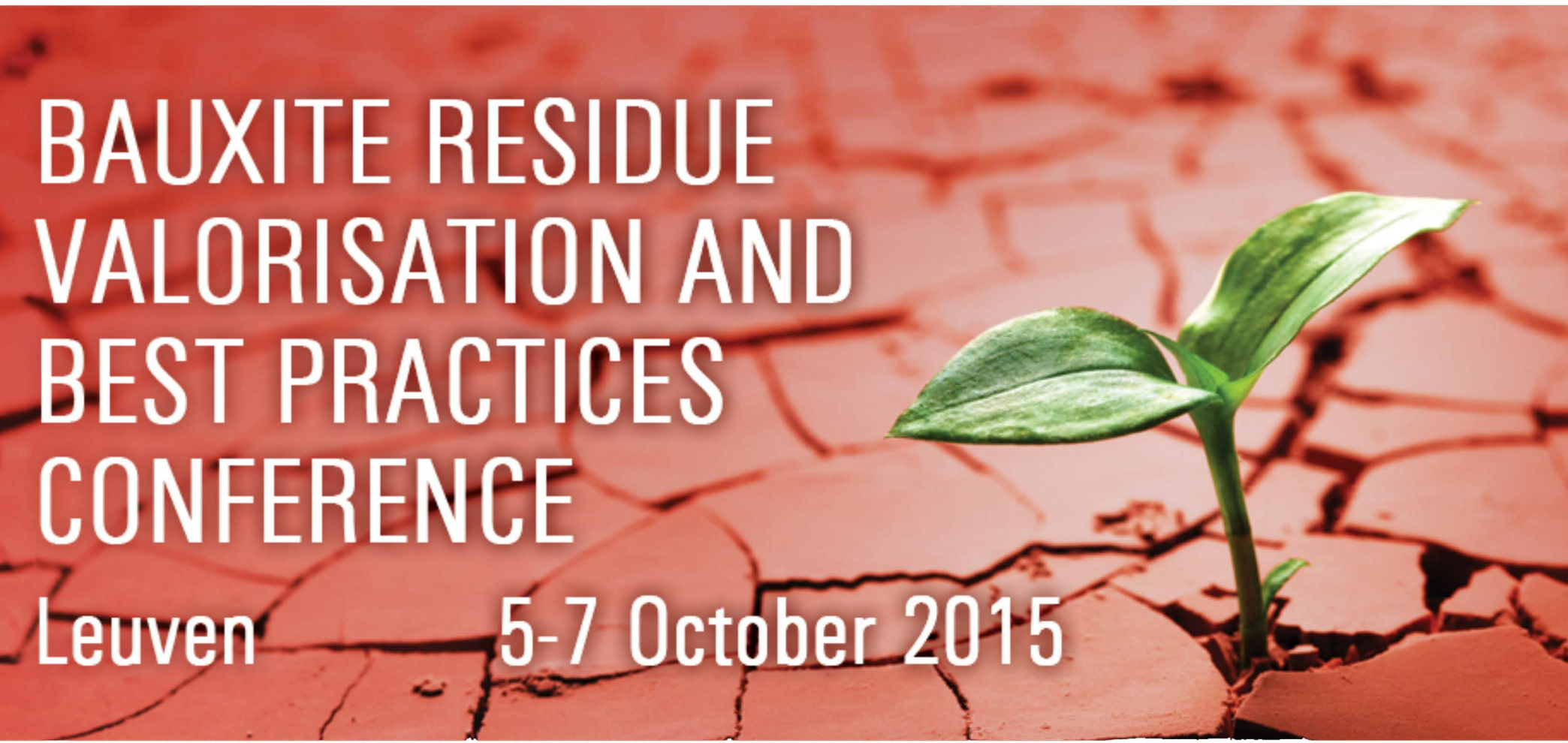
BAUXITE RESIDUE VALORISATION AND BEST PRACTICES CONFERENCE



Leuven 5-7 October 2015

Alternative valorisation of red mud as catalyst for sulphide oxidation in wastewater

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WHY?

Bauxite production
258 milion tons*

*2012-International Aluminium Institute

Bayer process

Alumina production
101 milion tons*

Aluminum
1 ton≅ 70,000 cans*

Bauxite residue
120 milion tons*

?

Annually repurposed 2 milion tons (< 2%) *

Potentially harmful Industrial waste ! –
-High alkalinity pH >12
-High content of heavy metals
- Usually deposited in landfills – soil contamination

HOW to solve the issue?

waste management firm Virotec (Australia)

neutralization

+ seawater or brine

NBR → **remediation of mining sites**

NBR → **filler to make bricks**

NBR → **sorbent (trap metals and P from wastewater.)**

Sulfidation (Iannicelli method*)

AZorb

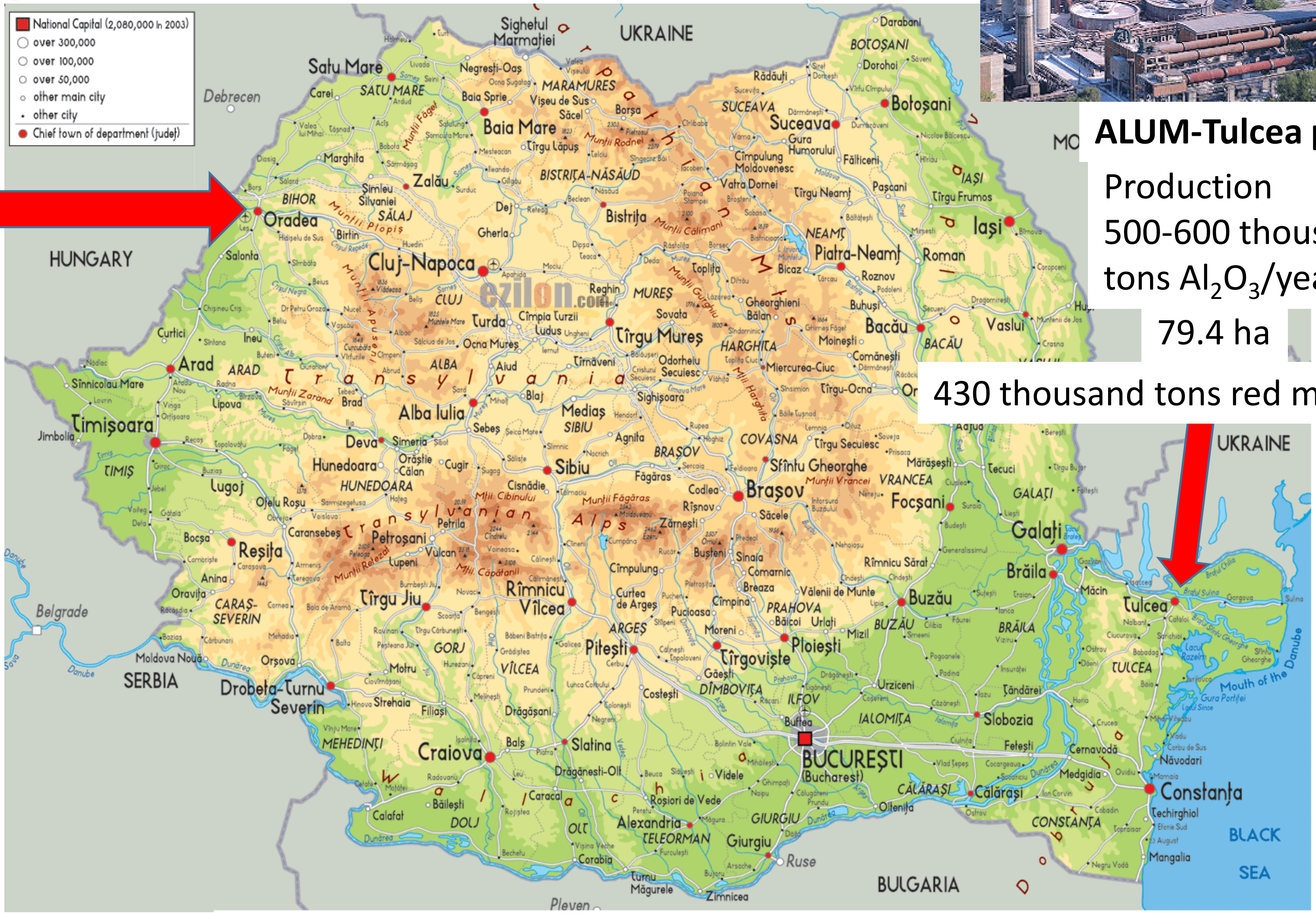
BR + CO_2 ***Aluminum producer Alcoa***

"red sand" → **cement and in road construction**

Recovery of iron and rare-earth metals

* STEPHEN K. RITTER , Making the most of red mud, C&EN WASHINGTON CEN 24,02,2014 page 33-35

Bauxite residue in Romania



80 ha

Oradea plant
stopped working in 2006

issues posed by the storage of red mud under secure conditions are still acting because the sludge (red mud) made infiltrations that polluted the soil and the water, and in windy conditions a red dust with caustic powders, due to the content of sodium hydroxide, is blown up

ALUM-Tulcea plant

Production 500-600 thousand tons Al_2O_3/year

79.4 ha

430 thousand tons red mud /year

Using BR as catalyst

Hydrogenation - *K.C. Pratt, and V. Christoverson*, "Hydrogenation of a model hydrogen-donor system using activated red mud catalyst", *Fuel*, **61** 460–462 (1982)

Hydrodechlorination - *S. Ordóñez, H. Sastre and F.V. Díez*, "Catalytic hydrodechlorination of tetrachloroethylene over red mud", *J. Hazard. Mater.*, **81** 103–114 (2001); *S. Ordóñez, F.V. Díez and H. Sastre*, "Hydrodechlorination of tetrachloroethylene over sulfided catalysts: kinetic study", *Catal. Today* **73** 325–331 (2002)

Hydrocarbon oxidation - *J.R. Paredes, S. Ordóñez, A. Vega and F.V. Díez*, "Catalytic combustion of methane over red mud-based catalysts" *Appl. Catal. B: Environmental,* **47** 37–45 (2004); *J.F. Lamonier, F. Wyralski, G. Leclercq, and A. Aboukais*, "Recycling of waste, red mud, as a catalyser for the elimination of volatile organic compounds", *Can. J. Chem. Eng*. **83** 737–741 (2005).

Our aim

To explore the catalytic activity of BR derived materials in the oxidation of sulphide ions from wastewaters

Why

1. There are no published data concerning the catalytic activity of BR derived materials referring to this subject

2. BR contain also TiO_2, SiO_2, Al_2O_3 besides high amounts of Fe_2O_3 and there are references concerning the utilization of iron oxide supported on TiO_2, SiO_2, Al_2O_3 or MgO as catalyst for the oxidation of sulphide ions to elementary sulphur in aqueous solutions – *[R. J. A. M. Terorde, P. J. van den Brink, L. M. Visser, A. J. van Dillen, and J.W. Geus, "Selective Oxidation of Hydrogen Sulfide to Elemental Sulfur Using Iron Oxide Catalysts on Various Supports", Catal. Today, **17** 217-225 (1993).; K.D. Jung, O.S. Joo, S.H. Cho, S.H. Han, "Catalytic wet oxidation of H_2S to sulfur on Fe/MgO catalyst", Appl. Catal. A: General, **240** 235-241 (2003).]*

3. Many sources of Sulphide ions pollutants - oil refineries, fossil fuel gasification plants, paper and pulp mills, the anaerobic oxidation of sewage water, certain well waters. The sulphide ions from water have to be removed due to their toxicity and obnoxious odour.

Hypotheses

- **Fe, Co and Cr Chelates in homogeneous systems have been proved to be useful catalysts for S^{2-} oxidation using oxygen from air as oxydation agent** [A. Cruceanu, R. Zavoianu, and E. Angelescu, E., "Catalytic Desulphurisation of Gaseous Streams Containing H_2S in the Presence of Fe, Co and Cr Chelates Catalysts", *Prog. Catal.*, 10 (1-2) 27-39 (2001)]

- **Fe (III) chelates immobilised on a solid base matrix have been proved to be useful catalysts for S^{2-} oxidation** [A. Cruceanu, R. Zavoianu, R. Bîrjega, M. Ropot, "Preliminary studies concerning catalytic oxidation of alkyl mercaptans from liquid petroleum cuts in the presence of Fe(III) chelates supported on hydrotalcite-like compounds", *Annals Univ. Bucharest.*, 1, 41-48 (2005)]

- **The reducing of the transitional metal ion by RS^- takes place simultaneously with the oxidation of the reduced species by the oxygen.**

- **BR could be used as Fe source due to the higher stability constants* of Fe complexes compared to those of the other metals existing in BR**

***[http://maxchelator.stanford.edu/xlsconstants.htm : 10/14/2002 for files of constants in: CMC1002S.TCM CMC1002E.TCM CMC1002S.CCM CMC1002E.CCM].**

Reactions to be avoided

$Fe^{2+} + HS^- \rightarrow FeS\downarrow + H^+$

$2Fe(OH)_3(s) + 3\ H_2S \rightarrow 2FeS(s)\downarrow + S^0\downarrow + 6H_2O$

$2Fe(OH)_3(s) + 3\ H_2S \rightarrow Fe_2S_3(s)\downarrow + 6H_2O$

Complexation =“functionalisation” of Fe(III) sites from bauxite residue by treatment with polycarboxylic acids.

Advantages:

-ability of Fe(III) to change the oxidation state during its involvement in the redox cycles

-+

- avoids precipitation as FeS or $Fe(OH)_3$ due to sufficiently strong coordination in the ligands field

Preparation

BR – E : molar ratio H_2Na_2EDTA / Fe = 1,5 / 1

BR-C : molar ratio Na_3CIT/Fe = 2/1

BR – E – C: molar ratio H_2Na_2EDTA /Fe=1/1; Na_3CIT /Fe=1/1

(weight ratio L/S=10:1) T=25°C,
6 days ; stirring (150 rpm) – 2h/day.

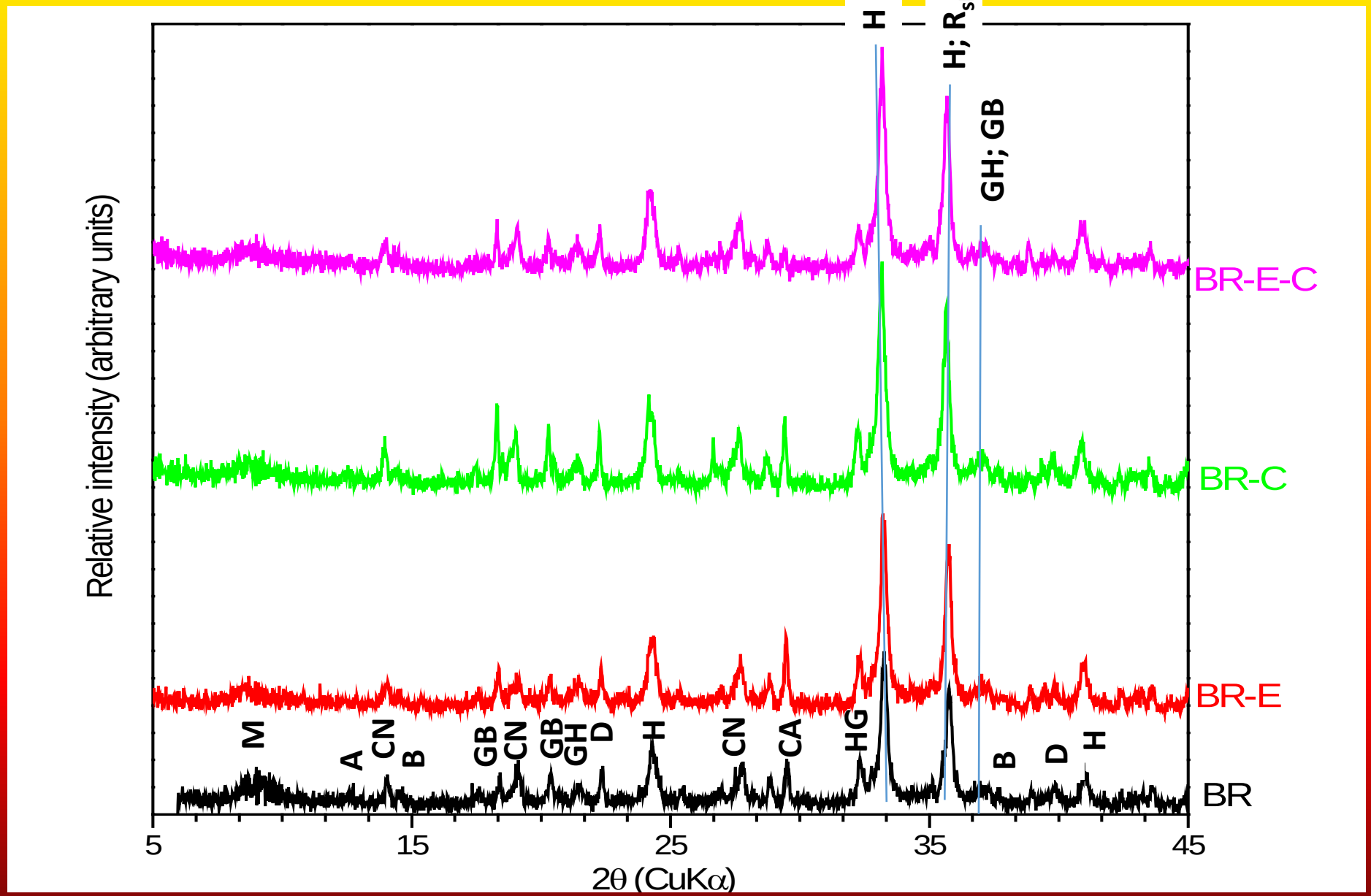
(BR) from ALUM Tulcea (Romania) - raw material for Fe containing catalysts.

chemical composition of the BR as determined by ICP-AES and chemical analyses

Fe	Al	Ti	Si	Na	K	Mg	Ca	Ba	C	F	
27	10.5	4.4	3.2	3.7	0.25	0.3	4.4	0.2	1.3	0.25	Wt%

Fe	Al	Ti	Si	Na	K	Mg	Ca	Ba	C	As oxides
39.2	20.2	7.5	7.0	5.1	0.3	0.5	6.3	0.2	6.6	Wt%

XRD


H
H; R_sh
GH; GB
BR-E-C
BR-C
BR-E
BR
M
A
CN
B
GB
CN
GB
GH
D
H
CN
CA
HG
B
D
H
Relative intensity (arbitrary units)
5
15
25
35
45
2θ (CuKα)

XRD - Semiquantitative phase analysis of BR

Abbreviation	Name	Chemical Formula	PDF[17]	Wt. %
H	**hematite**	**Fe_2O_3**	**1-087-1164**	**30.2**
GH	goethite	FeO(OH)	01-081-0464	9.7
D	diaspore	α-Al(O)OH	01-084-0175	7.5
B	bohemite	γ-Al(O)OH	01-083-1505	2.3
GB	gibbsite	$Al(OH)_3$	01-074-1775	10.5
HG	hydrogarnet	$Ca_3Al_2(OH)_{12}$	00-032-0147	4.7
CA	calcite	$CaCO_3$	r01-071-3699	9.2
CN	cancrinite	$Na_6Ca_2[(CO_3)_2\|Al_6Si_6O_{24}]\cdot 2H_2O$	01-089-8592	7.7
CS	cancrisilite	$Na_7(Al_5Si_7O_{24})(CO_3)\cdot 3H_2O$	01-089-8047	11.4
A	amesite	$Mg_2Al_2SiO_5(OH)_4$	01-087-2057	2.1
M	muscovite	$KAl_2(AlSi_3O_{10})(F,OH)_2$	00-007-0042	1.9
AN	anatase	TiO_2	00-021-1272	0.7
R	rutile	TiO_2	01-070-7347	2.2

Effects of the treatment with polycarboxylic acids :

Preservation of hematite characteristic diffraction lines → **Low solubilisation of Fe species.**

Higher intensity of the diffraction lines for iron containing phases compared to BR → **Removal of some amorphous phases from the bauxite residue by solubilisation.**

Disappearence of diffraction lines for amesite (A) and bohemite(B), lower intensities of lines corresponding to muscovite (M).

↓

Preferential solubilisation of Al, Ca and Mg from BR

↑ **Absence of the third diffraction line characteristic to gibbsite (GB) for BR-C and BR-E-C**

↑ **BR-E-C decrease of intensity for the calcite (CA) phase.**

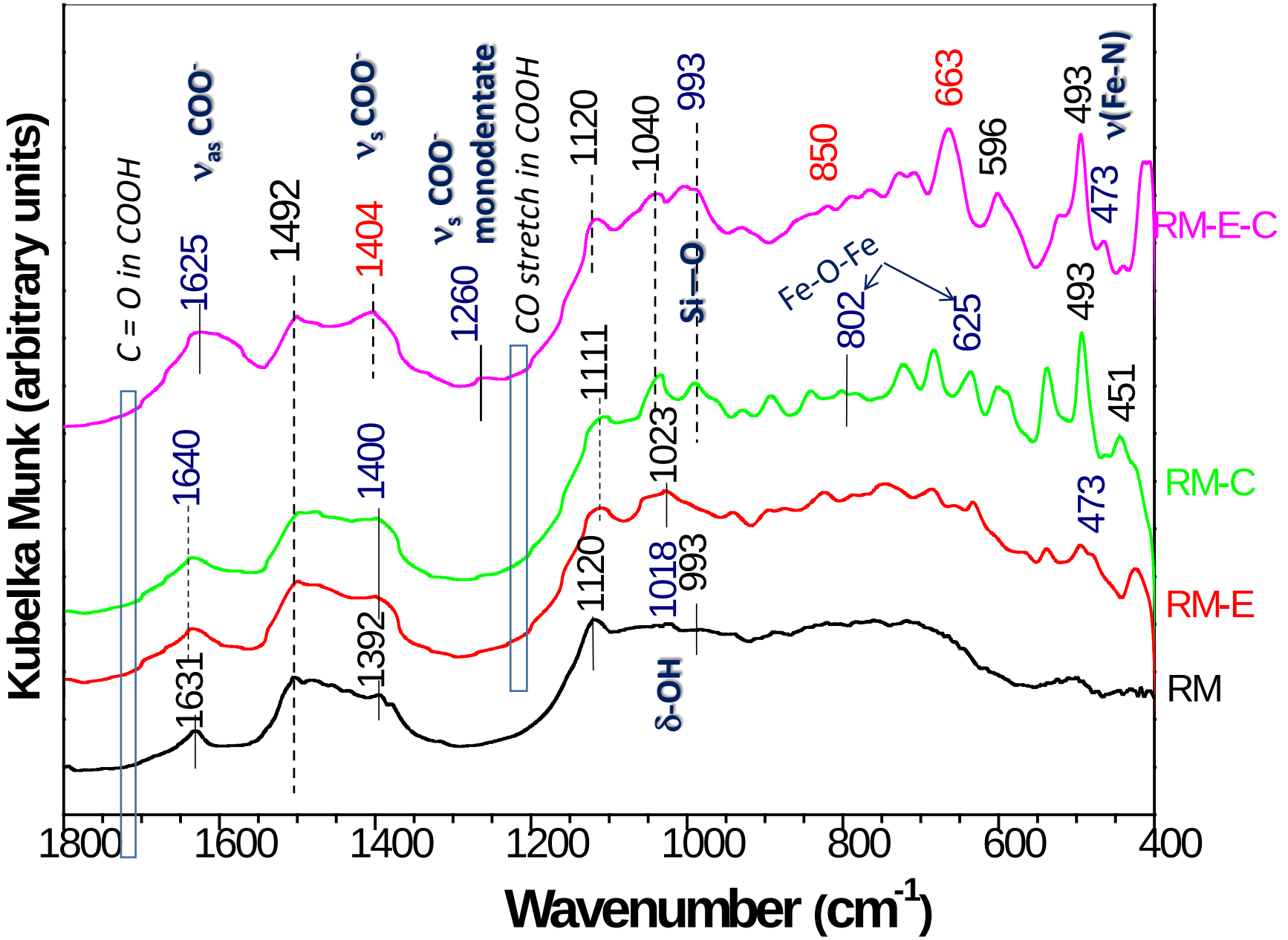
Metal content in the waste waters obtained after the synthesis

	Volume of waste water	Concentration (mg/L)					
Sample	(L)	Fe	Al	K	Mg	Ca	Ba
BR-E	0.920	1.2	533.4	0.5	32.2	230.7	1.6
BR-C	0.945	1.4	532.4	0.4	31.1	122.2	1.3
BR-E-C	0.960	1.0	529.9	0.3	33.3	354.6	1.7

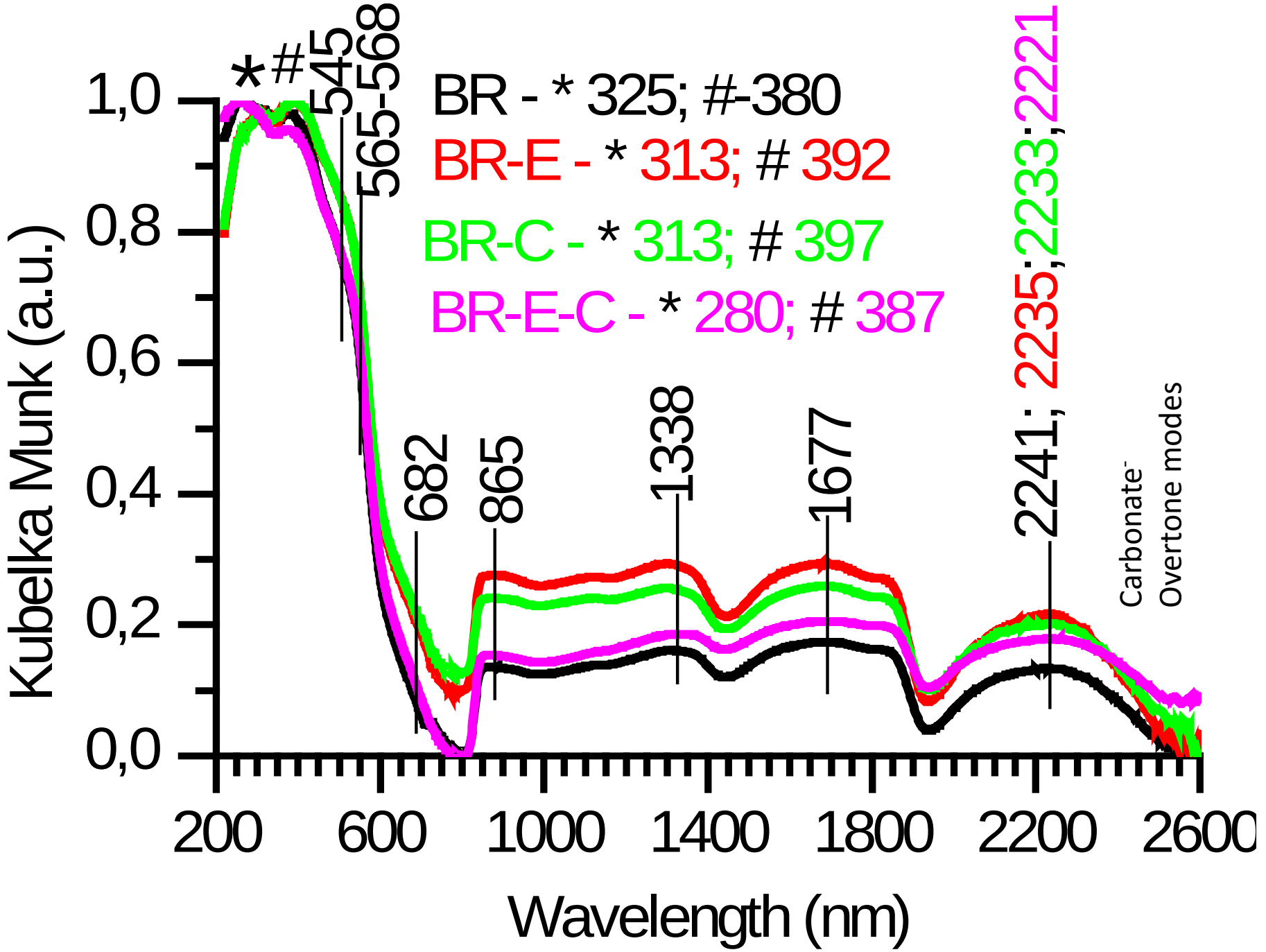
New lines corresponding to the complexes formed on the surface of BR

Sample	2 θ for the new diffraction lines
BR-E	9.88°, 21.43° and 42.5°,
BR-C	21.51°, 26.64° and 39.33°
BR-E-C	21.27°, 21.51°, 26.49°, 34.37° 38.84° and 42.34°

DRIFTS


Kubelka Munk (arbitrary units)
Wavenumber (cm-1)
1800
1600
1400
1200
1000
800
600
400
C = O in COOH
νas COO-
νs COO-
νs COO- monodentate
CO stretch in COOH
Si—O
δ-OH
Fe-O-Fe
ν(Fe-N)
1625
1492
1404
1260
1120
1040
993
850
663
596
493
473
1640
1400
1111
1023
802
625
493
451
1631
1392
1120
1018
993
473
RM-E-C
RM-C
RM-E
RM

DR UVVis NIR


*#
545
565-568
682
865
1338
1677
2241; 2235;2233;2221
Carbonate Overtone modes
BR - * 325; #-380
BR-E - * 313; # 392
BR-C - * 313; # 397
BR-E-C - * 280; # 387
Kubelka Munk (a.u.)
1,0
0,8
0,6
0,4
0,2
0,0
200
600
1000
1400
1800
2200
2600
Wavelength (nm)

Catalytic testing

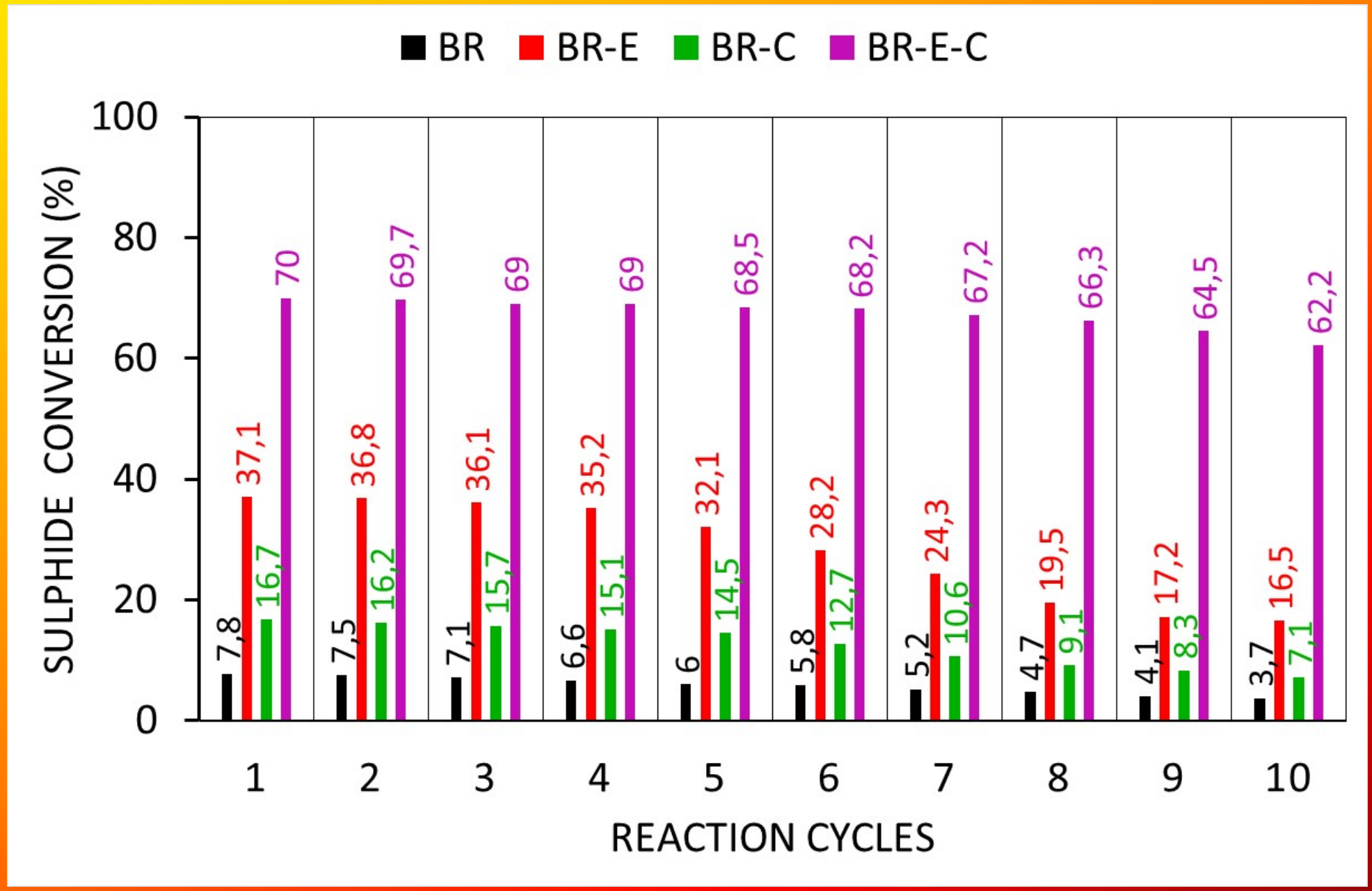
synthetic wastewater freshly prepared = $Na_2S \cdot 9H_2O$ in deoxygenated distilled water.

Reaction conditions

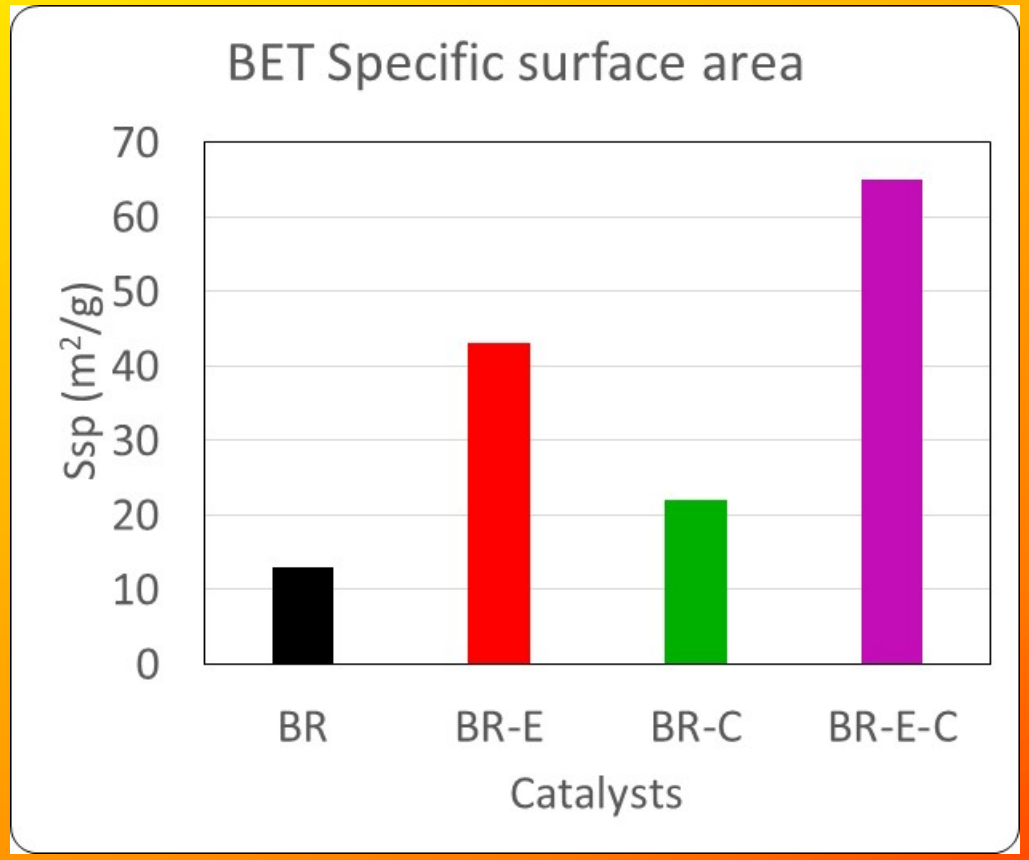
$C_{0,S^{2-}}$ = 1 g/L, 2 h reaction time;
4L/h air flow, 1.3 wt. % of catalyst in wastewater;
T= 25°C; p = 1 atm pH 8.5-9

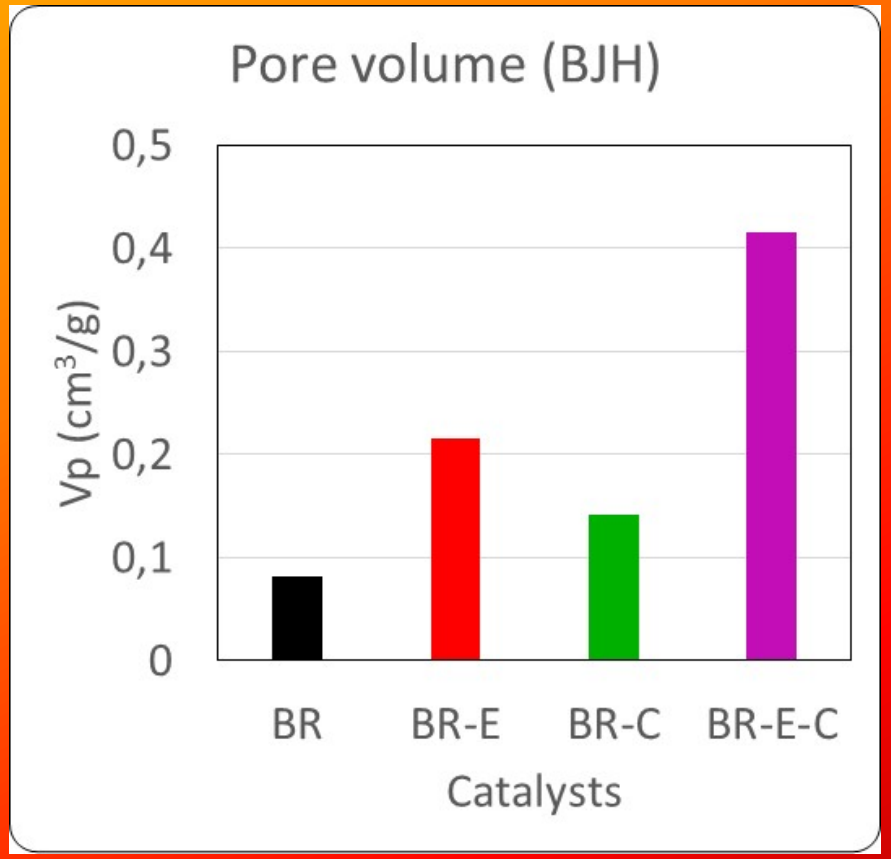
S^{2-} dosage – both by spectrophotometric method (λ-230nm) –(disadvantage – other oxidation products such as $S_2O_3^{2-}$, $S_4O_6^{2-}$ and SO_3^{2-} also absorb strongly in this region)

[*Chen & Morris, J. C. Environ. Sci. and Technol. 6(6), (1972) 529-537***] and by volumetric method (iodometric titration)**



The stability of the catalysts decreases following the same order as their catalytic activity: BR-E-C > BR-E > BR-C > BR.





The order of the catalytic activity seems to be well correlated to the textural properties of the solids

CONCLUSIONS

1. The functionalization of BR with disodium ethylenediamminotetraacetic acid (H_2Na_2EDTA) or/and trisodium citrate (Na_3CIT) yields active catalysts for the oxidation of sulphide ions from wastewaters using air as oxidation agent.

2. The preparation method allows both the formation of Fe(III) complexes on the surface of the bauxite residue, and the re-adsorption of the complexes formed in the solution following the dissolution of Fe by the complexation agents. This process may be responsible for the increase of the surface area of the functionalised catalysts.

BR-E-C - the most promissing catalyst

Acknowledgements

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Thank you very much for your kind attention!