



# International Symposium on the Industrial Applications of the Mössbauer Effect

Organized by Palacký University Olomouc, Czech Republic 11<sup>th</sup>–16<sup>th</sup> September 2022





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#### Welcome letter

Dear participants of ISIAME 2022 conference,

it is my great honour to invite you to attend the International Symposium on the Industrial Applications of the Mössbauer Effect, ISIAME 2022, which takes place in Olomouc, Czech Republic from 11<sup>th</sup> to 16<sup>th</sup> September 2022. Since travelling from some countries is still quite difficult, the conference is organized in a hybrid format, i.e. with both physical and virtual attendance. In the past, the symposium was organized every four years. However, due to the COVID-19 pandemic, ISIAME 2020 conference had to be postponed by two years. The participants are strongly encouraged to present their results, which are closely connected with industrial applications. During the conference, specific issues and methodology of applying Mössbauer spectroscopy results in industry are discussed thoroughly. The Scientific Executive Committee (SEC), which is composed mainly of the previous chairmen of the ISIAME series, supervises organization and program of ISIAME conferences. The main task of its members is to propose another organizers of the ISIAME and, generally, to keep tradition and main mission of the conference series.

Olomouc with its approx. 100 000 inhabitants is one of the most important and beautiful cities in the Czech Republic. Due to its rich history, time-honoured university, culture and crafts traditions, Olomouc has always been an attractive location for tourists, merchants, and business people. You can enjoy a lot of parks with green vegetation as well. Olomouc is easily accessible from Prague or Vienna, which are both approx. 250 km far, by using a train or bus. During the conference, you are cordially invited for a joint trip to TVARG brewery, where you can taste a good beer and special strongly-smelled cheese.

Olomouc is a typical university city with approx. 20 000 students. Palacký University Olomouc is the second oldest university in the Czech Republic comprising of 8 faculties. ISIAME 2022 conference is hosted by Faculty of Science in its modern-style building near the city centre. Mössbauer spectroscopy at Palacký University has a long-term history, particularly thanks to Prof. Miroslav Mashlan who has educated many specialists in the field.

On behalf of the Local Organizing Committee and as the chair of ISIAME 2022, I wish you fruitful and friendly meetings as well as enjoyable social events and stay in Olomouc.

Libor Machala

#### **Local Organizing Committee (LOC)**

Libor Machala - the chair of LOC

Josef Kopp

Jakub Navařík

Lukáš Richterek

Karolína Šišková

Pavla Šretrová

#### **Scientific Executive Committee (SEC)**

Massimo Carbucicchio (Italy) – the chair of SEC

Krish Bharuth-Ram (South Africa)

Desmond C. Cook (United States)

Ernö Kuzmann (Hungary)

Libor Machala (Czech Republic)

José. F. Marco (Spain)

Tetsuaki Nishida (Japan)

John G. Stevens (United States)

Frans B. Waanders (South Africa)

Tao Zhang (China)

#### **International Advisory Committee (IAC)**

Cesar Barrero (Colombia)

Frank J. Berry (United Kingdom)

Krish Bharuth-Ram (South Africa)

Massimo Carbucicchio (Italy)

Desmond C. Cook (United States)

Stanislaw Dubiel (Poland)

Yann Garcia (Belgium)

Jean-Marc Greneche (France)

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Ernö Kuzmann (Hungary) – SEC

Károly Lazár (Hungary)

Pierre-Emmanuel Lippens (France)

Libor Machala (Czech Republic)

José. F. Marco (Spain)

Miroslav Mashlan (Czech Republic)

Marcel Miglierini (Slovakia)

Tetsuaki Nishida (Japan)

Peter Schaaf (Germany)

Paulo de Souza (Australia)

John G. Stevens (United States)

Tadeusz Szumiata (Poland)

Frans B. Waanders (South Africa)

Tao Zhang (China)

#### The conference program

Sunday 11 <sup>th</sup> S	Sept	ember 2022		
-		Registration (Faculty of Science, 17.listopadu 1192/12)		
18:00-19:00	Exc	cursion to the Science	Centrum	
19:00-21:30	We	elcome reception (Scie	nce Centre)	
	_			
Monday 12 <sup>th</sup>	Sep	tember 2022	Registration desk 8:00-18:00	
9:00-9:30			Opening ceremony (Faculty of Science, 17. listopadu 1192/12)	
9:30-10:10	K1	PE. Lippens	Is tin an interesting element for energy transition?	
10:10-10:30	C1	J. Gałązka-Friedman	HOW MÖSSBAUER SPECTROSCOPY CAN HELP IN ACHIEVEMENT OF VALUABLE FOR INDUSTRY NATURAL RESOURCES FROM EXTRATERRESTRIAL OBJECTS	Chairman: J. F. Marco
10:30-11:00			Coffee break	
11:00-11:30	11	E. Tabor	MÖSSBAUER SPECTROSCOPY AS A CRUCIAL TOOL FOR DESIGNING OXIDATION CATALYSTS	
11:30-12:00	12	K. Lázár	STUDY OF INDUSTRIAL CATALYSTS AND CATALYTIC PROCESSES BY MÖSSBAUER SPECTROSCOPY	Chairman: T. Szumiata
12:00-12:20	C2	M. Kořenek	MÖSSBAUER SPECTROSCOPY OF IRON CATALYSED CARBON NANOSTRUCTURES	
12:30-14:00			Lunch	
14:00-14:30	13	J. Wang (online)	In-situ/operando Mössbauer Spectroscopic Characterizations of Iron-based Electrocatalysts	
14:30-15:00	C3	JM. Génin	Ordering of Fe <sup>3+</sup> cations in green rust related minerals within gleys: Mössbauer spectroscopy vs. X-ray diffraction	Chairman: E. Tabor
15:00-15:20	C4	S. Dubiel	Fe-GLUCONATE: STRUCTURE AND PROPERTIES	
15:20-15:50			Coffee break	
15:50-16:20	14	Y. Garcia	SMART SENSORS FOR CIVIL SECURITY APPLICATIONS	
16:20-16:40	C5	M. Robić	INFLUENCE OF SM AND Y MOLAR FRACTIONS ON THE PROPERTIES OF ELECTROSPUN (Fe, Sm) AND (Fe, Y) OXIDES	Chairman: PE. Lippens
16:40-17:00	C6	K. Bharuth-Ram	PARAMAGNETIC BEHAVIOUR OF Mn IMPLANTED ZnO	rippeiis
17:30-19:00			SEC meeting (Dept. of Experimental Physics, 4 <sup>th</sup> floor)	
18:00-19:30			Guided tour to the city center (optional)	

Tuesday 13 <sup>th</sup>	Septe	mber 2022	Registration desk 8:00-18:00	
			MÖSSBAUER SPECTROSCOPY IN ADDITIVE	
9:00-9:30	15	M. Mashlan	MANUFACTURING BY SELECTIVE LASER MELTING	
9:30-9:50	<b>C</b> 7	A. Sedláčková	STUDY OF STAINLESS STEEL SURFACE AFTER ANNEALING IN THE TEMPERATURE RANGE 550 - 1000 °C	Chairman: M. Miglierini
9:50-10:20	16	J. Pechoušek	NONDESTRUCTIVE DETERMINATION OF AUSTENITE IN STEELS	
10:20-10:50			Coffee break	
10:50-11:20	17	A. Quesada	DEVELOPING NOVEL MAGNETS AND ASSOCIATED PROCESSES TO REDUCE OUR DEPENDENCE ON RARE-EARTH ELEMENTS	
11:20-11:40	C8	P. Kohout	SURFACE CHANGES INVESTIGATION OF "MASHA" STEEL COMPONENTS BY MÖSSBAUER SPECTROSCOPY	Chairman: P. Bingham
11:40-12:10	C9	JM. Génin	Eh-pH Pourbaix diagrams of green rusts and CORTENTM steel	
12:30-14:00			Lunch	
14:00-16:00			Poster session, discussions of participants	
15:30-16:00			Coffee, snack	
16:00-18:00			Excursion to laboratories (optional)	
16:00-19:00			Guided tour to the city center of Olomouc (optional)	
Wednesday 14 <sup>th</sup> September 2022 Registration desk 8:00-14:00				
9:00-9:30 9:30-10:00 10:00-10:20	18 19 C10	P. Bingham M. Miglierini D. Košovský	APPLICATION OF MÖSSBAUER SPECTROSCOPY TO REAL-WORLD RADIOACTIVE WASTE IMMOBILISATION PROBLEMS METALLIC ALLOYS IN NUCLEAR INSTALLATIONS MICROSTRUCTURE OF HIGH-ENTROPY ALLOYS	Chairman: S. Dubiel
10:20-10:50			Coffee break	
10:50-11:20	110	N. Oka (online)	APPLICATION OF VANADATE GLASSES CONTAINING DIFFERENT METAL OXIDES TO RECHARGEABLE BATTERIES	
11:20-11:40	C11	A. Béres	SYNTHESIS, STRUCTURE AND PROPERTIES OF COMPLEX IRON(III) SALTS CONTAINING VARIOUS LIGANDS AND OXIDIZING ANIONS	Chairman: C. Barrero
11:40-12:00	C12	S. Dubiel	Simple Method of Determining Center Shift and Spectral Area of a Mössbauer Spectrum	
12:30-14:00			Lunch	
14:00-19:00			Half-day excursion ( <u>TVARG Velká Bystřice</u> )	

Thursday 15 <sup>th</sup> September 2022		ember 2022	Registration desk 8:00-18:00	
9:00-9:30	111	V. Garg (online)	INDUSTRIAL APPLICATIONS OF SUPERPARAMAGNETIC OF IRON OXIDE NANOPARTICLES	
9:30-9:50	C13	Marciuš	ONE POT SYNTHESIS OF Co AND NI DOPED MAGHEMITE NANOPARTICLES USING ACETYLCETONATE PRECURSORS	Chairman: M. Reissner
9:50-10:20	l12	K. Garcia	USE OF IRON OXYHYDROXIDES AS WATER DECONTAMINANTS: THE CASE OF AKAGANEITE	
10:20-10:50			Coffee break	
10:50-11:20	I13	S. Kubuki	HIGHLY COVALENT FEIII-O BOND CONFIRMED FROM MÖSSBAUER SPECTRA OF DOMESTIC WASTE MOLTEN SLAG SIMULATED SODA-LIME IRON-SILICATE	
11:20-11:50	114	T.Nishida (online)	INDUSTRIAL APPLICATIONS OF HIGHLY CONDUCTIVE VANADATE GLASS CONTAINING IRON(III)	Chairman: L. Machala
11:50-12:20		J. Navařík, V. Dutka, J. Pechoušek	Commercial presentations	
12:30-14:00			Lunch	
14:00-16:00			Poster session - ONLINE	
16:00-18:00			SEC meeting (Dept. of Experimental Physics, 4 <sup>th</sup> floor)	
19:00-23:00			Conference dinner ( <u>the rectorial canteen</u> )	
Friday 16 <sup>th</sup> September 2022 Registration desk 8:00-11:00				
9:00-9:20	C14	D. Balatskiy (online)	MÖSSBAUER STUDY OF Fe-RICH BERYL	
9:20-10:20			Discussion panel, ISIAME in future, organization of the next ISIAME	Chairman: E. Kuzmann
10:20-10:40			Closing of the symposium	
11:00-12:00			Lunch	

#### The conference proceedings

The conference proceedings will be published in the journal Hyperfine Interactions (published by Springer Nature). Invited talks as well as oral and poster presentations will be included in the conference proceedings. All manuscripts will be peer reviewed according to the standard international procedures before being accepted for publication in the conference proceedings.

#### **Submission**

The procedure for submitting manuscripts is the same as for other conference proceedings (e.g. ICAME) published in Hyperfine Interactions. It is important to notice that there is no a priori page limit. Authors are free to use as many pages as necessary. Referees might object to manuscripts which are unnecessarily long.

Papers have to be submitted via the Hyperfine Interactions website <a href="https://www.springer.com/journal/10751">https://www.springer.com/journal/10751</a> by clicking on the button "submit manuscript". Under the Details tab, the authors should choose the name of the conference from the drop-down list (ISIAME2022).

#### **Deadline**

Deadline for the electronic submission of manuscripts is 16<sup>th</sup> September 2022.

#### **Open Access**

With the consent of Springer Nature, publisher of Hyperfine Interactions, the final accepted version of all peer reviewed and accepted conference manuscripts will be published on the website of the Mössbauer Effect Data Center together with the conference manuscripts of the most recent ICAME, ISIAME and LACAME conferences. It is the purpose to keep using this database as a repository for Mössbauer conference proceedings in order to facilitate access for the scientific community. All these conference manuscripts can be downloaded from this website free of charge. To assist correct citation of the conference articles clear indications are given of the corresponding Hyperfine Interactions issues and page numbers. Please notice that this free open access offered to the conference participants and their community is different from the open access offered to the authors, against payment, by Springer Nature upon publication of their manuscript.

#### **About the Hyperfine Interactions journal**

Hyperfine Interactions was created in 1975 as a scientific journal with a strict peer review procedure, with the main purpose to publish conference proceedings in the border region between nuclear physics, atomic physics and solid state physics. The present publisher is Springer Nature. Since May 2015 the scope of this publisher has broadened through the merger of Springer Science & Business Media with the Nature Publishing Group, Palgrave Macmillan and Macmillan Education.

Articles published in Hyperfine Interactions are listed and fully indexed by search and indexing databases such as Web of Science, Google Scholar and Scopus. In 2008 Web of Science split their journals database into two: the traditional journals part and a new proceedings part, and they moved all journals they decided to be proceedings journals, including Hyperfine Interactions, into that new database. Since then Web of Science only publishes impact indices for journals in their journals database, not for journals in their proceedings database. However, citations to articles in Hyperfine Interactions are still measured and included as they had been before by Web of Science. Journal metrics values for Hyperfine Interactions can be found at the websites of different ranking agencies, such as:

Citescore 2017 = 0.66

[http://www.springer.com/physics/particle+and+nuclear+physics/journal/10751]

RG Impact Ranking 2018 = 0.92 [https://www.researchgate.net/journal/1572-9540 Hyperfine Interactions]

Guido Langouche, Editor of Chief

#### **Useful information**

#### The conference venue

The conference is hosted by Faculty of Science, Palacký University Olomouc. The conference venue is located in the main modern-style (dark marble) building at 17.listopadu 1192/12 street, which is nearby the city centre and approx. 1.5 km from the railway station. The lecture hall is located on the 2nd floor and its surroundings will be available for the posters, coffee breaks and discussions of the participants. The welcome reception is held at the Science Centre of Faculty of Science and the conference dinner at the Křížkovského canteen. All these places are at a "walk distance". See the map on the page 12.



#### Registration & Info Desk - location, opening hours

Sunday 11 <sup>th</sup> September	12:00pm – 8:00pm	Faculty of Science, the ground floor
Monday 12 <sup>th</sup> September	8:00am – 6:00pm	Faculty of Science, the 2 <sup>nd</sup> floor
Tuesday 13 <sup>th</sup> September	8:00am – 6:00pm	Faculty of Science, the 2 <sup>nd</sup> floor
Wednesday 14 <sup>th</sup> September	8:00am – 2:00pm	Faculty of Science, the 2 <sup>nd</sup> floor
Thursday 15 <sup>th</sup> September	8:00am – 6:00pm	Faculty of Science, the 2 <sup>nd</sup> floor
Friday 16 <sup>th</sup> September	8:00am – 11:00pm	Faculty of Science, the 2 <sup>nd</sup> floor

#### **Instructions for presenters**

All lectures (keynote, invited, contributed) will be transferred via Zoom platforms. All the speakers (participating physically) will be requested to provide their presentations in PPT or PDF format in advance to each session. The presentation will be downloaded on a local computer in the lecture hall. At the end of each session, the files will be deleted from the computer. The running presentation (either local or on-line) will be projected on the screen in the lecture hall. The computer screen will be at the same time shared via the Zoom platform to all registered and confirmed participants. Invitations and links to the Zoom platform will be daily sent by e-mail (to the address provided during registration) to each confirmed participant. All the time will be Central European Time (CET).

#### **Duration of lectures:**

Keynote lecture 30 minutes + 10 minutes discussion

Invited lecture 25 minutes + 5 minutes discussion

Contributed lecture 15 minutes + 5 minutes discussion

#### **Posters**

All the registered posters (of on-site as well as on-line participants) will be uploaded on the <u>conference website</u> and will be available (only) to all confirmed participants of the conference. On-site presenters will be asked to anchor their posters on the tables in the front of the lecture hall the first day of the conference. The recommended (and maximum) size of posters is A0 (w 841mm x h 1189mm). The on-site poster section will be held on Tuesday 13<sup>th</sup> September afternoon in the front of the lecture hall. The online poster session will be organized on Thursday 15<sup>th</sup> September afternoon by using a platform Zoom. The participants will be informed in detail by the organizers.

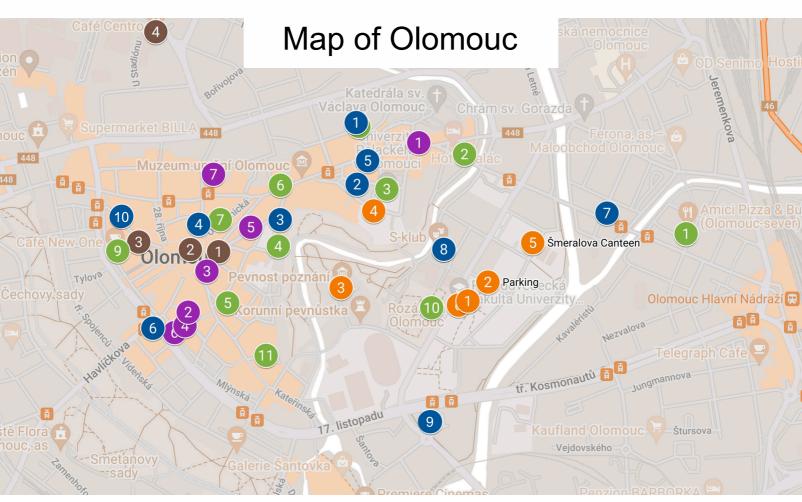
A free WIFI is available in the buildings of Palacký University Olomouc.

WIFI Username: upol

WIFI Password: wifiup2022



scan to join the WIFI



#### The important venues of the conference

- Faculty of Science, Palacký University
- 2 Parking
- 3 The Science Centre
- Křížkovského Canteen
- 5 Šmeralova Canteen
- 6 Bistro FreshUP

#### Pubs & bars

- 1 The BLACK STUFF Irish Pub & Whisky Bar
- OpenWine Latino Bar
- 3 Na břehu Rhôny
- 4 Koktejly & sny
- 6 Cuban Cocktail bar OSA
- 6 Giraldilla
- Jazz Tibet Club

#### Cafes & tearooms

- CAFE DELUX
- 2 Café 87
- 3 Coffee Library
- 4 Kafec
- 6 Naše Café
- 6 Kavárna Miss Sophie's Hotel
- Café La Fée
- 8 Long Story Short Cooking Bar Café
- Oafe New One
- 10 CoffeePark Rozarium
- 1 Dobrá Čajovna Olomouc

#### Others

- UPoint Information center & Palacký University Shop
- 2 Infopoint Olomouc
- 3 Exchange office UNNI Trading
- 4 Zmrzlinárium Café Centro

#### Restaurants

- 1 Long Story Short Eatery & Bakery
- 2 Svatováclavský pivovar
- 3 Konvikt Bistro & Bar
- Restaurant U Mořice
- 5 Bistro DaG
- 6 Restaurant Drápal
- La Scala
- 8 Kozlovna M3
- 9 Bistro Paulus
- 10 Burger & Beer Brothers



### **ABSTRACTS**

#### **Keynote lecture**

### IS TIN AN INTERESTING ELEMENT FOR ENERGY TRANSITION?

#### **Pierre-Emmanuel Lippens**

Institut Charles Gerhardt de Montpellier, UMR 5253 CNRS-UM-ENSCM, Montpellier, France

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The transformation from fossil-based to zero-carbon energy production is essential to reduce the global greenhouse gas emissions. Solar and wind energy sources are of particular importance due to their renewability and sustainability but they both suffer from intermittency. In addition, mobile systems such as electric vehicles or small electronic devices require autonomous and green energy sources. In these different cases, the electrochemical energy storage should be considered as a suitable solution and lithium-ion batteries are actually the best available technology, providing high energy density [1].

Basically, lithium-ion batteries consist of two electrodes to store both lithium ions and electrons, and an electrolyte for lithium ion transport. The commonly used positive electrode materials are metal oxides or phosphates while the negative electrodes are mainly based on carbon. However, since the first lithium-ion batteries commercialized by Sony in 1991, a tremendous number of works have been devoted to alternative electrode materials such as tin-based negative electrode materials. These include tin-based amorphous composite oxides in the Stalion batteries developed by Fujifilm Celltech Co. in 1997 and tin-based amorphous intermetallics in the Nexelion batteries commercialized by Sony in 2005 [2].

The present talk will show how <sup>119</sup>Sn Mössbauer spectroscopy can help to characterize electrode materials, understand the electrochemical mechanisms and improve the battery performance [3]. Some selected examples will be considered that include not only the lithium-ion batteries but also sodiumion and potassium-ion storage systems. In addition, future prospects on the application of Mössbauer spectroscopy to recently proposed tin-based electrode materials will be presented.

- [1] John B. Goodenough, M. Stanley Whittingham, Akira Yoshino, Nobel prize in Chemistry 2019 for the development of lithium-ion batteries. <a href="https://www.nobelprize.org/prizes/chemistry/2019/">https://www.nobelprize.org/prizes/chemistry/2019/</a>
- [2] F. Xin and M.S. Whittingham. Challenges and development of tin-based anode with high volumetric capacity for Li-ion batteries. Electrochem. Energ. Rev. **3**, 643–655 (2020). https://doi.org/10.1007/s41918-020-00082-3
- [3] P.E. Lippens. Application of Mössbauer spectroscopy to Li-ion and Na-ion batteries. Modern Mössbauer Spectroscopy. Topics in Applied Physics, vol. 137. Y. Yoshida and G. Langouche (eds), Springer, Singapore (2021). <a href="https://doi.org/10.1007/978-981-15-9422-9\_7">https://doi.org/10.1007/978-981-15-9422-9\_7</a>

#### **Invited lectures**

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### MÖSSBAUER SPECTROSCOPY AS A CRUCIAL TOOL FOR DESIGNING OXIDATION CATALYSTS

#### **Edyta Tabor**

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Iron zeolites represent one of the most promising types of heterogeneous catalysts. Zeolite-based iron actives sites can effectively eliminate  $N_2O$ , transform alkanes to alkenes or activate  $O_2$  and enable methane oxidation at room temperature. The catalytic performance of iron zeolites is controlled by type of iron species and zeolite matrix. Thus, the determination of iron sites active in a particular reaction is crucial for developing an efficient catalyst. Mössbauer spectroscopy is the best available method for studying iron-containing materials due to the fact that it can reveal all iron forms. Moreover, this method provides the essential information on the local structure of iron sites.

In this contribution, I will first discuss the influence of iron loading on Fe speciation in zeolites with various topologies (FER, \*BEA, and MFI). We have shown that using the combination of *in situ* Mössbauer and FTIR spectroscopies, the structure and oxidation state of active iron centres in Fe- FER, \*BEA, and MFI and their role in  $N_2O$  decomposition can be revealed.

Furthermore, we have demonstrated that the activity of Fe-MFI in the oxidation of propane to propene can be controlled by the structure of iron active sites. The Mössbauer spectroscopy proved to be an efficient tool to study the influence of post-synthesis treatment and reaction conditions on the structural changes of iron species.

Last but not least, we have designed a special arrangement of iron cations in the FER matrix. DFT calculations revealed that these Fe(II) ions can cooperate in  $N_2O$  and  $O_2$  splitting, providing the active form of oxygen stabilized on iron cations. The Mössbauer spectroscopy experimentally confirmed that  $N_2O$  is split over two Fe(II) centres in FER and the stabilized oxygen form exhibits high oxidation potential towards methane. For the first time, we have shown that molecular oxygen can be dissociated over Fe-FER and subsequently used for the oxidation of methane to methanol at room temperature.

### STUDY OF INDUSTRIAL CATALYSTS AND CATALYTIC PROCESSES BY MÖSSBAUER SPECTROSCOPY

#### Károly Lázár

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Conventionally, in large scale production the primary importance lies in the processes themselves, and the study of catalysts is only a partial, however important contribution to the complex interpretation. Usually industrial processes are performed under high pressures and temperatures, less accessible for an experimental Mössbauer assembly. Conventionally, the catalysts are studied before the processes in their pristine states and afterwards in spent forms and conclusions are drawn from comparison of these two states. The operando studies are less available for the method, however they provide essential information when completed in certain studies.

The present contribution is based on an overview of the recent literature taking into account the previous consideration as well. Two principal groups of catalysts will be discussed. First catalysts used in real large scale processes will be considered. Among these the conventional iron based catalysts used in Fischer-Tropsch and other hydrocarbon conversion processes are still significant part of recent studies, more related details are revealed in the last years. The oxide, nitride and other composed catalysts play also important role, they will be discussed, too.

The other wide group is composed from perspective materials not used currently in large scale, however they might be promising for future applications. The catalytic performances of these substances are evaluated and are compared to currently used catalysts, as well. In certain cases the catalysts and processes are developing in synergy, the wide scale successful application of the process may depend on the development of efficient catalysts.

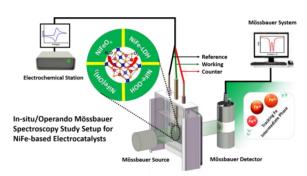
### IN-SITU/OPERANDO MÖSSBAUER SPECTROSCOPIC CHARACTERIZATIONS OF IRON-BASED ELECTROCATALYSTS

#### Junhu Wang

Center for Advanced Mössbauer Spectroscopy, Mössbauer Effect Data Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. Email: wangjh@dicp.ac.cn

The Mössbauer spectroscopy plays important role in study of Fe-based non-noble metal electrocatalysts. Mössbauer spectroscopy with high energy resolution can be applied to identify catalyst phases structure, active sites, catalytic mechanisms, and determining relationship between catalytic activity and coordination structure. The in-situ/operando Mössbauer spectroscopy is a technique based on hyperfine interactions between nucleus and electrons, gives the parameters of isomer shift, quadrupole splitting and magnetic hyperfine field to study oxidation state, electron spin configuration, symmetry, and magnetic information of Fe/Sn sites in catalyst under working conditions.

In this talk, the newly developed in-situ/operando Mössbauer spectroscopy for electrochemistry is introduced in detail, including in-situ/operando devices, spectrum measurement and results discussion by using the industrially potential study cases of Ni-Fe oxyhydroxide water oxidation catalyst and Fe-N-C oxygen reduction catalyst.



A schematic illustration of in-situ/operando <sup>57</sup>Fe Mössbauer spectroscopic electrochemical setup for the study of water oxidation catalyst

#### References

1) Jafar Hussain Shah, Qixian Xie, Zhichong Kuang, Rile Ge, Wenhui Zhou, Duorong Liu, Alexandre I. Rykov, Xuning Li, Jingshan Luo, Junhu Wang. *In-SitulOperando* 57Fe Mössbauer Spectroscopic Technique and Its Applications in NiFe-based Electrocatalysts for Oxygen Evolution Reaction [J]. Journal of Electrochemistry, 2022, 28(3): 2108541.

2) Zhichong Kuang, Song Liu, Xuning Li, Meng Wang, X. Ren, Jie Ding, Rile Ge, Wenhui Zhou, Alexandre I. Rykov, Moulay T. Sougrati, Pierre-Emmanuel Lippens, Yanqiang Huang, Junhu Wang, **Topotactically Constructed Nickel-iron (oxy)hydroxide with Abundant in-situ Produced High-valent Iron Species For Efficient Water Oxidation** [J]. Journal of Energy Chemistry, 2021, 57: 212-218.

3) Xinlong Xu, Xiaoming Zhang, Zhichong Kuang, Zhangxun Xia, Alexandre I. Rykov, Shansheng Yu, Junhu Wang, Suli Wang, Gongquan Sun, Investigation on the Demetallation of Fe-N-C for Oxygen Reduction Reaction: the Influence of Structure and Structural Evolution of Active Site [J]. Applied Catalysis B: Environmental, 2022, 309: 121290.

4) Xinlong Xu, Junhu Wang, Suli Wang, Application of 57Fe Mössbauer Spectroscopy in Studying Fe-N-C Catalysts for Oxygen Reduction Reaction in Polymer Electrolyte Membrane Fuel Cells, Book chapter submitted to the book titled "Mössbauer Spectroscopy: Applications in Chemistry and Materials Science" to be published by Wiley-VCH in 2023 (ISBN: 978-3527346912; Editors: Yann Garcia, Junhu Wang, Tao Zhang).

### STUDY OF INDUSTRIAL CATALYSTS AND CATALYTIC PROCESSES BY MÖSSBAUER SPECTROSCOPY

#### Yann Garcia

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In recent years, attention has been focused on the efficient detection of chemical pollutants, especially small volatile organic compounds (VOCs) and hazardous gases (HGs), as well as bacterial agents [1]. This area is very challenging because such molecules are relatively volatile at room temperature, even at low concentration levels. Such species can enter the body through normal breathing, and cause serious health issues [2]. Our investigations led us to focus on a series of azole based coordination polymers [3], for which intriguing iron(II) spin crossover properties were disclosed [4]. In particular, we have recently identified a a new colorimetric chemosensor of formula [Fe(H<sub>2</sub>btm)2(H<sub>2</sub>O)2]Cl (1) (H<sub>2</sub>btm = di(1H-tetrazol-5-yl)methane), allowing to detect at real time, with a high selectivity and ultra-sensitivity, 14 different VOCs and HGs [2]. In particular amines, which are detected very quickly (< 2 min) with very high sensitivity. The detection is accompanied by significant and fast colour changes detectable by the naked-eye at ambient conditions. In addition, different VOCs could be distinguished by simple and intuitive standard chemometric means using a handful smartphone-based analytical method, offering a large colour panel depending on detected molecules. The crystal lattice of (1) reconstructs after adsorbing VOCs vapours, reconstruction which is accompanied by a spin state and a colour change. In addition to its high thermal stability (up to 170 °C), the colorimetric sensor showed excellent reusability by consecutive 7 cycles of adsorption-desorption. This sensor is lowcost, environmentally friendly, easy to use, and shows excellent and fast detection performances. Such features offer attractive prospects for (1) which could be used for in-field detection and food safety control in environmental conditions. In this invited talk, I will review latest advances highlighting the impact of <sup>57</sup>Fe Mössbauer spectroscopy for quantitative analysis of spin states of selected iron(II) complexes, used as sensors for various toxic industrial chemicals (TICs) [5-11].

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### MÖSSBAUER SPECTROSCOPY IN ADDITIVE MANUFACTURING BY SELECTIVE LASER MELTING

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Selective laser melting (SLM) is an additive manufacturing technique used primarily for rapid prototyping. In SLM, the surface of the metal powder on the bed is melted by a laser, which scans the cross sections based on a 3D model of the part being manufactured. Once the cross section is fully scanned, the bed is lowered to allow a new layer of powder to be placed on the previous cross section. The laser rescans this layer and the whole process is repeated until the entire 3D model is scanned and the part is completed. Various experimental techniques (XRD, SEM, EDS) were used to improve the SLM process and to inspect the properties (surface morphology, microstructure, elemental composition) of components produced by SLM. Mössbauer spectroscopy is a suitable method for examining iron-based components. CEMS and CXMS allows surface layers to be studied selectively. CXMS contains information from depths of tens of micrometres, CEMS from depths of 0.3 µm. Transmission Mössbauer spectroscopy (TMS) of metal powders. The phase composition of stainless steel metal powders (CL20ES) and maraging steel powders (CL50WS) during annealing was studied in the temperature range of 500 - 1100 °C in air and inert atmosphere. When the CL20ES powder in an inert atmosphere, no phase changes were identified throughout the entire annealing temperature range. The Mössbauer spectra are represented by a narrow doublet (IS =  $(-0.8 \pm 0.02)$  mm/s, QS =  $(0.16 \pm 0.03)$  mm/s), which corresponds to austenitic steels. When CL50WS powder in an inert atmosphere, the phase composition of the powder changes depending on the temperature. The

Mössbauer spectra consist of two subspectra, which correspond to the austenitic and ferritic phases. The ferritic phase is represented in the Mössbauer spectrum by a sextet with a distribution of a hyperfine magnetic field (IS =  $(0.00 \pm 0.02)$  mm/s, mean value of B = 29.8 T). The ratio of the austenitic and ferritic phases varies depending on the annealing temperature.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and wüstite were identified for both powders depending on the annealing temperature in an oxidizing atmosphere.

CXMS and CEMS of parts made with SLM. CXMS and CEMS showed changes in the phase composition of the parts depending on the annealing temperature and atmosphere. At the same time, some changes occur only in the surface layer with a thickness of approximately 0.5 μm. These are changes in the ratio of the austenitic and ferritic phases. Various iron oxides also occur during surface oxidation. In accordance with XRD and EDS, it has been shown that some phase transformations occur as a result of the diffusion of alloying elements in the surface layers. This process is associated with an affinity of the alloying elements (Cr, Mn) for oxygen that is greater than the affinity of iron for oxygen. SEM shows the formation of a new crystalline layer on the surface of the samples by annealing. EDS confirmed an increase in the concentration of alloying elements (Cr and Mn), and XRD identified Cr<sub>2</sub>O<sub>3</sub> and Mn<sub>2</sub>NiO<sub>4</sub> on the surface. SEM showed an inhomogeneity of the emerging surface layer, which unfortunately results in difficulties in the registration of CEMS spectra.

### NONDESTRUCTIVE DETERMINATION OF AUSTENITE IN STEELS

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Determination of the austenite amount in steels and its products is an important process for the quality description and durability predicting of steel products. Retained austenite occurrence critically affects the steel properties in both positive and negative ways. We can highlight two statements, i.e., (1) as the retained austenite is soft, it is an undesirable constituent of quench-hardened steel. On the other hand, (2) it was shown that higher amount of retained austenite can enhance the ductility in highstrength steels. Nowadays, the microscopic metallography and XRD methods are conventionally used for austenite amount determination in the industry. As non-destructive measurement is one of the main requirements for steel products inspection, the backscattering Mössbauer spectroscopy can be favourably used and provide very valuable information. The industrial applications of the Mössbauer spectroscopy for austenite determination in steels have been known for more than four decades. From the very beginning of use, industrial solutions including experimental setups proposals and approaches of simple data evaluation were published [1,2], i.e. Taking into consideration Mössbauer spectroscopy features, we can ask a question "Why the Mössbauer spectroscopy is still not widespread in an industry?" From the author's point of view, there are some disadvantages which can play an important role and will be discussed. In the last years, a new version of Austenitemeter concept was designed [3,4], and applied [5,6] in steels characterization. Also new approaches are under the investigations.

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## PROCESSES TO REDUCE OUR DEPENDENCE ON RARE-EARTH ELEMENTS

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As a consequence of their capacity to transform mechanical energy into electrical (and vice versa), permanent magnets are key elements in the technologies upon which we rely our sustainable future. Nowadays, green energy generation (wind turbines) and green mobility (hybrid and electric vehicles, E-motors) operate with permanent magnets that contain rare-earth elements (REE) and thus their demand is expected to significantly increase in the next decade. However, REE are critical raw materials that present important environmental, price and supply issues, and an urgent need exists to reduce our current and future dependence. This situation urgently demands innovations that lead to a substitution of REE by noncritical materials in these devices. In this framework, ferrites present important advantages especially in terms of their price and availability, and efforts are being made to already attempt the substitution in wind turbines and E-motors with state-of-the-art ferrites. In this framework, even mild improvements in their performance could lead to a considerable amount of endusers substituting REE by ferrites in their applications. The demand for ferrites is thus expected to increase as well, and ensuring the sustainability of the ferrite value chain is of great importance for the long term sustainable development goals and CO2 emission targets. The main goal of our research is to develop innovative and improved ferrite-based magnets that substitute REE in applications for the green transition, and enhance the recycling rate of current ferrite magnets. Based on recent patented technology, we are focusing on:

- 1. Design and develop improved magnetically hard-soft composite powders and magnets based on ferrites through establishing the correlation between structure and magnetic properties,
- 2. Implement new energy efficient consolidation processes in the production of ferrite magnets,
- 3. Enhance the recycling rate of ferrite magnet production in collaboration with European waste managers and magnet manufacturers.

## APPLICATION OF MÖSSBAUER SPECTROSCOPY TO REAL-WORLD RADIOACTIVE WASTE IMMOBILISATION PROBLEMS

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Mössbauer spectroscopy is a key technique in the development of solutions for global radioactive waste immobilization problems. Presently ~55M US gallons of radioactive waste is stored in steel tanks at the Hanford site, USA [1]. This waste exists in mixed solid-liquid phases [2] and poses an environmental risk to the immediate area and nearby settlements. The US Dept. of Energy has decided that the waste be vitrified into borosilicate glass using "direct feed" vitrification [3]. A consequence of this approach is that the final waste forms will be highly complex, and the effects of these complexities must be better understood prior to the commencement of the large-scale vitrification efforts. One such complexity is high concentrations of Fe within the -4 -3 waste [2]. Three borosilicate glass series were designed to investigate the composition-property-phase relations in borosilicate glass. Mössbauer spectroscopy was used to show that the iron predominantly exists as Fe<sup>3+</sup> in four-coordinated structures with little change as function of Fe-content (Figure 1). However, further study has shown marked differences in the partitioning / clustering of Fe ions as a function of glass matrix.

During vitrification, foam evolution must be understood to mitigate risks of blockages [4]. Feeds such as the U.S. Hanford high-iron high-level waste feed, can foam up to 10 times its original volume [4]. This study examined the melting behaviour of the feed and the mechanisms behind gas release and foam creation. Elucidating the structure of iron at distinct temperatures, in the context of evolved gas analysis and feed volume expansion, allowed the precise mechanisms of gas evolution from melting reactions to be understood. During melting the crystalline iron in the feed progressed from Fe<sub>2</sub>O<sub>3</sub> to an Fe<sub>3</sub>O<sub>4</sub>-like spinel compound, while the content of iron in the amorphous phase increased. O<sub>2</sub> evolution corresponded with these temperatures.



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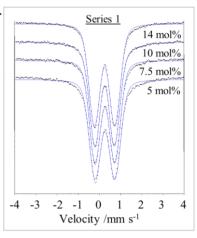


Figure 1. <sup>57</sup>Fe Mössbauer spectra for Fe-alasses

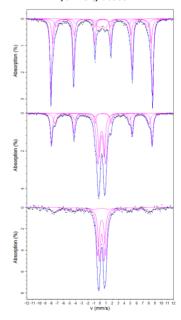


Figure 2. Evolution of iron in waste feed at 600, 1000 and 1150  $^{\circ}$ C.

#### METALLIC ALLOYS IN NUCLEAR INSTALLATIONS

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Metallic alloys used in nuclear installations are frequently exposed to harsh conditions featuring not only elevated temperature, corrosion but also intense ionizing radiation. Because microstructure of materials is sensitive to any external modifications their resulting physical properties might be also affected. Considerable worldwide research effort is dedicated to the design, production, and prediction of resulting properties of especially new compositions that are supposed to be used in extreme environments including those found in nuclear installations. In this respect, knowledge of microstructural arrangement of any materials is crucial as it affects the resulting macroscopic properties. Here, Mössbauer spectrometry, which is able to identify minute modifications in the local atomic arrangement of the resonant atoms, plays an unmatched and very important role.

In this contribution, two types of metallic alloys that are principally different from the point of view of their structural arrangement will be discussed. Namely, stainless steels (SS) with well-defined long-range order and amorphous metallic alloys (AMA) featuring disordered structure. While the former are widely used as constructions materials the latter are perspective materials for the use as magnetic cores of accelerator radio frequency cavities or surface coatings of containers for spent nuclear fuel. We present examinations of various mechanical treatments including hardening, cutting, grinding, and polishing on the microstructure of selected SS samples. In the second part, identification of radiation induced effects (neutrons and ions) upon Fe-based AMA will be discussed.

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<sup>3</sup> Slovak Spectroscopic Society, member of the Association of Slovak Scientific and Technological Societies, Ilkovičova 6, 842 15 Bratislava, Slovakia

### APPLICATION OF VANADATE GLASSES CONTAINING DIFFERENT METAL OXIDES TO RECHARGEABLE BATTERIES

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Cathode materials with high charge-discharge capacity are expected for Li-ion battery and metal-air battery to be applied to hybrid and electric cars. In this study, new cathode materials for these rechargeable batteries have been developed using conductive vanadate glasses with different metal oxides. Conductivity of barium iron vanadate glass, 20BaO·10Fe<sub>2</sub>O<sub>3</sub>·70V<sub>2</sub>O<sub>5</sub>, could be "tuneable" over a wide range (10<sup>-7</sup>-10<sup>-1</sup> S·cm<sup>-1</sup>) when the local distortion of the glass skeleton was diminished by isothermal annealing [1].

In this symposium, we present the results of air-electrode (cathode) catalysts containing vanadate glasses for metal-air rechargeable battery. This rechargeable battery needs bifunctional catalytic material, which involves effective oxygen reduction (ORR)/evolution reactions (OER) at the air electrode at the discharge/charge process. Conductive vanadate glass containing different metal oxides was synthesized by the melt-quench method. Prepared vanadate glasses were annealed at 450 °C for various times. For the preparation of the air electrode, pulverized vanadate glass was mixed with powder of 7.5 mass% of poly(tetrafluoroethylene), which was hot-pressed on the gas diffusion layer over a Ni metal mesh. 8M KOH aqueous solution and a Pt mesh were used as the electrolyte and the counter electrode, respectively. The prepared vanadate glass electrode showed an excellent bifunctional oxygen reduction/evolution activity, being comparable to that of the materials reported in the literature, such as polycrystalline LaNiO<sub>3</sub> [2]. At the symposium, we will also present the application of the conductive vanadate glass to Li-ion battery.

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### INDUSTRIAL APPLICATIONS OF SUPERPARAMAGNETIC IRON OXIDE NANOPARTICLES

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In 1963, Steve Papell of NASA created ferrofluid for use as rocket fuel. His team of NASA scientists were investigating methods of directing fluids in space and realized that magnetic fluids could be completely controlled by the application and variation of a magnetic field. Ferrofluids are also the focus of current scientific research and have the potential to be used in many medical applications, industrial electric transformers, oil pollution cleaners, memory devices in IT industry. In magnetic drug targeting for example, where drugs could be enclosed by ferrofluid and, once injected into the specific body area requiring treatment, a magnetic field could be applied to keep the drugs in this target area. The localization would limit exposure to the rest of the body and enable the dosage level to be decreased, reducing the adverse side effects experienced by the patient. Hard drives use magnetic memory to store giga- and terabytes of data in computers. Information is written to and read from the storage medium as it moves past devices called read-and-write heads that operate very close (often tens of manometers) over the magnetic surface. The read-and-write head is used to detect and modify the magnetization of the material immediately under it. Magnetite (Fe<sub>3</sub>O<sub>4</sub>) and is ferrimagnetic is the most magnetic of naturally-occurring minerals. the Nanotechnology an emerging field, with thousand research paper only using Mössbauer spectroscopy that covers a wide range of new technologies under development in nanoscale (1 to 100 manometers) to produce new products and methodology.

Superparamagnetic iron oxide nanoparticles (SPIONs) with appropriate surface chemistry have numerous applications such as diagnosis, targeted drug delivery, magnetic labelling, magnetic isolations, magnetic carriers, cell separation, magnetic resonance imaging contrast enhancement, tissue repair, immunoassay, detoxification of biological fluids, and hyperthermia. Magnetic nanoparticles can bind to drugs, proteins, enzymes, antibodies, or nucleotides and can also be directed to an organ, tissue, or specific location using an external magnetic field or can be heated in alternating magnetic fields for use in hyperthermia. In the last decade, increased investigations with several types of iron oxides have been carried out in the field of man-sized magnetic particles (mostly maghemite, α-Fe<sub>2</sub>O<sub>3</sub>, or magnetite, Fe<sub>3</sub>O<sub>4</sub>, single domains of about 5–20 nm in diameter), among which magnetite is a very promising candidate since its biocompatibility has already been proven. Magnetite, Fe<sub>3</sub>O<sub>4</sub>, is a common magnetic iron oxide that has a cubic inverse spinel structure with oxygen forming an fcc closed packing and Fe cations occupying interstitial tetrahedral sites and octahedral sites. The electrons can hop between Fe<sup>2+</sup> and Fe<sup>3+</sup> ions in the octahedral sites at room temperature, rendering magnetite an important class of half-metallic materials. With proper surface coating, these magnetic nanoparticles can be dispersed into suitable solvents, forming homogeneous suspensions (ferrofluids). Such a suspension can interact with an external magnetic field and be positioned to a specific area, facilitating magnetic resonance imaging for medical diagnosis, and AC magnetic

field-assisted cancer therapy. Because of growing interest preparation of nanoparticles (NPs) to have distinctive properties related to high surface area at volume ratio. The quantum effects of NPs have created notable interest to engineers, biologists, chemists and physicists. Various SPION assisted drug delivery systems and SPIONs are commercially available. Interestingly, naturally occurring nanoparticles (NNPs) are present in all spheres of the Earth (atmosphere, hydrosphere, lithosphere and even in the biosphere). Natural Organic Matter (NOM) could largely contribute to the formation of metal nanoparticles, like by silver and gold nanoparticles (AgNPs and AuNPs) in the environment. The formation of metal nanoparticles entails the reaction of reactive oxygen species and NOM complexes with dissolved metal ions. The formation of AgNPs and AuNPs is enhanced by elevated temperature and/or exposure to light. Water properties (pH, redox conditions, presence of ions/ionic strength, and concentrations are also important factors. Various types of (NOM) determine the growth and stability of NPs in the aquatic environment. Organic matter-coated natural metal nanoparticles display less toxicity than ENPs that are surface coated by polymers and/or surfactants. Different materials have different size and size distribution, applications and advantages. We have synthesized gold, layered double (LDH), and iron-oxide zeolite composite superparamagnetic nanoparticles. Goldhas been used in eastern civilizations for centuries and in west it is still being used in cosmetic surgery. Stabilized gold nanoparticles (AuNPs) Au to buthyldithiol stoichiometry were prepared using modified Brust synthesis. The size of the particles falls into the 1.3-4.0 nm range in which the molecular cluster – metallic particle transition occurred. A Mössbauer study of the effect of pH on Fe valence in iron-polygalacturonate as a medicine for human anaemia was conducted. We have synthesized SPIONs Fe<sub>3</sub>O<sub>4</sub>-Zeolite composites. Zeolite can act as a drug carrier and both the constituents of composites are biocompatible. Fe<sub>3</sub>O<sub>4</sub>–Zeolite composites in different concentration of Zeolite .Superparamagnetic to ferrimagnetic transitions in cubic iron oxides could be tuned by varying zeolite concentration in composite. Shift of γ-Fe<sub>2</sub>O<sub>3</sub> to α-Fe<sub>2</sub>O<sub>3</sub> phase transition from lower to higher temperature confirmed increase in thermal stability of iron oxide nanoparticles with higher zeolite concentration. Saturation magnetization decreased with increase in Zeolite concentration due to increase in superparamagnetic composition. Above 200 mg of zeolite, the slight decrease in saturation magnetization was due to increase in the zeolite content. We also prepared Fe<sub>3</sub>O<sub>4</sub>–Zeolite composite samples with different incubation, and digestion time but we could not obtain clean samples giving a paramagnetic doublet.

### USE OF IRON OXYHYDROXIDES AS WATER DECONTAMINANTS: THE CASE OF AKAGANEITE

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Humanity recognizes the vital importance of adequate access to safe drinking water for a population that is growing in number. However, various human activities along with climate change can lead to an increase in contaminated water. Therefore, the minimization of the content of water contaminants has long been the subject of worldwide research. Within the various methods that exist to remove contaminants in aqueous media, there is the use of adsorbents based on iron oxides and oxyhydroxides. In this sense, the most commonly used samples for adsorption are ferrihydrite, goethite, feroxyhyte, hematite, and magnetite. Comparatively, akageneite has been less employed, in spite their unique properties for the efficient removal of water pollutants [1]. In this work, we review our contributions to both: (i) the synthesis of pure and co-precipitated akaganeites in presence of different cations such as aluminium, chromium, copper, mercury, antimony and arsenic, and also (ii) the study of the adsorption kinetics of mercury, antimony, and arsenic onto some modified akageneite nanoparticles [2]. We reported that: (i) it seems that the investigated cations did not replace iron in their crystallographic sites, (ii) some cations produced important particle size reductions and changes in the Mössbauer parameters, and (iii) the nanosized akaganeites had much better adsorption capacities than pure akaganeites. Finally, many adsorptions kinetic models have been reported in the literature, but only very few of them have been used to fit the kinetic experimental data. It is important to know the kinetic characteristics, because it allows a prediction of the rate of removal of contaminants using adsorbents, which is a crucial factor for the design and operation of an effective adsorption system. In this work, 22 models have been explored and it was found that the fractal kinetic models were the ones that better described the kinetic adsorption processes.

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## HIGHLY COVALENT Fe<sup>III</sup>-O BOND CONFIRMED FROM MÖSSBAUER SPECTRA OF DOMESTIC WASTE MOLTEN SLAG SIMULATED SODA-LIME IRON-SILICATE

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The local structure of iron-containing soda-lime aluminosilicate glass and glass-ceramics simulated as domestic waste slag exhausted from municipal waste combustion plants in Japan was investigated by  $^{57}$ Fe-Mössbauer spectroscopy. Photo-Fenton catalytic ability was evaluated by a degradation test using methylene blue aqueous solution (MBaq). The visible-light activated photocatalytic effect was first observed by the MB degradation test of  $15\text{Na}_2\text{O} \cdot 15\text{CaO} \cdot 20\text{SiO}_2 \cdot 50\text{Fe}_2\text{O}_3$  (in mass%, abbreviated as 50NCSF) glass which was heat-treated at  $1000~^{\circ}\text{C}$  for 100~min. Under this reaction, MBaq concentration decreased from  $10.0~\text{to}~0.0~\text{µmol} \cdot \text{L}^{-1}$  for 24~h with an apparent rate constant (k) of  $4.78 \cdot 10^{-4}~\text{min}^{-1}$ . RT  $^{57}$ Fe-Mössbauer spectrum of 50NCSF was composed of a paramagnetic doublet with isomer shift ( $\delta$ ) of  $0.24~\text{mm} \cdot \text{s}^{-1}$  and quadrupole splitting ( $\Delta$ ) of  $0.99~\text{mm} \cdot \text{s}^{-1}$  due to distorted Fe<sup>III</sup>O<sub>4</sub> tetrahedra, superimposed on a magnetic sextet with  $\delta$  of  $0.36~\text{mm} \cdot \text{s}^{-1}$  and internal magnetic field ( $H_{\text{int}}$ ) of 51.8~T due to hematite. A larger k value of  $9.26 \cdot 10^{-3}~\text{min}^{-1}$  was recorded in heat-treated  $15\text{Na}_2\text{O} \cdot 15\text{CaO} \cdot 11\text{Al}_2\text{O}_3 \cdot 19\text{SiO}_2 \cdot 40\text{Fe}_2\text{O}_3$  glass, of which  $^{57}$ Fe-Mössbauer spectrum was composed of a sextet with  $\delta$  and  $H_{\text{int}}$  of  $0.37~\text{mm} \cdot \text{s}^{-1}$  and 51.2~T due to hematite.

Very recently, Ali *et al.* revealed that heat-treated  $5Na_2O \cdot 41.4CaO \cdot 20Al_2O_3 \cdot 27.6SiO_2 \cdot 6Fe_2O_3$  glass showed a considerably large *k* value of  $115 \cdot 10^{-3}$  min<sup>-1</sup> by the introduction of 0.4 mol·L<sup>-1</sup>H<sub>2</sub>O<sub>2</sub> into this system which was caused by highly covalent distorted Fe<sup>III</sup>O<sub>4</sub> tetrahedra with  $\delta$  and  $\Delta$  of 0.12 and 1.88 mm·s<sup>-1</sup>, respectively. The smaller *k* value of  $16.6 \cdot 10^{-3}$  min<sup>-1</sup> was evaluated by the catalyst prepared from the domestic waste molten slag in Tokyo. It is concluded that hematite and highly distorted Fe<sup>III</sup>O<sub>4</sub> tetrahedra with high covalency found in domestic waste molten slag simulated soda-lime iron-silicate achieved highly active Photo-Fenton catalytic ability. This new catalyst prepared by recycling waste slag will be realized by excluding the impurities in domestic waste molten slag in Tokyo.

### INDUSTRIAL APPLICATIONS OF HIGHLY CONDUCTIVE VANADATE GLASS CONTAINING IRON(III)

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"Glass is liquid with a mask of solid". When a melt is quenched, it remains as a "supercooled liquid" below the melting point  $(T_m)$ , and finally becomes "glass" at a glass transition temperature  $(T_g)$ . A linear relationship, termed  $T_g$ - $\Delta$  rule [1], was discovered in different iron(III)-containing oxide glasses between  $T_g$ , ranging from 180 to 800 °C, and quadrupole splitting ( $\Delta$ ) of Fe<sup>III</sup> ranging from 0.44 to 1.30 mm·s<sup>-1</sup>. A  $T_g$ -vs.- $\Delta$  plot yields a straight line with an "identical" slope of 680 K·mm<sup>-1</sup>·s when Fe<sup>III</sup> atoms occupy distorted tetrahedral sites as network former (NWF) in different oxide glasses. This experimental rule revealed that  $T_g$  of oxide glasses could be primarily determined by the local distortion of NWF-oxygen polyhedra. Thermodynamic studies of "polymers", "Adam-Gibbs theory" and "conformer model", could satisfactorily explain the principles of  $T_g$ - $\Delta$  rule [2].

Conducting oxide glasses were invented by annealing vanadate glasses at temperatures higher than  $T_g$  or crystallization temperature ( $T_c$ ) [3-7]. Room-temperature DC resistivity ( $\rho$ ) remarkably decreased from the order of M $\Omega$ ·cm to several  $\Omega$ ·cm after the annealing. These glasses have been applied to the busbar electrode of solar cell, conducting glass paste, discharge needle, *etc*. Introduction of CuO ( $E_g$ : 1.2-1.5 eV) and Cu<sub>2</sub>O (2.1-2.2 eV) into vanadate glass was effective to achieve a low resistivity of 3.1-5.0  $\Omega$ ·cm [5] after the annealing. In the case of ZnO ( $E_g$ : 3.3-3.4 eV)- and SnO<sub>2</sub> (3.4-3.6 eV)-containing vanadate glasses, low  $\rho$  values of 4.8 [6] and 5.0  $\Omega$ ·cm [7] were respectively achieved. Conduction mechanism of these glasses could be explained by taking account of the band gap energy ( $E_g$ ) of each component and that of prepared glass samples [8]. Together with the remarkable decrease in  $\rho$ , a marked decrease in  $\Delta$  of Fe<sup>III</sup> is generally observed, proving that Mössbauer spectroscopy could be a powerful tool for the development of cutting-edge materials.

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#### **Contributed lectures**

#### **C1**

# HOW MÖSSBAUER SPECTROSCOPY CAN HELP IN ACHIEVEMENT OF VALUABLE FOR INDUSTRY NATURAL RESOURCES FROM EXTRATERRESTRIAL OBJECTS

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Cosmic agencies are working on the project of bringing down asteroids which contain natural resources valuable for industry. It was determined based on meteorites samples studies that the most useful source of raw materials of our interest could be parent bodies of ordinary chondrites type H. The identification of the type of the ordinary chondrites with the use of classical method (determination of the Fa/Fs ratio (fayalite versus ferrosilite) by measurements made by electron microprobe) cannot be performed on the surface of asteroids for technical reasons. It may, however, be done based on Mössbauer measurements followed by the application of 4M method [1, 2, 3]. The very name of the method – 4M, comes from four words: Meteorites, Mössbauer spectroscopy, Multidimensional Discriminant Analysis and Mahalanobis distance. Following the success of Mössbauer spectroscopy in the mission on Mars [4, 5], there are suggestions to use the same method for investigation of the surface of asteroids. In our experimental study, in which 4 Mössbauer laboratories took part we assessed objectivity and effectiveness of 4M method by comparison of the results obtained for Mössbauer studies of ordinary chondrites type H, L and LL. In our presentation details of the study and problems related to the effectiveness of the 4M method will be discussed.

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## MÖSSBAUER SPECTROSCOPY OF IRON CATALYSED CARBON NANOSTRUCTURES

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The phase evolution of the trapped iron catalyst in grown up carbon nanostructures was studied. Synthesis was carried out by chemical vapour deposition at temperatures between 700 and 1100 °C using mainly toluene as a carbon precursor. In other cases, a pure ferrocene or ferrocene-toluene solution was used as the carbon precursor. Here, ferrocene also played the role of an iron source for the formation of catalytic particles required in the process of carbon nanostructures growth. Alternatively, nanoparticles of zero-valent iron Fe(0) NANOFER STAR (NANO IRON, s. r. o., Czech Republic) were used as catalyst. The phase composition of the final products was analysed by Mössbauer spectroscopy (MS) and X-ray powder diffraction (XRD). Scanning electron microscopy (SEM) in combination with energy dispersive spectroscopy (EDS) was used to visualize the morphology of the resulting structures. Analysis by MS of the phase composition of trapped catalytic iron particles revealed four main phases, namely alpha-Fe, gamma-Fe, Fe<sub>3</sub>C and Fe<sub>3</sub>O<sub>4</sub>. The ratio of iron-containing phases differs depending on the catalyst used and the temperature. Alpha-Fe, ce-mentite Fe<sub>3</sub>C and Fe<sub>3</sub>O<sub>4</sub> phases were identified in the case of direct decomposition of pure ferrocene at 900 °C. Alpha-Fe, Fe<sub>3</sub>C and gamma-Fe were identified in the decomposition of the ferrocene-toluene solution at 850 and 900 °C. In the case of synthesis with zero-valent iron alpha-Fe and Fe<sub>3</sub>C phase were identified in all products synthetized at temperatures from 700 to 1100 °C. Samples prepared at lower temperatures (700 and 800 °C) contained a Fe<sub>3</sub>O<sub>4</sub> phase. The products of synthesis at higher temperatures (950 and 1100 °C) did not contain the Fe<sub>3</sub>O<sub>4</sub> phase, but instead gamma-Fe. XRD confirmed the presence of the same phases as in MS in all samples. SEM and EDS of the final products confirmed a morphology similar to that of a carbon nano-tube/nanofiber.

# ORDERING OF Fe<sup>3+</sup> CATIONS IN GREEN RUSTS RELATED MINERALS WITHIN GLEYS; MÖSSBAUER SPECTROSCOPY VS. X RAY DIFFRACTION

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Corrosion of iron and steels, which is of utmost importance in every day life, depends on the way they form during the oxidation process. In both cases, a blueish-green compound or mineral appears, which is denominated "green rust" because it contains Fe<sup>2+</sup> and Fe<sup>3+</sup> cations and its color seems that of triclinic clays. The crystal structure displays that of a trigonal double layered hydroxide (DLH), which is the stacking of layers with divalent M<sub>1</sub> and trivalent M<sub>2</sub> metallic cations, and of interlayers comprising anions and water molecules; its general formula can be written [M<sub>1</sub><sup>2+</sup>(1-x) M<sub>2</sub><sup>3+</sup>x]<sup>x+</sup> [A<sup>n-</sup>](x/n). y H<sub>2</sub>O. In the case where both cations are those of iron, the formula is now Fe<sup>2+</sup>6(1-x) Fe<sup>3+</sup>6x O<sub>12</sub> H<sub>2</sub>(7-3x) CO<sub>3</sub>. y H<sub>2</sub>O since the intercalated ion is carbonate CO<sub>3</sub><sup>2-</sup>; this hydroxycarbonate (green rust) was identified by <sup>57</sup>Fe Mössbauer spectroscopy in hydromorphous gley soils, described firstly by the Ukrainian pedologist Georgii Nikolaiev Vysotskii in 1905. The stacking of a DLH is observed by XRD and Mössbauer spectra revealing a long-range order of Fe<sup>3+</sup> ions in layers as due to electrostatic repulsion so that each Fe<sup>3+</sup> ion is surrounded by six Fe<sup>2+</sup> ions; consequently, the CO<sub>3</sub><sup>2-</sup> ions are ordered and do not move during the the oxido-reduction reaction. The similarity between spectra of synthetic samples and those extracted from the field in gleys under the water table allowed the International Mineralogical Association (IMA 2012-049) to name three new minerals

- (i) fougèrite at x = 1/3,
- (ii) *trébeurdenite* at x = 2/3 and
- (iii) *mössbauerite* at x = 1; the biogenesis operates in anoxic conditions. The compound at x = 0 has never be found in the field. Finally, there are two oxido-reduction processes of iron, either the slow dissolution-reprecipitation leading to the usual corrosion of iron and steels, or the fast *in-situ* deprotonation-protonation;  $E_h$ -pH Pourbaix diagrams will be discussed later.

#### Fe-GLUCONATE: STRUCTURE AND PROPERTIES

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Ferrous gluconate (Fe-gluconate) is a salt of the gluconic acid:  $C_{12}H_{22}FeO_{14}\cdot xH_2O$  with  $0 \le x \le 2$ . The compound has mainly applications in medical and food additive industries. Regarding the former it has been satisfactorily used in the cure of hypochromic anemia and sold under various trade names e. g. Ascofer, Fergon and Ferate to list some of them. Respecting the latter, it has been applied for coloring foods, e. g. Black olives and beverages. But Fe-gluconate was also used as an effective inhibitor for carbon steel, gluconate-based electrolytes were also successfully used to electroplate various metals or alloys. The Fe content lies between 11.8 and 12.5 percent, and it is present in two forms: a major ferrous Fe<sup>2+</sup> or Fe(II) ion and a minor ferric (Fe<sup>3+</sup>) or Fe(III) ion. The relative contribution of the minor fraction amounts to ~10-15%, as detected by Mössbauer spectroscopy and it seems to decrease with time. We have recently found that, in addition to already known crystalline Fegluconate, its amorphous form can be obtained [1]. Furthermore, we revealed that the crystalline Fegluconate can have two different crystallographic structures depending on the amount of water: dry sample (x=0) crystallizes in the triclinic unit cell (space group PI), while fully hydrated sample (x=2) exhibits the monoclinic unit cell (space group I2) [2]. Results on the dynamics of Fe atoms and indications on low temperature magnetism will be reported, too [3].

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### INFLUENCE OF SM AND Y MOLAR FRACTIONS ON THE PROPERTIES OF ELECTROSPUN (Fe, Sm) AND (Fe, Y) OXIDES

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Iron oxides (general term for iron-hydroxides, -oxyhydroxides, and -oxides) are widespread and abundant in nature. In addition to oxides found in nature, there are also synthetic iron oxides, which are important materials in advanced technologies. Researchers are trying to pronounce some properties of these materials, such as magnetic, electrical, optical, photocatalytic, and other properties. These properties are strongly influenced by the nano/microstructure of iron oxides, which mostly depends on the preparation method, as well as by doping with various metal cations. In the present work, we report the phase composition and nano/microstructural changes of the thermal decomposition products of electrospun composite nanofibres of polyvinylpyrrolidone (PVP) and Fe(III)-Sm(III) or Fe(III)-Y(III) nitrate. The thermal decomposition products obtained from electrospun precursor composite fibres were determined using XRPD and <sup>57</sup>Fe Mössbauer spectroscopy, while fibre morphology was inspected using FE SEM and TEM. Magnetic properties were studied by <sup>57</sup>Fe Mössbauer spectroscopy and SQUID magnetometry. Depending on the Sm and Y molar fractions in (Fe, Sm) and (Fe, Y) oxide systems, as well as calcination temperatures, the following crystal phases were formed: α-Fe<sub>2</sub>O<sub>3</sub>, γ-Fe<sub>2</sub>O<sub>3</sub>, Sm<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>, Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>, SmFeO<sub>3</sub>, YFeO<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, and Y<sub>2</sub>O<sub>3</sub>. In the reference sample (containing only Fe<sup>3+</sup> cations) the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase and a minor amount of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phase were present. The amount of these crystalline phases in electrospun products depended on the Sm and Y molar fractions with a significant decrease in crystallinity in samples containing a higher content of samarium or yttrium.

#### PARAMAGNETIC BEHAVIOUR OF Mn IMPLANTED ZnO

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Following the prediction of room temperature ferromagnetism in ZnO and GaN doped with ~5 at. % Mn, we have conducted CEMS and VSM studies of ZnO implanted with Mn ions to 3 and 6 at. % concentration. For CEMS measurements, the substrates were co-implanted with  $5 \times 1015$  cm<sup>-2</sup> 60 keV <sup>57</sup>Fe ions. Data were collected after annealing the samples at temperatures up to 900 °C. The implantation damage anneals rapidly, and after the 900 °C anneal, the spectra are characterized by paramagnetic doublets with isomer shift consistent with Fe<sup>3+</sup>, as expected for Fe replacing the Zn<sup>2+</sup> in ZnO. The quadrupole splittings are considerably reduced for the 6% implanted sample, reflecting the formation of larger clusters than in the 3% implanted sample. The spectra display no evidence of ferromagnetic behaviour is observed. The magnetization curves collected at temperatures 2 K – 30 K and at RT are well represented by the Langevin function and confirm the formation of nano-sized clusters of the implanted ions.

### STUDY OF STAINLESS STEEL SURFACE AFTER ANNEALING IN THE TEMPERATURE RANGE 550 - 1000 °C

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Conversion electron Mössbauer spectroscopy (CEMS) and conversion X-ray Mössbauer spectroscopy (CXMS) were used as the main methods to study the surface of specimens made from stainless steel powder (CL20ES) by selective laser melting. Other study methods were X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). Samples measuring 25x25x2 mm<sup>3</sup> were prepared on a Concept Laser M2-cusing system (Concept Laser, Germany) by selective laser melting. After 3D printing, the samples were sandblasted with corundum powder. The annealed in a LE 15/11 furnace (LAC, at temperatures of 550, 700, 800, 900 and 1000 °C for 0.5, 1, 2, 4, 8, 16 and 32 hours. The CXMS spectra of all samples contained only the narrow doublet of the corresponding austenitic stainless steel (isomer shift; IS = -0.08 mm/s, quadrupole splitting; OS = 0.15 mm/s). These CXMS spectra are identical to the Mössbauer spectra of the starting metal powder (CL20ES) registered in the transmission geometry of the Mössbauer experiment. Changes related to oxidation in the surface layer with a thickness of about 0.3  $\mu$ m were identified in the CEMS spectra. A doublet with IS = 0.33 mm/s and QS = 0.55 mm/s appears in the CEMS spectra. According to the isomeric shift, this doublet corresponds to Fe<sup>3+</sup>. CEMS spectra did not register on all samples. This is related to the diffusion of alloying elements to the surface of the samples where they oxidize. This process is associated with an affinity of the alloying elements (Cr, Mn) for oxygen that is greater than the affinity of iron for oxygen. A thin surface layer formed by oxides of alloying elements and this layer prevents the penetration of conversion electrons emitted during deexcitation of <sup>57</sup>Fe nuclei. SEM shows a new crystalline layer on the surface of the samples after annealing. At the same time, EDS confirmed an increase in the concentration of alloying elements (Cr and Mn). XRD identified Cr<sub>2</sub>O<sub>3</sub> and Mn<sub>2</sub>NiO<sub>4</sub> on the surface. Transformation of the austenitic phase to the ferritic phase was observed in samples annealed at 550 °C. In the CEMS spectra, the subspectrum of the ferritic phase appears outside the subspectra of the austenitic phase and the oxide phase. The new ferritic phase (IS = 0.02 mm/s and B = 33.5 T) was observed only by CEMS. It was not commonly identified in CXMS spectra. Only in the extremely long period (430 hours) of registration of the CXMS spectrum does an indication of this ferritic phase appear. It is clear that the ferritic phase is present only in the surface layer up to about 1 µm. XRD confirmed the formation of a ferritic phase after annealing at 550 °C.

## SURFACE CHANGES INVESTIGATION OF "MASHA" STEEL COMPONENTS BY MÖSSBAUER SPECTROSCOPY

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MASHA (Mass Analyzer of Superheavy Atoms) is an experimental setup located on one of the beamlines of U400M synchrotron in Flerov Laboratory of Nuclear reactions, Joint Institute of Nuclear Research in Dubna. It is used for determination of mass of newly produced isotopes of superheavy elements. The defects of steel components of MASHA experimental setup are studied using Mössbauer spectroscopy. The determination the structural changes of surface properties are analysed in detail. These changes can negatively involve the pathway of primary beam and products in the SHE synthesis and characterization experiments. Vacuum chambers, tubes as well as special chambers (hot catcher, cryo-chambers) surface properties are crucial for attracting the products of SHE experiments due to the changes in electronic properties of phase components, porosity etc. due to the continuous irradiation at high doses. Backscattering  $^{57}$ Fe Mössbauer spectroscopy allows non-destructive material analysis for study of both large and small samples, for determination of iron-bearing phases occurrence with the accuracy below  $\pm 1\%$ . MS applications in metallurgy and engineering are significant for determination of residual austenite content. All iron bearing phases can be distinguished i.e. ferrites, oxides, amorphous forms, carbides etc. Phase component changes due to the irradiation are studied also.

# $E_h$ -ph pourbaix diagrams of green rusts and ${\sf CORTEN^{\sf TM} \ STEEL}$

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Thermodynamically speaking, an obvious similarity does exist between the properties of iron-carbon alloys, i.e. steels, and those of the products of aqueous corrosion of iron and steels. In both cases, one must distinguish between a slow process where stable equilibria are observed and a fast process where metastable equilibria are obtained. Let us firstly consider iron and steel. By slow cooling, many phases form, essentially two allotropic phases: bcc, body-centered cubic ferrite ( $\alpha$ ,  $\beta$ ,  $\delta$ )) and fcc, facecentered cubic austenite  $\gamma$  whereas carbides such as cementite Fe<sub>3</sub>C precipitate. In contrast, fast cooling by quenching from high temperature austenite  $\gamma$  allows to obtain a body-centered-tetragonal bct martensite  $\alpha'$ , which owns a high hardness. The carbides do not form so that the carbon atoms stay trapped inside the  $\alpha$ ' lattice, which becomes tetragonal; martensite quenching was invented long ago by Hittites who defeated Ramses II at Oadesh around 1200 BC, thus starting the Age of Iron by leaving the Bronze Age. For giving perennity to the outer envelope of the barrels where are stored the radioactive wastes in Cigéo Center at (F55290) Bure, which are brought from the European Nuclear Reactors, EPRs, that produce nuclear electricity, we propose to choose the weathering CORTEN<sup>TM</sup> steel which cannot be corroded since it is covered by the ferric double layered hydroxycarbonate of formula  $Fe^{3+}_{6}$   $O_{12}$   $H_{8}$ . n  $H_{2}O$ , which is found in soils, the glevs within maritime marshes and named **CORTEN**<sup>TM</sup> mössbauerite. For drawing the  $E_h$ -pH Pourbaix diagram of the *in-situ* deprotonation reaction becomes  $GR^*(x + dx) + dx H^+ + dx e^- \Leftrightarrow GR^*(x)$ , represented by a straight line according to Nernst's law;  $E_h$ -pH diagrams can be compared for the redox reactions of the two processes, slow dissolution-precipitation versus fast *in-situ* deprotonation; the fast process is obtained by pouring a strong oxidant such as hydrogen peroxide H<sub>2</sub>O<sub>2</sub>, on a coprecipitated  $GR1(CO_3^{2-})$  with a ferric ionic ratio x of 1/3, inside a glove box with pressurized nitrogen gas. Blackmailing from any gas producer is irrelevant and thanks to all green nuclear electricity by using weathering CORTEN<sup>TM</sup> steel.

#### MICROSTRUCTURE OF HIGH-ENTROPY ALLOYS

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In conventional alloys, additional alloying elements are added to the primary (major) element to improve their mechanical, chemical, and physical properties. Since 2018, there has been an increase in interest in high-entropy alloys (HEA) which consist of up to five primary elements. The multi-dimensional compositional space that can be tackled with this approach is practically limitless, and only several types of HEA have been investigated so far. Nevertheless, some HEA have already been shown to possess exceptional properties, exceeding those of conventional alloys. Other outstanding HEA are likely to be discovered in the future. In this work, we analysed mainly microstructural properties of three high-entropy alloys (Fe<sub>28</sub>Co<sub>28</sub>Ni<sub>28</sub>Al<sub>8</sub>Mn<sub>8</sub>, Fe<sub>20</sub>Co<sub>20</sub>Ni<sub>20</sub>Al<sub>20</sub>Mn<sub>20</sub> and Fe<sub>11</sub>Co<sub>11</sub>Ni<sub>11</sub>Al<sub>33.5</sub>Mn<sub>33.5</sub>). In doing so, less common approach, which makes use of the Mössbauer effect, was adopted. The materials' subsurface layers were analysed by conversion electron Mössbauer spectroscopy and their bulk was studied by transmission Mössbauer spectroscopy. The composition of HEA was verified using energy dispersive X-ray fluorescence, chemical analysis (F-AAS), and particle-induced X-ray emission technique. We use also X-ray diffraction to determine the crystalline phases present in the investigated HEA.

This work was supported by the projects VEGA 1/0130/20, by the European Regional Development Fund-Project "Centre for Advanced Applied Sciences", grant number CZ.02.1.01/0.0/0.0/16\_019/0000778 and by the Slovak Spectroscopic Society, member of the Association of Slovak Scientific and Technological Societies with the following logo:



#### **C11**

# SYNTHESIS, STRUCTURE AND PROPERTIES OF COMPLEX IRON(III) SALTS CONTAINING VARIOUS LIGANDS AND OXIDIZING ANIONS

### <u>Kende Attila Béres,</u> Ildikó Firalszky, Zoltán Homonnay, Libor Kvítek, Martina Kubiková, László Kótai

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The aim of our work was a continuing our previous efforts [1-3], i.e. preparation and structural characterization of various iron(III) complexes having different kinds of (reducing) ligands (urea, N-methylurea, N,N- and N,N'-dimethylurea, tetramethylurea) and oxidizing anions (NO<sup>3-</sup>, MnO<sup>4-</sup>, ClO<sup>4-</sup> etc.). Structural characterization has been performed by single crystal X-ray diffraction and various spectroscopic (Mössbauer, IR, Raman) methods.

## SIMPLE METHOD OF DETERMINING CENTER SHIFT AND SPECTRAL AREA OF A MÖSSBAUER SPECTRUM

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The most simple method is outlined for determining the center (isomer) shift, CS, and the spectral area, A, of a Mössbauer spectrum. Its usefulness has been demonstrated by an analysis of two sets of the spectra measured in the temperature range of 78-295 K on a powder sample of a natural pyrite,  $FeS_2$  and on a powder sample of a sigma-phase  $Fe_{0.525}Cr_{0.455}Ni_{0.020}$  intermetallic compound. For comparison, all the recorded spectra were also analyzed using a standard procedure i.e. the spectra of  $FeS_2$  were fitted to one doublet, and those of  $\sigma$ - $Fe_{0.525}Cr_{0.455}Ni_{0.020}$  to five doublets related to five different lattice sites. The obtained sets of the CS(T)- and A(T)-data were analyzed in terms of the relevant Debye model yielding values of the Debye temperature,  $T_D$ . For the pyrite  $T_D$ =590(10) K for the simple method and  $T_D$ =600(6) K for the standard approach were obtained based on the CS(T)-data. The corresponding values found from the A(T)-data are  $T_D$ =274(4) K and  $T_D$ =278(17) K, respectively. The  $T_D$ -values found for the  $\sigma$ -phase sample using the set of the CS(T)-data are 437(7) K and 450(12) K, for the standard and the simple methods, respectively. In turn, the analysis of the A(T)-data gave  $T_D$ =379(5) K and  $T_D$ =367(30) K, respectively.

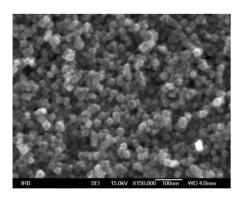
## ONE POT SYNTHESIS OF Co AND NI DOPED MAGHEMITE NANOPARTICLES USING ACETYLCETONATE PRECURSORS

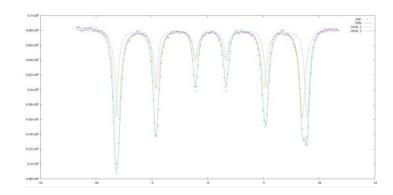
### Marijan Marciuš<sup>1</sup>, Mira Ristić<sup>1</sup>, Jean-Marc Grenèche<sup>2</sup>, Stjepko Krehula<sup>1</sup> and Svetozar Musić<sup>1,3</sup>

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Spinel ferrites are important materials which find various applications in modern technology. For this reason scientist and engineers show permanent interest in their synthesis and properties. Maghemite  $(\gamma\text{-Fe}_2\text{O}_3)$  which shows very interesting magnetic properties is also a semiconductor. Due to the characteristic crystal structure it can be doped in wide range with various cations for fine tuning of semiconducting as well as gas sensing properties. Recently we reported [1] one pot synthesis of Mn-doped maghemite nanoparticles using acetylacetonate precursors. In present work the acetylacetonates of iron and cobalt or nickel were mixed and heated at proper temperatures to form the nickel or cobalt doped maghemite samples or ferrites. The samples produced were characterized with XRD, Mössbauer, FE-SEM and EDS. The changes in crystallographic parameters in dependence on the fraction of cobalt or nickel were measured. Also, the effect of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  dopant on Mössbauer parameters was noticed. Low temperature (77 K) measurements of Ni doped maghemite samples showed almost no change in Mössbauer parameters with doping level. Electron microscopy (FE-SEM) showed unusual nanosized particles of high uniformity. The high uniformity of nanoparticles is due to the thermal decomposition of acetylacetonate precursors mixture above the melting point.





[1] M. Marciuš, M. Ristić, J.-M. Grenèche, S. Musić, S. Krehula, E. Kuzmann, Z. Homonnay, J. Radioanal. Nucl. Chem. 328 (2021) 1181-1187.

#### MÖSSBAUER STUDY OF Fe-RICH BERYL

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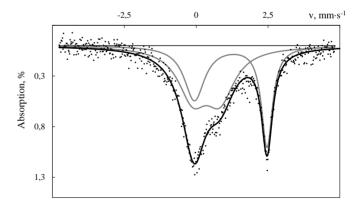
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Colored beryls are of considerable interest to the jewelry industry because of their high refractive index and rich color. Synthetic beryls are used in optical engineering. Iron is a typical impurity in natural beryls. The color of the mineral is associated not only with the total amount of iron, but also with the ratio of ferric and ferrous iron as well as their positions in the crystal lattice. Mössbauer spectroscopy is the optimal method for determining this parameter. The routine analysis of the Mössbauer spectra of beryls is complicated by the fact that the components of the spectrum (doublets) can be asymmetric [1]. The figure shows the room-temperature Mössbauer spectrum a Fe-rich beryl sample from Pamir containing about 5 wt.% of iron, which we have characterized in detail by several techniques.

The spectrum can be satisfactorily described by an asymmetric doublet of iron(II) and a symmetric doublet of iron(III);  ${}^{RT}IS_{\alpha}$ Fe=1.20±0.06 mm·s<sup>-1</sup>, RTQS=2.5±0.1 mm·s<sup>-1</sup>,  $FWHM_L=0.9\pm0.1 \text{ mm} \cdot \text{s}^{-1}, FWHM_R=0.5\pm0.1$  $^{RT}IS_{\alpha\text{-Fe}}=0.36\pm0.08 \text{ mm}\cdot\text{s}^{-1}$  $\text{mm} \cdot \text{s}^{-1}$ and  $^{RT}QS=0.9\pm0.2 \text{ mm}\cdot\text{s}^{-1}$ , FWHM=1.2±0.1  $\text{mm} \cdot \text{s}^{-1}$ respectively, Fe(II):Fe(III)≈1:1. These parameters are consistent with those known for beryls [2]. However, the accuracy of their determination is not satisfactory from



a practical point of view. It is known that the asymmetry may reversibly disappear at low (<14K) and high temperatures ( $>\approx500^{\circ}C$ ) [2]. This can be used to simplify modeling.

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#### **Poster contributions**

**P1** 

### PHYSICO-CHEMICAL CHARACTERIZATION OF SYNTHETIC HEMOZOIN CRYSTAL

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Plasmodium is a parasite that is transmitted to man by the bite of a mosquito of the Anopheles genus that causes malaria. In one of the stages of the life cycle of the parasite in the human body, the plasmodium degrades hemoglobin and forms a crystal called hemozoin, as the main protection mechanism. For this reason, a complete understanding of the formation mechanisms and the physical-chemical characteristics exhibited by this crystal are very important to understand and control the malaria disease. Additionally, this crystal is also the target of several antimalarial drugs. An approach for this type of research is to manufacture in the laboratory, under diverse and controlled conditions and in the presence of various drugs, the synthetic analogue of hemozoin, which is called the  $\beta$ -hematin crystal. We present the kinetic studies, in aqueous medium, of conversion of hemin to  $\beta$ -hematin both in pure form and in the presence of chloroquine, a commonly used antimalarial drug. The results suggested that, under the conditions of the present experiments and based on three statistical values for the goodness of the fit, the order from the best to the worst models for all kinetics are: lineal combination of Avrami and first order > Avrami > hyperbolic tangent > order 1 > order 0. Furthermore, all crystals were characterized by X-ray diffraction, Mössbauer and infrared spectroscopy, and transmission electron microscopy.

#### FORMATION OF Fe<sub>2</sub>O<sub>3</sub> CLUSTERS ON FE IMPLANTED AL<sub>2</sub>O<sub>3</sub>

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Our earlier study on  $Al_2O_3$  implanted with 4 at. % Fe by conversion electron Mössbauer spectroscopy (CEMS) and magnetization measurements showed the formation of paramagnetic Fe clusters 2-3 nm in size. Our search for formation of ferromagnetic nanoclusters was now extended to studies on samples implanted with 50 keV Fe to a concentration of 8 at. %. For the as-implanted situation, the CEM spectrum shows the expected presence of implantation induced broad paramagnetic doublets due to incorporated Fe<sup>3+</sup> and Fe<sup>2+</sup>. On annealing at 900°C, the CEMS spectrum evolves into a strong ferromagnetic sextet with parameters consistent with those of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, together with a paramagnetic doublet due to nanoclusters. The magnetization curves show hysteresis loops with a small non-zero coercive field. The Langevin function for superparamagnetic particles is unable to fit the low temperature magnetic isotherms, confirming the finite size of the clusters.

## MÖSSBAUER SPECTROSCOPY STUDY OF CHROMIUM RICH BCC $\alpha'$ PHASE PRECIPITATION IN Fe20Cr ODS ALLOY

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Martin Petriska<sup>1</sup>, and Michal Kotvas<sup>1</sup>

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The ferritic, dual-phase and martensitic steels with the Cr content higher than 12 wt. % are known for their ageing degradation due to so-called "475 °C embrittlement", which can significantly influence their mechanical properties and consequently narrow the range of their applications. This phenomenon is attributed to the phase separation of the  $\alpha$ -(Fe, Cr) ferrite phase into Fe-rich ferrite ( $\alpha$ ) and the Crrich ferrite ( $\alpha$ ') phases in the miscibility gap, below 500 °C. In the present work, we focus on the determination of  $\alpha$ ' precipitation in PM2000 (Fe20Cr) steel by the Mössbauer spectroscopy technique. The obtained results are complemented by non-destructive techniques such as magnetic Barkhausen noise (MBN) and positron annihilation spectroscopy (PAS). These non-destructive techniques were used in a complementary manner to determine the  $\alpha$ ' phase in the PM2000 samples isothermally annealed at 475 °C up to 1000 h. The same annealing was performed on T91 (Fe8Cr) steel to compare the differences in the obtained results with the alloys where  $\alpha$ ' development is not expected.

The authors acknowledge the contribution of the Slovak Research and Development Agency under the project APVV-20-0010. The authors further acknowledge financial contributions from the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic and the Slovak Academy of Sciences, grant numbers VEGA 1/0382/20 and VEGA 1/0395/20 and from the European Regional Development Fund, project No. ITMS2014+:313011W085.

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# THE EFFECT OF ANNEALING ATMOSPHERE ON THE STRUCTURAL PROPERTIES OF FeSiBPCu ALLOYS WITH DIFFERENT SILICON CONTENT

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Structural and magnetic properties of the as-cast and nanocrystalline NANOMET-type soft magnetic alloys of two different compositions differing in silicon content, i.e., Fe<sub>82</sub>Si<sub>4</sub>B<sub>10</sub>P<sub>3</sub>Cu<sub>1</sub> and Fe<sub>78</sub>Si<sub>8</sub>B<sub>10</sub>P<sub>3</sub>Cu<sub>1</sub>, were studied. Nanocrystalline alloys were prepared by annealing the amorphous precursors at a temperature of 420°C for 20 and 60 minutes in vacuum and in Ar atmosphere. The effect of the annealing time and atmosphere on the alloy properties were investigated by Mössbauer spectroscopy (MS), magnetic measurements, atomic force microscopy (AFM) and X-ray diffraction (XRD) for both studied compositions. Mössbauer spectroscopy disclosed the effect of the silicon content on the annealed alloys microstructure, i.e., the lower relative volumetric fraction of the crystalline phase component for the alloy with 8% of Si as compared to the alloy with lower silicon content of 4%. Variations of the parameters reflecting the magnetic microstructure were also observed and are discussed with relation to different annealing times and atmospheres. Magnetic measurements indicated that longer annealing times are reflected in the resulting coercivity. Better soft magnetic properties showed sample with 8% of Si after annealing for 20 minutes whose coercivity was lower as well as the determined magnetization work. The AFM measurements inspecting the morphology of the sample surfaces manifested the differences in the grain height and the number of grain agglomerates for the studied alloy compositions with relation to the annealing duration and atmosphere. The XRD measurements followed the expansion of crystalline phase in annealed samples.

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# MÖSSBAUER AND MAGNETIC PROPERTIES STUDIES OF Fe<sub>84.5-x</sub>Co<sub>x</sub>Nb<sub>5</sub>B<sub>8.5</sub>P<sub>2</sub> NANOCRYSTALLINE ALLOYS FOR APPLICATIONS IN HIGH-POWER CONVERSION SYSTEMS

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Amorphous and nanocrystalline iron-based soft magnetic materials play an important role in a broad area of energy conversion, especially in miniaturization- and mobility-related applications. Current development of these materials is focused on fabrication of relatively cheap and easy-to-produce materials with a high-set expectation bar as concerns the soft magnetic properties.

The aim of the work was to determine the most optimal alloy's composition and conditions of thermomagnetic treatment of Pyroperm-type  $Fe_{84.5-x}Co_xNb_5B_{8.5}P_2$  (x=0-20 at.%) materials in order to obtain the magnetic parameters suitable for possible applications in induction heating devices. The amorphous ribbons were produced on semi-industrial scale using the melt-spinning equipment. Next, a special thermo-magnetic treatment was applied to obtain nanocrystalline cores with induced transverse magnetic anisotropy. The structure and magnetic properties of the nanocrystalline alloys were investigated by Mössbauer spectroscopy, hysteresis loop analyses and vibrating sample magnetometry. Magnetic parameters, such as saturation induction, remanence, coercivity, magnetic permeability and core losses, were determined.

Mössbauer spectroscopy studies confirmed the presence of Co in the nanocrystalline bcc phase and the influence of the transverse magnetic field during annealing on spin orientation. Conversion electron Mössbauer spectroscopy measurements allowed us to compare surface vs. bulk crystallization of the alloys. As concerns magnetic properties it was found that the maximum value of the induced magnetic anisotropy (637 J/m³) while maintaining a high value of saturation magnetization (1.7 T) was obtained for the heat treatment at 525 °C for 20 min. in the presence of 140 kA/m transverse magnetic field for the alloy with the highest Co content [1]. High-frequency tests performed on the Fe<sub>64.5</sub>Co<sub>20</sub>Nb<sub>5</sub>B<sub>8.5</sub>P<sub>2</sub> cores confirmed high stability of their magnetic parameters as a function of frequency proving that they are suitable for applications in power electronics in high-frequency and high-power conversion systems. As an example, the nanocrystalline Fe<sub>64.5</sub>Co<sub>20</sub>Nb<sub>5</sub>B<sub>8.5</sub>P<sub>2</sub> cores were successfully installed in industrially available mobile heating equipment [2].

<sup>[1]</sup> A. Kolano-Burian, P. Zackiewicz, A. Grabias, A. Wojcik, W. Maziarz, M. Szlezynger, P. Wlodarczyk, M. Kowalczyk, L. Hawelek, Materials 14 (2021) 3433.

 $<sup>[2] \ \</sup>underline{https://www.efd-induction.com/-/media/pdf/brochures/minac/the-new--generation-minac.ashx}$ 

#### PHOTODEGRADATION OF IRON(III) CITRATE

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Iron is an essential cofactor for all livings. Due to environmental factors iron limitation of the agricultural lands of the world is significant. As a consequence, iron deficiency is one of the most challenging limiting factors of crop production. Since plants represent the major iron source in human nutrition, iron deficiency in plants not only leads to a reduced quality and quantity of plant products, but also promotes development of iron deficiency in human bodies, which is recognized as one of the most common nutritional disorder in the world. Despite this, iron metabolism of mesophyll cells has not been fully revealed yet. It is suggested that iron in the xylem is transported as a citrate complex. Therefore, Fe<sup>III</sup> citrate is widely applied as the standard iron source for plant nutrition. Since leaves as photosynthetic organs are generally exposed to illumination in daytime, photoreaction of ferric species may have biological relevance in iron metabolism, the relevance of which is poorly understood. In present work Fe<sup>III</sup> citrate transformation during the photodegradation in solution and after foliar application on leaves was studied by Mössbauer analysis directly. Four model solutions of Fe<sup>III</sup> citrate at different pH values (1.5, 3.3, 5.5, and 7.0) were exposed to light in a plant growth chamber. Highly acidic conditions led to a complete reduction of Fe together with the formation of Fe<sup>II</sup> citrate and hexaaqua complexes in equal concentration. At higher pH (Fig. 1), the only product of the photoreduction was Fe<sup>II</sup> citrate, which was later reoxidized, resulting in the formation of polynuclear stable ferric compound. To test biological relevance, leaves of cabbage were treated with Fe<sup>III</sup> citrate solution. X-ray fluorescence imaging indicated the accumulation of iron in the treated leaf parts. Mössbauer analysis revealed the presence of several ferric species incorporated into the biological structure. The iron speciation observed should be considered in biological systems where Fe<sup>III</sup> citrate has a ubiquitous role in iron metabolism.

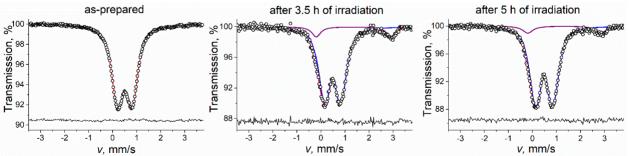


Fig. 1. Mössbauer spectra of the frozen iron(III) + citric acid solutions at pH = 5.5: as-prepared (left) and after 3.5 (center) and 5 (right) hours of light irradiation.

## DEVELOPMENT OF POLARIZED <sup>57</sup>Fe MÖSSBAUER SOURCES USING AN ELECTRON LINEAR ACCELERATOR

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Fundamental quantum optics studies in the X-ray and  $\gamma$ -ray region have attracted increasing attention, and Mössbauer  $\gamma$ -rays have been applied to various studies in this region such as electromagnetically induced transmission phenomena and coherent waveform control. Compared with visible light,  $\gamma$  rays have high spatial resolution and high penetrability to objects with optical thickness. In particular, Mössbauer  $\gamma$  rays have a high energy resolution as high as  $\Delta E/E \sim 10^{-13}$  and the polarization and time structure can be controlled by the transmission process of the absorber, therefore it seems to have extremely promising potential. For quantum optics research in the  $\gamma$ -ray region, it is desirable to use polarized  $\gamma$ -ray sources easily. In order to satisfy this requirement, we produced a magnetically split  $^{57}$ Fe Mössbauer source by irradiating natural Ni foil with X-rays at KURNS-LINAC(Kyoto University, Institute for Integrated Radiation and Nuclear Science - Linear Accelerator). This method requires no special chemical treatment for radioactive material and the prepared source is easy to handle, making it highly valuable for practical use. The polarization source is expected to be used for controlling polarization by applying an external magnetic field, implementing quantum bits, and analyzing hyperfine structure in single crystals.

# MÖSSBAUER SPECTROSCOPY MONITORING OF THE FERRATE(VI) CONTENT OF A POTENTIAL INDUSTRIAL WASTE WATER TREATMENT PRODUCT ON LONG TERM STORAGE

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Ferrate(VI) technology for waste water treatment has been in focus for a long time [1]. While ferrate(VI) has several advantages as compared to chlorine containing products (hypochlorite or chlorine gas), the lack of its stability poses a great challenge to researchers in the R&D sector.

When potassium ferrate(VI), K<sub>2</sub>FeO<sub>4</sub> is synthesized and brought to a dry solid form, it is thermodynamically stable, but the presence of water vapor and CO<sub>2</sub> triggers decay to Fe<sup>III</sup> compounds. A further problem is that when the dry product is added to water, the most probably close to neutral pH initiates fast decay and self decomposition with the release of oxygen which reduces the efficiency of the removal of organic pollutants from the water.

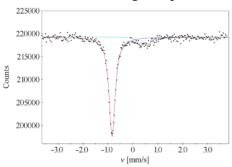


Figure 1. Mössbauer spectrum of a ferrate product after storage in a refrigerator for several months.

Ferrate ions are stable at high pH, therefore for long term storage of a commercial product high pH conditions may be secured. In our study, ferrate(VI) was synthesized by anodic oxidation of iron metal at high pH, and after precipitation it was filtered off. The precipitate was not dried completely so that some liquid film could cover the solid grains providing high pH. This material was sealed and stored in a refrigerator. Under these conditions the initial ~90 % ferrate content did not change significantly for several months (Figure 1). The ferrate content during storage was monitored by Mössbauer Spectroscopy, and identification of the degradation products was attempted.

[1] Virender K. Sharma (editor), Ferrates, Synthesis, Properties, and Applications in Water and Wastewater Treatment, ACS Symposium Series 985, American Chemical Society, 2008.

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# STUDY ON THE MECHANISM OF MECHANOCHEMICAL TRANSFORMATIONS AND THEIR IMPACT ON THE CATALYTIC PROPERTIES OF WASTE-DERIVED AMORPHOUS ALLOYS

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This paper investigates the potential to apply mechanochemistry toward improvement of photocatalytic properties of damaged ferromagnetic amorphous alloys for waste water remediation. Series of mechanochemical experiments are arranged for treatment of the tested material, Fe<sub>81</sub>B<sub>13.5</sub>Si<sub>3.5</sub>C<sub>2</sub> ribbons. Mossbauer spectroscopy was used to study the mechanism of mechanochemical transformations and their impact on the catalytic properties of these wastederived amorphous alloys. Planetary ball mill PM 100, Retsch GmbH, Germany with a stainless-steel vial, stainless-steel balls and ethanol milling media are used in all mechanochemical experiments. Comparative investigation of the bulk and the surface of samples is made by transmission mode Mössbauer spectroscopy (at room and liquid nitrogen temperature) and by conversion electron Mössbauer spectroscopy (CEMS). Additional information about the changes in studied materials was obtained by X-ray diffraction and SEM/EDX method. The ball milling parameters, where the surface chemical rearrangement and clustering of amorphous alloy is highly beneficial for its catalytic oxidation properties, are established as a result of the study. It was registered, that the mechanism of mechanochemical transformations and the created chemical and structural rearrangement in the amorphous material significantly impact the formation of catalytically active phases in studied materials. So, this study is dealing with application of mechanochemical treatment for both the preparation of highly active catalytic materials and the reuse of waste-derived amorphous alloys. Acknowledgements: The authors gratefully acknowledge the financial support of the Bulgarian National Science Fund at the Ministry of Education and Science - Project № KΠ-06-KOCT/18/2019. This article is based on the project activities of COST Action CA 18112 "Mechanochemistry for Sustainable Industry" (Mech@SustInd), supported by COST (European Cooperation in Science and Technology). The financial support from the Bulgarian Academy of Sciences (Bilateral grant agreement between BAS and University of Belgrade, ICTM) is also gratefully acknowledged.

# <sup>57</sup>Fe MÖSSBAUER STUDY OF Zn ADDITION IN Co<sub>1-x</sub>Zn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> SPINEL NANO FERRITES

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Ferrimagnetic spinel nano ferrites exhibit face centred cubic structure, have two inter-penetrating sublattices tetrahedral (A), octahedral (B) respectively allocated by divalent, trivalent metal ions, and are represented by formula M<sup>2+</sup>Fe<sub>2</sub><sup>3+</sup>O<sub>4</sub>. Control over magnetic properties can be achieved via: presence of specific cations, synthesis technique, thermal treatment, distributions of cations on A, B sites, Thus, tunability of properties makes them attractive in various applications, including those in high frequency devices, bioscience (hyperthermia, MRI), gas sensing, multilayer chip inductor, magnetic cores etc. Present work reports sol gel auto-combustion synthesis of  $Co_{1-x}Zn_xFe_2O_4$  (x = 0.0 - 0.56) ferrites, using nitrate-citrate precursors. Prepared 'dry gel' samples were characterized at room temperature by x-ray diffraction (XRD), <sup>57</sup>Fe Mössbauer, magnetic measurements. XRD validates the formation of pure spinel phase (grain size: 14.7 nm - 29.1 nm), incorporation of  $\text{Zn}^{2+}$  ion in the spinel structure evidenced by increase of lattice parameter from 0.8318 nm to 8394 nm, ascribable to variation of ionic radii of Co<sup>2+</sup> (0.072 nm), Zn<sup>2+</sup> (0.074 nm). Specific surface area between 38.8 – 75.4 m<sup>2</sup>/g suggests usefulness of current samples in heterogeneous catalysis. Cationic distribution suggests that while Fe<sup>3+</sup>, Co<sup>2+</sup> ions reside on both A, B sites, but majority of Zn<sup>2+</sup>, Co<sup>2+</sup> ions are populated respectively on A, B sites, leading to modification of: A-A, A-B, B-B super-exchange interaction, inversion degree (0.46 - 0.86), oxygen parameter (0.3786 - 0.3870) suggesting variation of disorder. With increasing Zn-content: i) coercivity reduction, and equivalent grain size suggest that studied ferrites are in single-multi domain overlap regions, ii) decrease of saturation magnetization is attributable to the replacement of a magnetic ion (Co<sup>2+</sup>) with a non-magnetic ion (Zn<sup>2+</sup>), shows tunability of magnetic properties. Isomer shift values reveal that Fe has 3+ oxidation state, and component with higher effective internal field (BHF) is assigned to the tetrahedral co-ordination, and shows significant re-distribution of Fe<sup>3+</sup> among A, B sites, and reveal increase of paramagnetic doublet area with Zn addition. Data for  $x \ge 0.16$  is analyzed with distribution of hyperfine fields, and shows noticeable changes. B<sub>HF</sub> decrease shows that more Fe atoms are surrounded by Zn atoms as first-near neighbours. Observed changes in magnetic properties are consistent with cation distribution obtained jointly from Mössbauer and XRD analyses.

## DEVELOPMENT OF MÖSSBAUER SOURCES FOR <sup>161</sup>Dy, <sup>166</sup>Er, AND <sup>169</sup>Tm

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Mössbauer spectroscopy is one of the most powerful tools for investigation of rare earth elements, since most of rare earth elements include Mössbauer isotopes. To promote their Mössbauer spectroscopy, short-lived Mössbauer sources are necessary to be developed. In this study, several practical sources are reported for <sup>161</sup>Dy, <sup>166</sup>Er, and <sup>169</sup>Tm Mössbauer spectroscopy. The sources are obtained by neutron irradiation at the Kyoto University Reactor (KUR). For the <sup>161</sup>Dy Mössbauer spectroscopy, Dy<sub>0.5</sub>Gd<sub>0.5</sub>F<sub>3</sub> was irradiated at KUR to obtain a <sup>161</sup>Tb source. The <sup>161</sup>Tb was generated from beta-decay of <sup>161</sup>Gd. Gd metal powder irradiated at KUR was also used as another practical <sup>161</sup>Tb source. An attempt for alternative source production methods for <sup>161</sup>Dy using the electron linear accelerator is discussed. For the <sup>166</sup>Er spectroscopy, HoAl<sub>2</sub> was irradiated to obtain a <sup>166</sup>Ho source. The HoAl<sub>2</sub> was used at the temperatures above 40 K, since it shows magnetic broadening below 40 K. For low temperature measurements, a synthesis method of Ho<sub>0.4</sub>Y<sub>0.6</sub>H<sub>2</sub> was developed using TiH<sub>2</sub> as a H<sub>2</sub> source. This compound can be used as a <sup>166</sup>Ho source even below 40 K. For the <sup>169</sup>Tm Mössbauer spectroscopy, Er-Al alloys are used to obtain an <sup>169</sup>Er source. Each source was confirmed to show a single-line spectrum by using a single-line absorber. Mössbauer spectra with some typical Dy, Er, and Tm compounds have been measured to demonstrate availability for the application using the obtained sources. These sources are promising for investigations of various materials including Dy, Er or Tm.

## MOSSBAUER STUDY OF THE MATERIAL OF THE ELECTRIC POWER TRANSFORMERS

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Fe-Si alloy is a soft magnetic material used as the core of electric power transformers. One method of molding the core is to press the powdered alloy into the shape of the core. In our study, the X-ray diffraction measurements performed on this processed material, we observed that the peak intensity of ordered phase Fe<sub>3</sub>Si was decreased in the pressed sample. The amount of ordered phase is important for the magnetic material. We performed Fe-57 Mossbauer spectroscopy to elucidate this decrease in the ordered phase. The Fe-Si alloy powders (Fe-5.0wt%Si and Fe-6.5wt%Si) were prepared by the gas atomizing process. To investigate the influence on the amount of the ordered phase, we pressed the powders at 883MPa and annealed them at 750°C. We used the Co-57 in Rh source and the conventional Mossbauer spectrometer for Mossbauer spectroscopy. The obtained spectra consisted of spectra of the Fe-Si alloy at low Si concentration and the small of the Fe<sub>3</sub>Si ordered phase. The obtained Mossbauer spectra were almost unchanged before and after pressing and annealing. There was no change in the amount of Fe<sub>3</sub>Si, too. The only difference was the full width at half the maximum of the peak, and the pressed sample was broader. This broadening is due to the crystal lattice distortion due to press working. Since there was no change in the intensity ratio of the Mossbauer spectrum, we consider that the percentage of the Fe<sub>3</sub>Si ordered phase did not change. And we think that the difference in the peak intensity of the X-ray diffraction comes from the distortion, which reduces interference and reduces the peak intensity.

## INFLUENCE OF SAMARIUM DOPING ON THE PROPERTIES OF HEMATITE ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) NANORODS

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In addition to being an important source of iron for the steel industry, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is also an important material for some other industrial applications, such as a catalyst in several industrial chemical reactions, particulate pigment for industrial production of paints, coatings, coloured plastic, rubber, ceramics, glass and concrete, as well as for production of magnetic pigments and ferrites [1]. In recent times, synthetic hematite samples have been intensely investigated for usage in several advanced applications such as photoelectrodes for photoelectrochemical hydrogen production using sunlight [2], sensors for detection of toxic and flammable gases [3] or photocatalysts for the degradation of toxic organic compounds [4]. Properties of hematite samples and their performance in different applications strongly depend on the particle size and shape, as well as on the substitution of Fe<sup>3+</sup> ions in crystal structure of hematite by other metal cations.

In the present work, the effects of the presence of Sm<sup>3+</sup> ions during the synthesis of hematite nanorods on their structural, magnetic and optical properties were investigated. Due to the same charge, but very different radius (95.8 pm), electron configuration (4f<sup>5</sup>) and magnetic moment (0.85 BM) of Sm<sup>3+</sup> ions compared to Fe<sup>3+</sup> ions (64.5 pm, 3d<sup>5</sup> and 5.92 BM, respectively), it could be possible that Sm<sup>3+</sup> ions replace a small amount Fe<sup>3+</sup> ions in hematite samples with a measurable change of their properties. Hematite nanorods were prepared by a two-step method which includes hydrothermal synthesis of goethite (α-FeOOH) nanorods and their calcination. Samarium doping caused an increase of the unit cell volume of hematite which indicates a substitution of certain amount of Fe<sup>3+</sup> ions by larger Sm<sup>3+</sup> ions. Besides, Sm<sup>3+</sup> doping of hematite nanorods caused a change of particle shape, decrease of hyperfine magnetic field, lowering of the Morin transition temperature, increased absorption of visible light and decrease of the optical band gap.

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## FABRICATION OF AMORPHOUS Fe BY SWIFT HEAVY ION IRRADIATION

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It is well known that rapidly quenched Fe-based metal-metal or metal-metalloid alloys are widely used in the industry due to their favourable properties. However, pure iron cannot be produced by rapid quenching technology since this would require extremely high cooling rates. We have previously demonstrated [1-2] that irradiation with swift heavy ions is capable of partial (15-35%) amorphization of alpha iron. In the present work, we present a case where very high amorphization rate was obtained when amorphous Fe was produced by swift heavy ion irradiation.

<sup>57</sup>Fe conversion electron Mössbauer spectroscopy was used to study the radiation effect of swift heavy ions on <sup>57</sup>Fe thin films vacuum deposited onto SiO<sub>2</sub>/Si substrate. The swift heavy ion irradiation of the metallic <sup>57</sup>Fe layer was carried out with 160 MeV energy <sup>132</sup>Xe<sup>26+</sup> ions up to a fluence of 10<sup>14</sup> ion cm<sup>-2</sup> at room temperature, at a current density of 0.01 μA cm<sup>-2</sup> and a pressure of about 10<sup>-3</sup> Pa, at the IC-100 cyclotron of the Flerov Laboratory of Nuclear Reactions, JINR, Dubna, Russia.

#### CEMS spectra (Fig. 1) revealed that

- in the non-irradiated deposit dominantly metallic crystalline  $\alpha$ -Fe is present besides minor Fe<sup>III</sup> oxide/oxyhydroxide phases
- the formation of amorphous pure iron and the formation of silicon-iron-oxides develops upon swift heavy ion irradiation
- the irradiation induced transformation of  $\alpha\mbox{-}$  Fe into amorphous Fe is almost completed

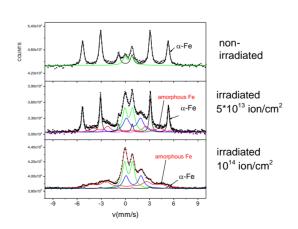


Fig. 1. <sup>57</sup>Fe CEM spectra of <sup>57</sup>Fe thin on SiO<sub>2</sub>/Si

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## INFLUENCE OF SINTERING IN THE STRUCTURAL AND MAGNETIC PROPERTIES OF DIFFERENT LITHIUM FERRITES

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Lithium ferrites (i.e, LiFeO<sub>2</sub>, LiFe<sub>5</sub>O<sub>8</sub>) are materials of great technological interest due to their multiple properties and the varied applications derived. LiFeO<sub>2</sub> is an antiferromagnet (AFM) with a rock-salt structure in which both Li<sup>+</sup> and Fe<sup>3+</sup> share octahedral sites (Oh) while LiFe<sub>5</sub>O<sub>8</sub> crystallizes in a spinel-type structure in which Li<sup>+</sup> occupy Oh while Fe<sup>3+</sup> distribute between Oh and tetrahedral (Td) positions, yielding a ferrimagnetic structure (FiM). The Li-content on Li ferrites has been seen to have a great influence over some physical properties, therefore conditioning the performance of functional devices based on these materials.

In this paper we have investigated using XRD, XANES, EXFAS and <sup>57</sup>Fe Mössbauer spectroscopy at different temperatures the effect that a process of sintering, aimed at producing denser materials, has on the phase composition, structural properties and magnetic ordering temperature of various lithium ferrites with different Fe/Li ratios.

Increasing the Fe/Li ratio in the precursors, produces materials having different crystalline structures, from rock salt LiFeO<sub>2</sub> for Fe/Li=1, to mixed rock salt and spinel phases for Fe/Li=3, to spinel LiFe<sub>5</sub>O<sub>8</sub> for Fe/Li=5.

The data have been evaluated using different fitting models in order to gain insight on the nature of the Li and Fe distribution, either ordered or disordered. The different models and their viability are commented in the light of the EXAFS structural results.

# ENERGY DOMAIN SYNCHROTRON RADIATION BASED MÖSSBAUER SPECTROSCOPY OF EuH<sub>2</sub> UNDER A FEW GPa HYDROGEN PRESSURE

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Many metals absorb hydrogen and show properties different from their base materials: volume expansion, structural phase transition, and magnetic phase transition, and so forth. Europium metal also absorbs hydrogen; its hydride EuH<sub>2</sub> is stable and shows *Pnma* structure and ferromagnetism, while europium metal shows  $Im\bar{3}m(bcc)$  structure and anti-ferromagnetism. Recently, the progress of high-pressure technique enables experiments under high hydrogen pressure. As for europium, some novel hydride phases of EuHx ( $x \ge 2$ ) were found under high hydrogen pressure below 16 GPa. Further phases were theoretically predicted under higher hydrogen pressures of about 100 GPa.

To study the local electronic structure of europium hydrides,  $^{151}$ Eu Mössbauer spectroscopy have been used. It had clearly showed Eu<sup>2+</sup> ionic state at EuH<sub>2</sub> and Eu<sup>2+</sup>-like metallic state at Eu metal. Eu hydride phases under high hydrogen pressure were also studied by energy-domain synchrotron radiation based Mössbauer spectroscopy: Eu<sup>3+</sup> ionic state was clearly observed at EuHx (x > 2) phase under 14 GPa hydrogen pressure. These ionicity change was observed through the clear difference in isomer shift in Mössbauer spectroscopy: furthermore, isomer shift is also affected by volume change and minor charge transfer between the europium and hydrogen even in the same ionicity. For the detailed discussion on the local states of europium in hydride phases, it is important to evaluate the shift by the volume and minor charge transfer.

In this presentation, we report our recent results on isomer shift in the  $EuH_2$  phase under a few gigapascal hydrogen pressure through the  $^{151}Eu$  energy-domain synchrotron radiation based Mössbauer spectroscopy performed at BL11XU of SPring-8. The relation between isomer shift change and volume change of  $EuH_2$  are discussed, compared with that of Eu metal.

### <sup>57</sup>Fe MÖSSBAUER SPECTROSCOPIC ANALYSIS OF Fe-BEARING PHASES IN THE INDUSTRIAL PRODUCTION OF TiO<sub>2</sub> WHITE PIGMENT

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Fe-bearing phases, present in the manufacture of TiO<sub>2</sub> pigment by sulphate process, were analysed by <sup>57</sup>Fe Mössbauer spectroscopy and supporting techniques. XRD analysis of ilmenite ore from Australia showed the presence of crystalline phases: ilmenite (FeTiO<sub>3</sub>), rutile (TiO<sub>2</sub>) and pseudorutile (Fe<sub>2</sub>Ti<sub>3</sub>O<sub>9</sub>). Mössbauer spectrum of ilmenite ore at 293 K showed the superposition of three quadrupole doublets, two of them corresponding to Fe<sup>2+</sup> and Fe<sup>3+</sup> in ilmenite, whereas the third doublet was discussed in the sense of electron charge transfer mechanism. With decreasing temperature, the hyperfine magnetic splitting components appeared. Mössbauer spectrum of ilmenite ore at 18 K showed very complex nature and possible assignations are given. Copperas (FeSO<sub>4</sub>·7H<sub>2</sub>O) is waste product in the manufacture of TiO<sub>2</sub> pigment by the sulphate process. Mössbauer analysis was also used in the characterization of commercial FeSO<sub>4</sub>·7H<sub>2</sub>O (as declared) and the effect of ageing of this hydrated iron(II) sulphate. Also, Mössbauer spectroscopy was applied in the analysis of ash produced by calcination of copperas in the production of H<sub>2</sub>SO<sub>4</sub> as well as in the characterization of iron oxide pigments produced from copperas.

# Simultaneous detection of gamma radiation transmission, conversion electrons and x-rays in a single Mössbauer experimental setup

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This poster is illustrating three typical Mössbauer measurements merged into a single setup, which creates the opportunity to run them at once. The technical solution, developed at CATRIN, is based on the combination of two gas flow detectors (CEMS and CXMS) and one scintillation detector (TMS). The main advantages are experimental time savings and perfect match of the experimental results as all data are acquired with exactly the same instrument, the same source activity and thus the same experimental conditions. The poster outlines the main ideas of the technical solution as well as the experimental results.

## STATUS OF THE DEVELOPMENT OF A REPOSITORY FOR MÖSSBAUER SPECTRA

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Nowadays it is unquestioned not enough to publish only the results of investigations, but it is necessary to present also the raw data in an open-access manner together with all the information essential to reproduce the measurements. In times where papers have to be shorter and shorter, the traceability of described results often impossible. Sometimes data in supplementary appendices, but important information about how the data were gained are lacking. This information, described by so-called metadata can be a quite large data set. The way to publish all the metadata, connected to a published data set, is their storage in a repository. Such repository should fulfil the FAIR principles for data [1]: Findable, Accessible, Interoperable and Reusable. Findable and accessible means that data should be findable easy in internet and should have open access. Interoperable means that data should be compatible with similar systems. That needs use of standardized metadata which are independent of the subject. Main task is to define internal metadata which are domain relevant. These are necessary for reusability. A lot of such repositories have been created in last years for different domains, sometimes for the same subjects at different places. Up to now no such repository dedicated solely to Mössbauer spectroscopy exists. Therefore, at the meeting of the International Board of the Applications of the Mössbauer Effect (IBAME) during the International Conference on the Applications of the Mössbauer Effect 2019 (ICAME 2019) in Dalian (China) the proposal for the creation of a repository for Mössbauer measurements was discussed and by majority of the delegates supported. The initiative was based on the fact that in 2019 TU Wien started to build up a system in which individual repositories could be created in simple way. This offered the possibility to establish a Mössbauer repository without large input of money and personal resources, because programming is done by the IT group of the university. A further advantage is that the repository is not fixed to a special person. Now after some delay, due to the pandemic, the main system is ready to be use. A test repository for Mössbauer was created and in the next step the internal metadata have to be defined. Some ideas about Mössbauer specific meta data have been discussed by D. Nagy at ICAME 2021 in Brasov [2], and should be discussed in a larger group. Some ideas will be presented at the poster.

#### **References:**

- [1] https://www.go-fair.org/fair-principles/
- [2] D.L.Nagy, H.Spiering, E.Szilágyi, Book of Abstracts ICAME 2021, page 99

# STRUCTURAL AND LOCAL STUDY OF THE ALLOY AI(X)Fe(1-X) (X=0.25, 0.5 Y 0.75) OBTAINED BY ARC FURNACE

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Over the past three decades, it has provided much attention to the synthesis of nanoparticles: many routes have been developed to prepare magnetic nanoparticles well controlled. Thus, in the present work, the study structural and magnetic is carried out by X-ray diffraction and Mössbauer spectrocopy of the  $Al_xFe(1-x)$  alloy with x = 0.25, 0.5 and 0.75. Samples were synthesized by the technique arc furnace (HA) and were subsequently treated at temperatures of 600 °C, 950 °C and 1000 °C for 48, 290 and 48 hours, respectively. After the heat treatment corresponding to the temperature of 600 °C, is observed for the composition  $Al_{25}Fe_{75}$  and  $Al_{50}Fe_{50}$  ferromagnetic and paramagnetic, together to the solid solution Fe(Al) rich and poor in iron, for the composition  $Al_{75}Fe_{25}$ , the formation of the intermetallic  $Al_{13}Fe_4$  and the solid solution Fe(Al), both paramagnetic, is observed [1].

#### **References:**

1) V. A. Peña Rodríguez, J. Medina Medina, J. Quispe Marcatoma, Ch. Rojas Ayala, C. V. Landauro, E. M. Baggio-Saitovitch E. C. Passamani, Hyperfine Interact., 202, 145 (2011).

# THE INFLUENCE OF FE SPECIES FROM RED MUD ON THE MECHANICAL PROPERTIES OF GEOPOLYMER BINDER

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Bauxite residue, often called red mud, is an aluminosilicate waste material rich in iron generated in the Bayer alumina production process. Due to the high pH, which is a consequence of residual NaOH from the Bayer process, the bauxite residue proves to be a potential candidate for use in new, alternative types of mineral binders such as geopolymers. Also, this waste material is rich in Fe species (from which red colour comes) and some research indicates that Fe species ascend into Si-O-T geopolymer structure (where T = Si or Al) and replace part of  $Al^{3+}$  ions, which ultimately gives new material binders obtained by properties. Geopolymer are reacting aluminosilicate a solution of alkali oxide and/or its silicate (usually Na, K and Cs). This type of binder has a great advantage over Portland cement in terms of environmental protection and reduction of CO<sub>2</sub> emissions because it most often uses waste aluminosilicate materials, mainly fly ash and slag, and recently, for the above reasons, bauxite residue. In order to examine the influence of Fe species from red mud (bauxite residue) on the structure and properties of geopolymer, the structural characterization of the industrial waste red mud sample and prepared red mud containing geopolymer sample (composed of 20 wt.% of bauxite residue and 80 wt.% of metakaolin) was performed using XRD, SEM/EDS and <sup>57</sup>Fe Mössbauer spectroscopy. Mössbauer spectra of both samples showed the presence of a sextet with asymmetrically broadened lines, which can be attributed to the magnetically ordered Fe(III) in Al-containing hematite, and an asymmetric quadrupole doublet, which could be attributed to Fe(III) in octahedral and tetrahedral sites of aluminosilicate cancrinite and katoite detected in samples by XRD and/or to superparamagnetic Fe oxide nanoparticles. Also, the compressive strength of geopolymer paste, considered as a main engineering property of construction materials, was tested in this research.

## Mössbauer study of the stainless steel surface after annealing in the temperature range 700 - 1000 ° C

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Mössbauer conversion electron spectroscopy (CEMS) and secondary conversion X-ray spectroscopy (CXMS) were used as the main method for studying the surface of specimens made from CL20ES steel powder by selective laser melting. Other study methods were X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS).

Samples measuring 25x25x2 mm<sup>3</sup> were prepared on a Concept Laser M2-cusing system (Concept Laser, Germany). After 3D printing, the samples were sandblasted with corundum powder and annealed at 700°C - 1000°C for 0.5, 1, 2, 4, 8, 16 and 32 hours in air with the step 100°C.

The CXMS spectra (e.g., samples annealed for 0.5 hours in Fig. 1 (left)) of all samples contained only the singlet line of the corresponding austenitic stainless steel. These CXMS spectra are identical to the Mössbauer spectra of the starting metal powder (CL20ES) registered in the transmission geometry of the Mössbauer experiment. Changes related to oxidation in the surface layer with a thickness of about 0.5 µm were identified in the CEMS spectra. These changes were observed, for example, in the CEMS spectra of the annealed samples for 0.5 hours (Fig. 1(right)). Note that the CEMS spectra did not register on all samples. This is related to the diffusion of alloying elements to the surface of the samples where they oxidize. This process is associated with an affinity of the alloying elements (Cr, Mn) for oxygen that is greater than the affinity of iron for oxygen. A thin surface layer formed by oxides of alloying elements is formed. This layer prevents the exit of conversion electrons formed during deexcitation of <sup>57</sup>Fe nuclei. The passage of these electrons in the material is less than 0.5 mm and the corresponding surface layer does not contain iron. Therefore, CEMS cannot be registered. A doublet with IS = 0.33 mm/s and OS = 0.55 mm/s appears in the CEMS spectra. According to the isomeric shift, this doublet corresponds to Fe<sup>3+</sup>. Using the SEM method, it was found that a new oxide layer forms on the surface of the sample due to temperature annealing. At the same time, EDS confirmed an increase in the concentration of alloying elements (Cr and Mn). XRD identified Cr<sub>2</sub>O<sub>3</sub> and Mn<sub>2</sub>NiO<sub>4</sub> on the surface for samples annealed at 1000°C. According to the Cr in Cr<sub>2</sub>O<sub>3</sub> may be partially substituted for iron, which may the existence of a doublet (IS = 0.33 mm/s and QS = 0.55 mm/s) in the CEMS spectrum. SEM showed an inhomogeneity of the emerging surface layer, which unfortunately results in difficulties in the registration of CEMS spectra. CEMS spectra could not be recorded at all in some samples, and the shape of these spectra shows a certain chaos.

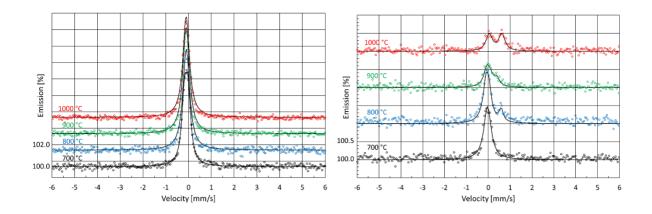


Figure 1. CXMS spectra of annealed samples for 0.5 hours at different temperatures (left) and CEMS spectra of annealed samples for 0.5 hours at different temperatures (right).

### The list of participants (alphabetical order)

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39	Mr.	Lin	Yubo	China	personal	
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### Iron Analytics Mössbauer Spectrometer

based on 30 years of experience

#### 4th Generation



#### modern instruments for modern science

What you can imagine, we can create!









### **Typical Configurations**



Transmission Setup with Sample Exchanger Sample volume investigation

#### Sample Types:

- Powder
- Thin bulk samples

#### **Conversion Setup**

Sample surface investigation

#### Sample Types:

- Thick bulk samples
- Thin layers





#### **Combined Transmission & Conversion Setup**

Simultaneous sample volume and surface investigation

#### Sample Types:

- Powder
- Thin bulk samples, thin layers

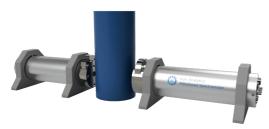
#### **High-temperature Transmission Setup**

High-temperature sample volume investigation

#### Sample Types:

- Powder
- Thin bulk samples





#### **Low-temperature Transmission setup**

Low-temperature sample volume investigation

#### Sample Types:

- Powder
- Thin bulk samples



# Components/modules

Can be tailor-made according to customer needs Can be combined with 3rd party products

### **Basic Components**

#### 4th Generation Transmission Detector

Scintillation based detector, high voltage supply, amplifiers and single-channel analyzer built-in, complete independent detection system, including spectrum registration and software (Windows OS compatible), USB control interface

#### 4th Generation Velocity Transducer

PID velocity regulator and velocity generator built-in, complete independent velocity system, including software (Windows OS compatible), USB control interface

#### Calibration and Installation Set

Dual channel oscilloscope (USB), standard aplha-Fe absorber, sample handling consumables, tools required for spectrometer installation and inspection

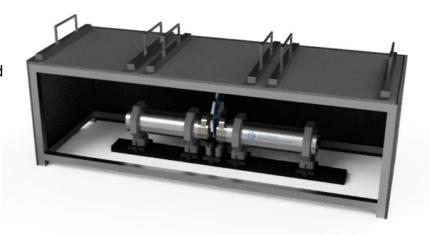
Power supply, experimental bench and PC included in complete setup

### **Optional Components**

Detector CEMS or CXMS
Sample Exchanger
Liquid Nitrogen Bath Cryostat
HT Furnace 1000°C
HT Furnace 1000°C vacuum sealed
HT Furnace 1400°C
Additional Shielding

### **Third Party Products**

- MossWinn Interpretation SW
- Radioactive source



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## References

Diferrent variants of the MS96 Mössbauer Spectrometers and/or its components have been installed at various places around the world, including both universities and scientific research centres.



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### **MAIN ADVANTAGES**

- toroidal design for almost  $2\pi$  detection
- non-destructive analyzation
- CXMS, BGMS and TMS mode
- basic shielding included
- optional choice
  - improved shielding
  - high voltage supply and preamplifier

### **CONTACTS**

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### **TECHNICAL PARAMETERS**

- dural body
- outer diameter 87 mm
- circular wolfram anode
- gas input / output connections (3 mm tube)
- SHV high voltage connector
- optimized with 90% Ar + 10% CH<sub>4</sub> mixture
- output gas pressure stabilization
- mylar windows (aluminized)

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### **MAIN ADVANTAGES**

- non-destructive nuclear analytical tool
- precise iron phases content analysis in steels
- rapid retained austenite determination
- measurement statistics enhacement
- simple geometric setup adjustment
- results without surface texture effects

### **TECHNICAL PARAMETERS**

- based on Conversion X-rays Mössbauer Spectroscopy method (CXMS)
- radioactive source <sup>57</sup>Co (max. 50 mCi)
- uses proportional gas flow counter filled with Ar + CH<sub>4</sub> mixture
- combination of lead and brass shielding
- measurement head and control box unit

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## **AMA - Advanced Materials Analytics**

Advanced Materials Analytics is a specialized laboratory focused on the analysis of nanomaterials. We make the unique analytic infrastructure and highly qualified staff of Palacký University Olomouc available for commercial partners.

Advanced Materials Analytics provides analytic services to a dozen of partners around the world, especially in the pharmaceutical industry. We also manufacture and provide our partners with specific nanomaterials, such as magnetic nanoparticles for RNA isolation, etc.

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### Available techniques

Mössbauer spectroscopy (MS)

Vibrating Sample Magnetometry (VSM/SQUID)

**Electron Paramagnetic Resonance (EPR/ESR)** 

X-Ray diffraction (XRD)

Transmission Electron Microscopy (TEM)

and many others...

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