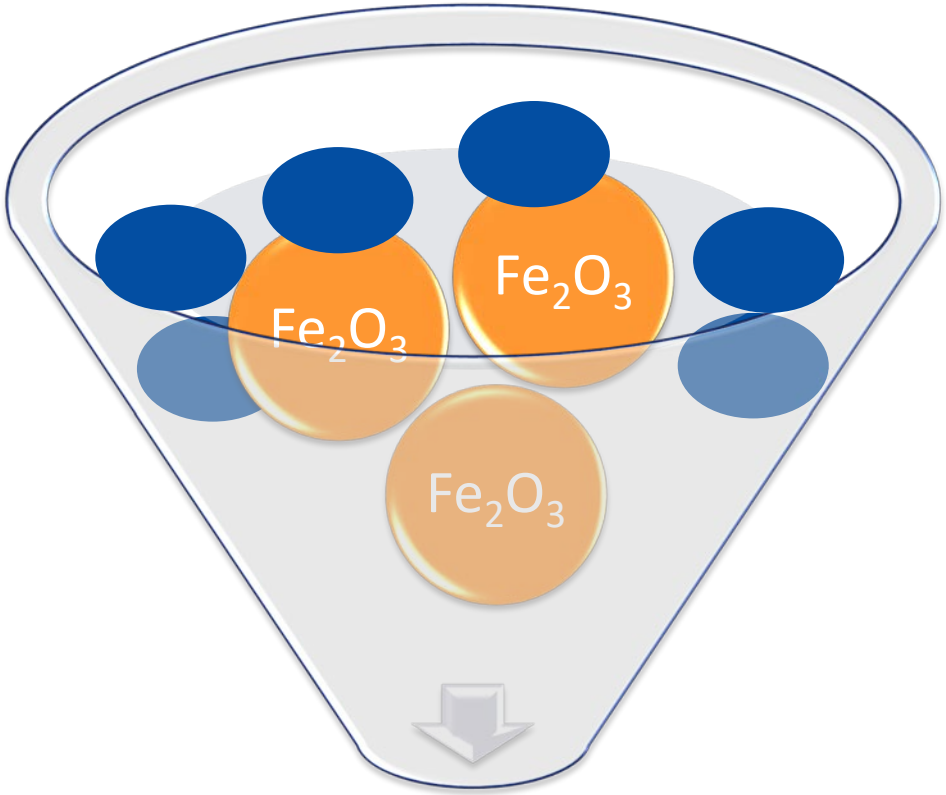
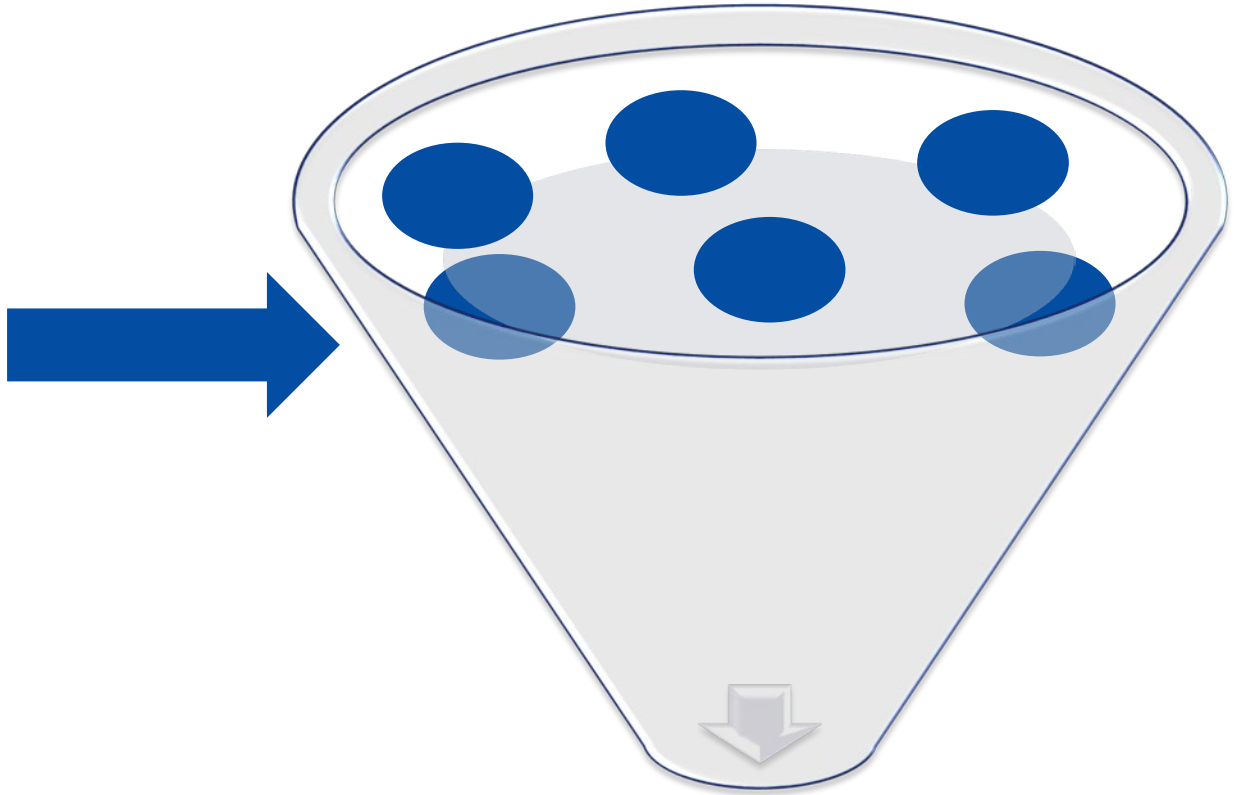
What if we remove the iron component ???





Removal of cca 50% Fe_2O_3

Doubling of other components !!!

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What are we trying:
Transforming hematite into other forms of iron oxides

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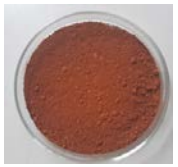
hematit + kvarc porijeklom iz piritne rude → magnetit

$FeS_2 \rightarrow FeSx + (2 - x)S$ x = 1–2 (450-750 °C)

$FeS_2 + 4Fe_2O_3 \rightarrow 3Fe_3O_4 + 2S$

$2S + 12Fe_2O_3 \rightarrow 8Fe_3O_4 + 2SO_2$

Tempereature	600 °C
Time at final T	0,5 h
Heat rate	10 °C/min
Nitrogen flow	50 L/h
Cooling	In N2 flow down to 25 °C



Apyrite forms

Red mud

Mixing

Heat treatment

Separation

- N2 adsorption
- FTIR
- XRD

characterisations

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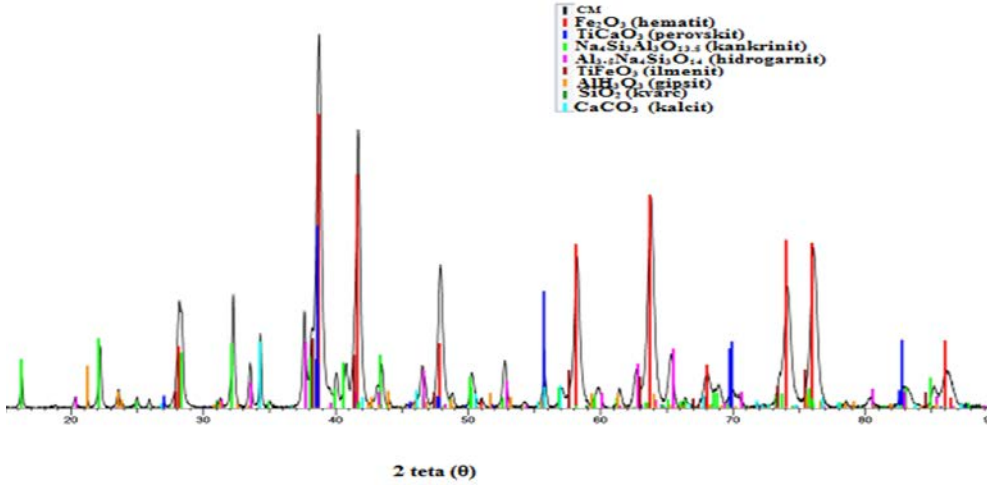
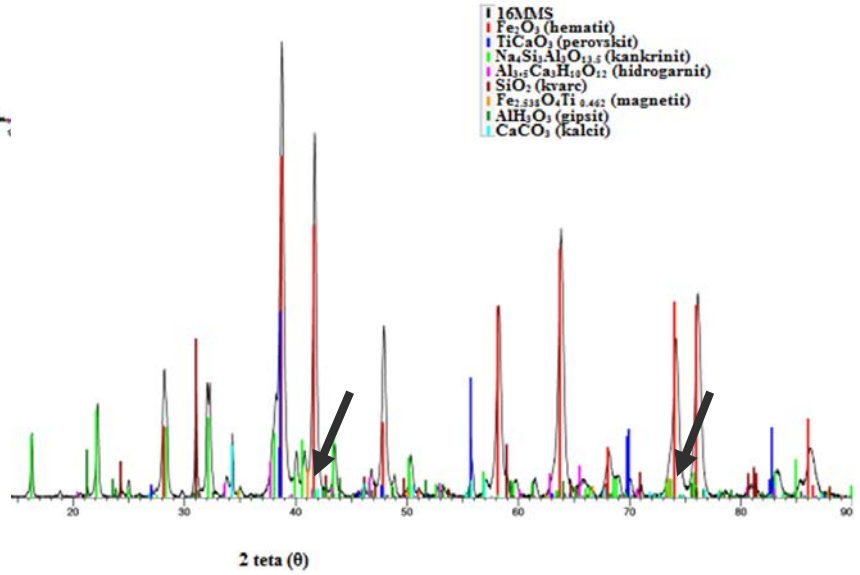
XRD

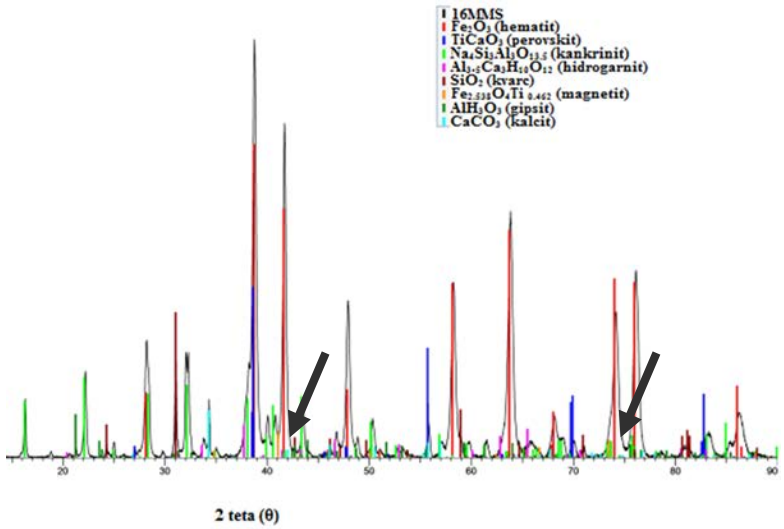


- Raw red mud: hematite species dominant

- Red mud treated with pyrite-dressed quartz: appearance of the magnaetite peaks 41°, 73°

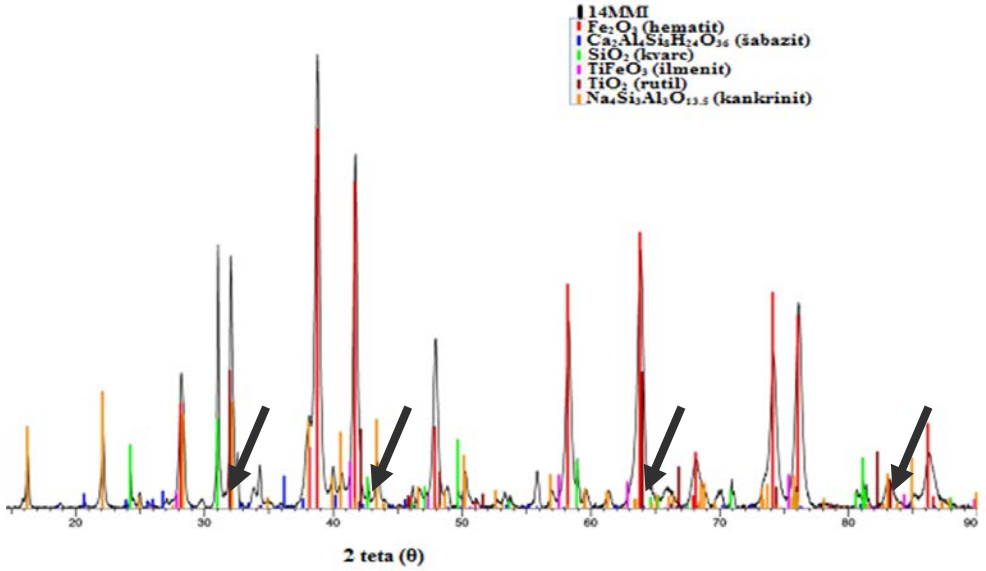


XRD

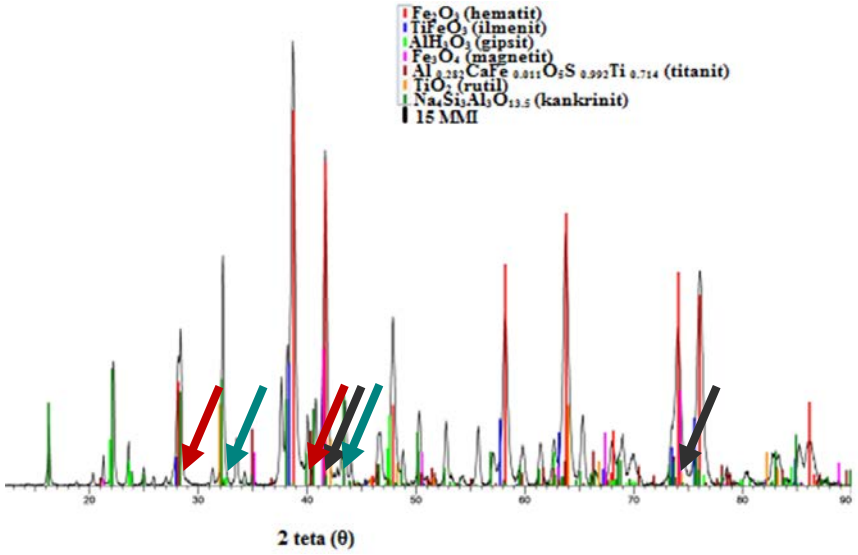


- Different treatments appearance of (TiO_2): 32°, 43°, 64°, 83°

- Red mud treated with pyrite-dressed quartz: appearance of the magnaetite peaks 41°, 73°

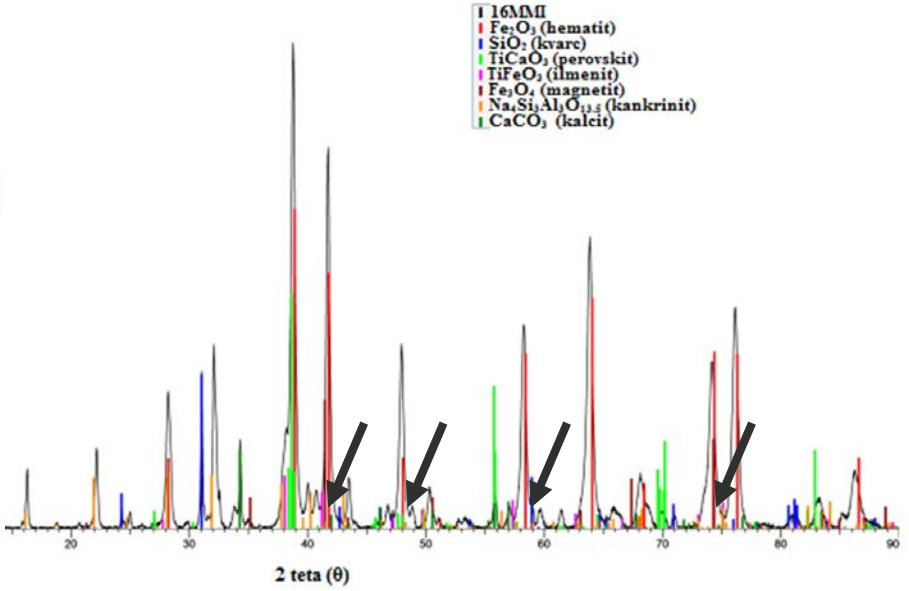


XRD



- Again magneatite: 42°, 48°, 58°, 74°

- Other forms of tiatinum dioxide (rutile and titanite):
  41.5°, 74°, 32°, 42°, 28°, 40°



Plan: to make use of the domestic abandoned pyrite mine in Ključ

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Historical data on pyrite in Bosnia

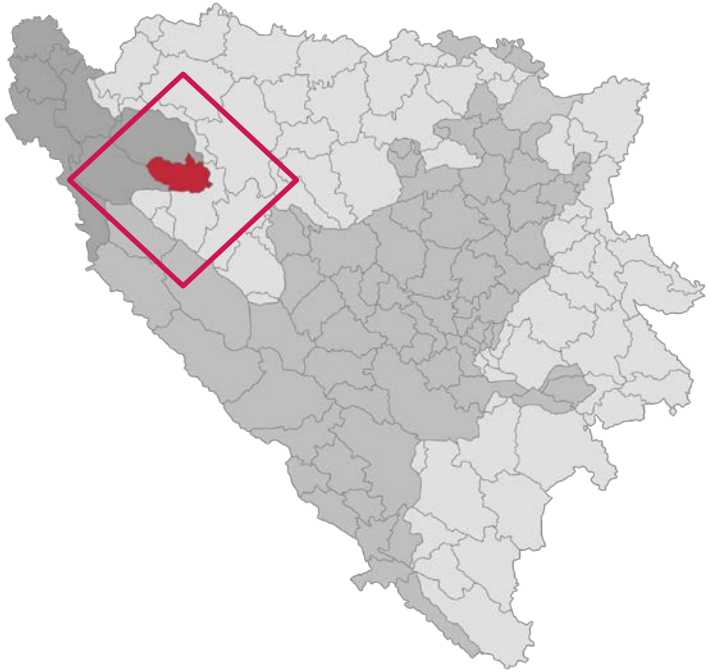
PIRIT

Sjeverozapadno od Ključa, u području Muhamedbegove Prisjeke, nalazi se pi[illegible] orudnjenje, koje je još početkom ovog stoljeća istraživano, a prije II svjetskog rata i eksploatirano. Detaljnim istražnim radovima samo su djelimično obuhvaćene lokalnosti Šikman i Osoje, čija međusobna udaljenost iznosi oko 600 m, vazdušne linije.

Ležište Šikman izgrađeno je od tri rudna tijela međusobno po[illegible]. Vjerovatno čine cjelinu, ali zbog pomanjkanja istražnih radova to nije utvrđeno. Morfologija ležišta je veoma nepravilna. Ležište Osoje ima oblik izduženog nepravilnog sočiva. Duža osa mu je orijentirana u pravcu sjeverozapad—jugoistok. Zalijeganje mu je vertikalno. Prosječena dužina iznosi 36 m, debljina je neujednačena i kreće se od 1—5 m.

Na osnovu postojećih podataka može se zaključiti da orudnjenje pirita kod Muhamedbegove Prisjeke po genetskim karakteristikama pripada metamorfnom tipu ležišta, koja su nastala dinamometamorfozom sedimentnih submarinsko-eshalacionih tvorevina.

31



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Success story: Alumina company

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- Over 1500 employes
  - Absolute European leader

- Customers at 5 continents
  - Products reaching 40 countries

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Maybe titanium ?

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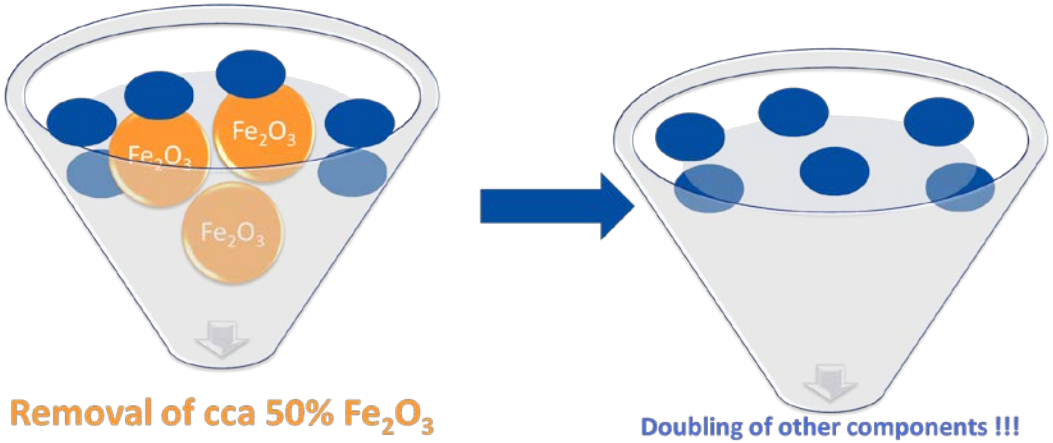

TiO_2 6% becomes 12% !

- **Titanum ores rutil and anatas contain cca 90% of Ti-oxides**
- **HOWEVER, in „soft“ ores, titanium extraction is economical even at 1%**
- **Red mud is very „soft“ !!!**

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Conclusions:

- It is important to recognize a need for awakening of the mining in Europe
- The mining can be done in a „green“ manner

=

- Not only ore deposits, but tailings as well hold a potential for raw material exploitation
- One direction of the tailings application should be in nanotechnologies
- Red mud tailings lead the way as one with a very diverse composition

Supported by:

This activity has received funding from the European Institute of Innovation and Technology (EIT), a body of the European Union, under the Horizon 2020, the EU Framework Programme for Research and Innovation

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Thank you for kindly your attention!

Questions & Suggestions?

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