



# ARIES 1st Annual Meeting WP3 - the Industrial and Societal Applications of Particle Accelerators New applications of low energy electron beams

This project has received funding from the European Union's Horizon 2020 Research and Innovation programme under Grant Agreement No 730871.

ANDRZEJ G. CHMIELEWSKI INSTITUTE OF NUCLEAR CHEMISTRY AND TECHNOLOGY





Riga, Latvia, May 22nd, 20178

#### Mile Stone 13



#### ARIES

Accelerator Research and Innovation for European Science and Society Horizon 2020 Research Infrastructures GA n° 730871

#### **MILESTONE REPORT**

#### **Current applications of electron beam accelerators up to 10 MeV**

#### MILESTONE: MS13

Document identifier:	ARIES-MS13
Due date of deliverable:	05 2018
Justification for delay:	-
Report release date:	25/05/2018
Work package:	WP3: Industrial and Social Applications (ISA)-NA
Lead beneficiary:	INCT
Document status:	Draft

#### ABSTRACT

Current applications of electron beam accelerators up to 10 MeV in R&D study and industrial implementation are described. Report is written to evaluate the fields of radiation technology and future prospects for accelerator technology implementation.







# TABLE OF CONTENTS

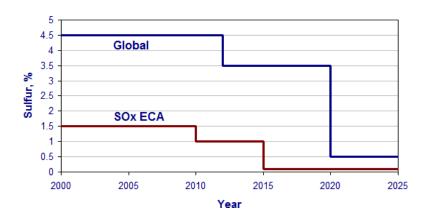
- 1. INTRDUCTION
- 2. HISTORY AND PERSPECTIVES OF PARTICLE ACCELERATORS
- 2.1. PROGRESS IN ACCELERATOR TECHNOLOGY DEVELOPMENT FOR RADIATION PRCESSING
- 2.2. CURRENT STATUS OF ACCELERATOR TECHNOLOGY
- 2.3. TRENDS IN ACCELERATOR TECHNOLOGY DEVELOPMENT
- 3. FIELDS OF RADIATION PROCESSING IMPLEMENTATION
- 3.1. CHARACTERISTIC FEATURES OF RADIATION PROCESSING
- 3.2. MATERIALS MODIFICATION
- 3.2.1. Polymers modification
- 3.2.2. Semiconductor modification
- 3.2.3. Surface curing
- 3.3. BIOLOGICAL APPLICATIONS
- 3.4. ENVIRONMENTAL APPLICATIONS
- 3.5. EMERGING TECHNOLOGY IN RADIATION PROCESSING
- 4. CONCLUSIONS
- 5. REFERENCES
- 6. GLOSSARY



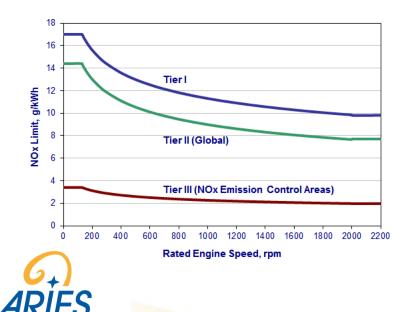


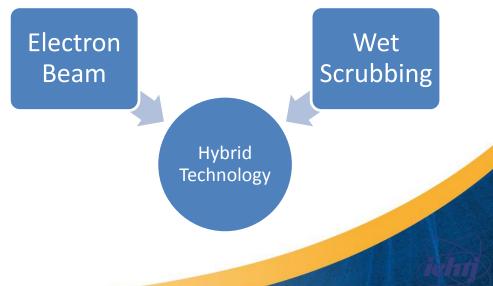
# DIESEL OFF GASES EB TREATMENT – TANGO 2 PROJECT



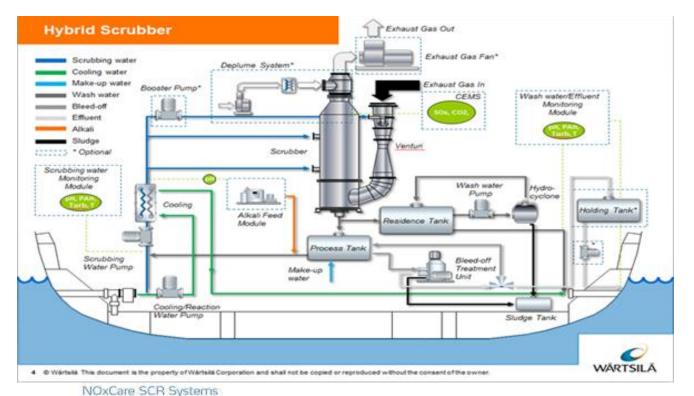


Diesel exhaust gas compositionNOx50-1500 ppmSO2Proportional to sulphur<br/>content in fuel; 500-<br/>2000 ppmHC50-500 ppmCO100-1000 ppm



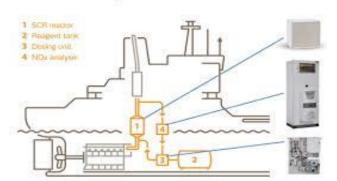


# FGD (up) + SCR (bottom)





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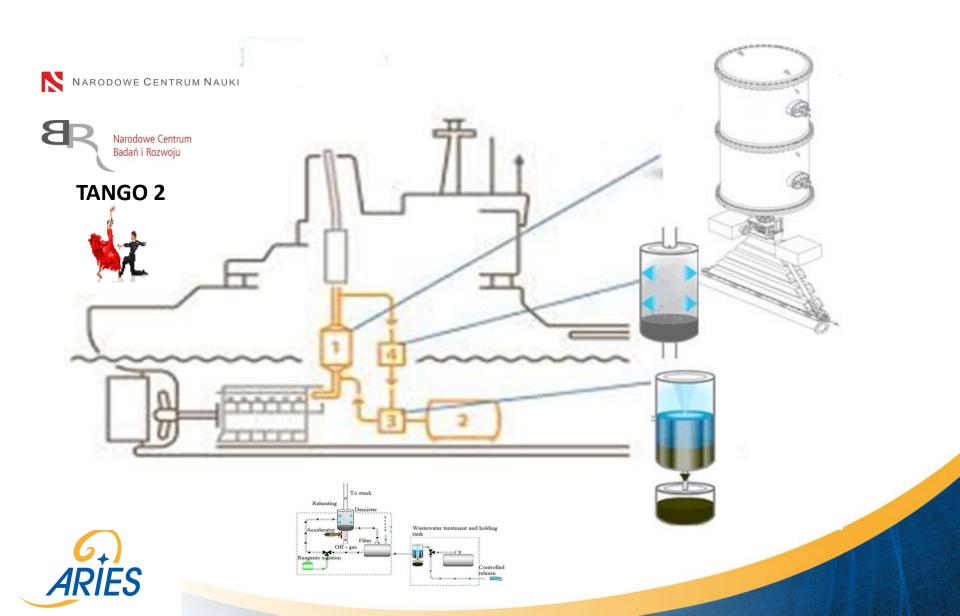








### New application of EB FGT







# Plazmowa technologia usuwania tlenków azotu z gazów spalinowych

#### Projekt: Tango 2 Numer umowy TANGO2/341079/NCBR/2017 Faza K

Kierownik Projektu: prof. dr hab. inż. Andrzej



16.05.2018 NCBiR Ewaluation



#### Experimental set up







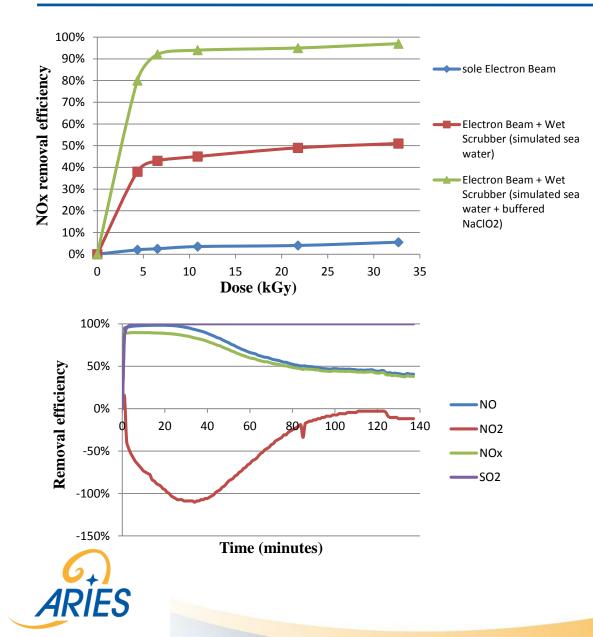


#### Analytical equipment





#### SO<sub>2</sub> and NO<sub>x</sub> removal using a hybrid electron beam technology



#### **Results:**

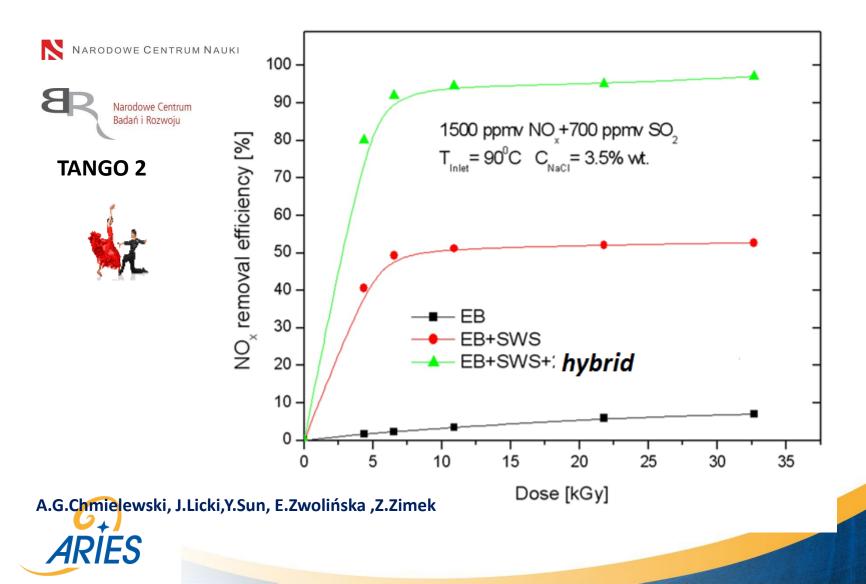
• The addition of liquid oxidant increases the removal efficiency of the NO<sub>x</sub> to over 90% (15 min experiments), which complies with the requirements imposed by the regulations

Plans:

- Reasearch on the other liquid oxidants influence
- Research on the installation configuration

<sup>•</sup> SO<sub>2</sub> removal is 100%

#### Hybrid new solution ! Futher developments underway.



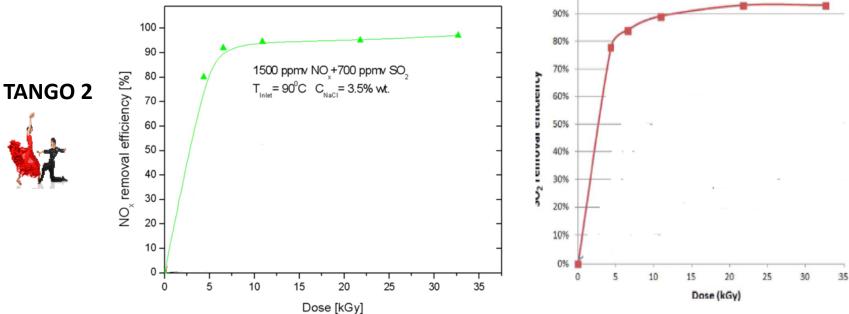
#### **Hybrid new solution ! Futher developments underway.**





R

100% 90% 80% 1500 ppmv NO<sub>x</sub>+700 ppmv SO<sub>2</sub> 70%  $T_{inlet} = 90^{\circ}C C_{NaCl} = 3.5\%$  wt. 60%





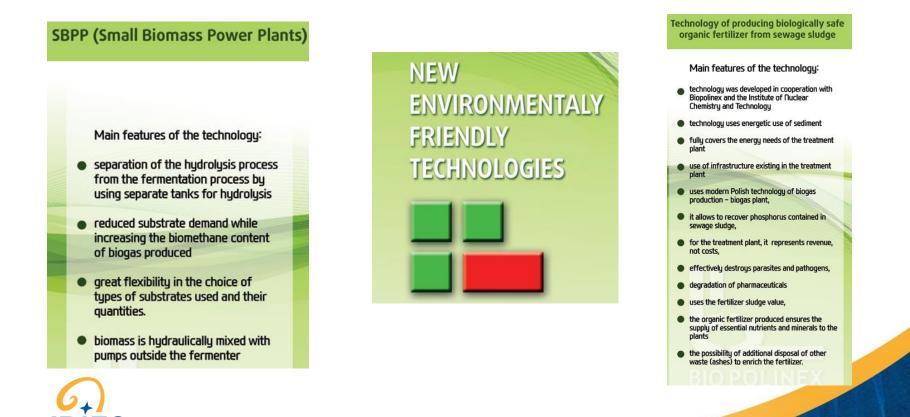
A.G.Chmielewski, J.Licki,Y.Sun, E.Zwolińska,,Z.Zimek

### Industrial partner





- Biopolinex Sp. z o. o. is building on the basis of owned patent rights, the socalled "MEB system" (small bio-methane heat and power stations) which are the perfect solution for agricultural farms, processing plants, dairies, manufacturers of pig and cattle meat as well as others with resources of biomass.
- BIOGAS POWER PLANTS; БИОГАЗОВЫЕ ЭЛЕКТРОСТАНЦИИ; BIOGAZOWNIE



1.Be Creative - a small business must always be creative, do thing differently from what others are doing. Focus on the niche marketing and stay away from the stiff competition.

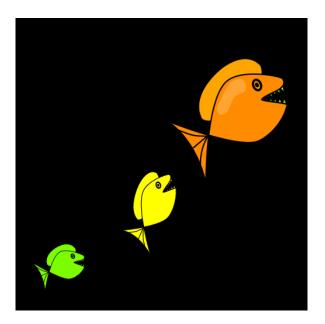
2.Be Flexible - a small business must be flexible enough to change and adapt to the business environment, flow with the trends and design a business model on what the market needs.

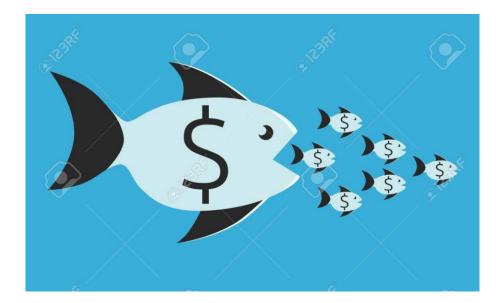
3.Be Collaborative - a small business must willing to collaborate with other small businesses, leverage our resources and work with other potential partners, only then we can grow big and strong together.

















#### Shipyard – Gdańsk



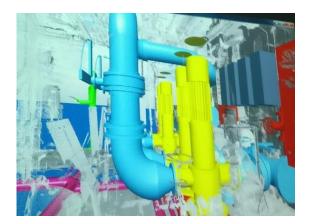


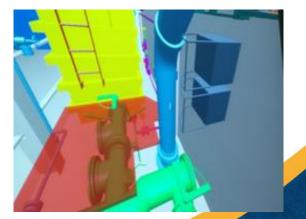
















### Meeting in Genova, Italy









Ministero delle Infrastrutture e dei Trasporti CAPITANERIA DI PORTO GENOVA

> Indirizzo p.e.c. dm.genova@pec.mit.gov.it

Indirizzo mail <u>cpgenova@mit.gov.it</u> Protocollo n. 11755 del 31 marzo 2018

16126 - Genova P.d.C:.CF Massimo Mosconi 010 2777434

A/ European Organization for Nuclear research – Organisation européenne pour la recherche nucléaire C.Att. Dr. Maurizio VRETENAR ARIES Coordinator

OGGETTO: Electron beam treatment technology for the marine diesel exhaust gases.

#### Dear Sirs,

I'm writing in my capacity of Commandant of the Italian Coast Guard Regional District in Genova, and on behalf of the Italian Coast Guard Headquarters.

As you know Italy is an IMO Member State and partner of the most important conventions and initiatives in the maritime field. The Italian Coast Guard is responsible for the preservation of the environment in the core-part of the Mediterranean Sea.

Nowadays a growing demand for a safe and sane marine environment comes from Italian citizens, especially in city-ports like Genova, where shipsourced pollution has a considerable impact on the environment and where it has to be considered together with other polluting agents coming e.g. from the industry and land transport. This cause environmental conditions trapped in a vicious circle of negative externalities which are clearly perceived by citizens and faced every day by Italian Coast Guard local Offices.

For those reasons the Italian Coast Guard strongly support all initiatives aimed at reducing pollution and ship emissions and was honoured to host the second meeting of *Electron beam treatment of marine diesel exhaust gases project* in Genova, probably the most important port in Northern Mediterranean Sea.

We are then very honoured to give our full support to this initiative, believing that developing research in this specific subject is of the utmost importance to achieving the goal of a safer and more sane marine environment.

Yours faithfully

IL COMANDANTE Amm. Isp. (Of Airota GARLONE



#### RIGATU + SHIPYARD



Riga Technical University, Reg. No. 90000068977, Kalku Street 1, Riga, LV-1658, Latvia Phone: +371 67089999, fax: +371 67089710, e-nail: fru@rtu./v, www.rtu./v Rigas Tehniskā universitāte, Reģ. Nr. 90000068977, Kaļku iela 1, Riga, LV-1658, Latvija Tālir. 67069999, faks.s 67089710, e-pasts: rtu@rtu./v, www.rtu.iv

Riga

#### TO WHOM IT MAY CONCERN

Center of High Energy Physics and Accelerator Technologies of Riga Technical University is cooperating with Riga Shipyard, which is one of the largest ship repair facilities in the Baltic States, providing dry-docking as well as afloat repairs. Shipyard is perforing conversion, modernization and refurbishment of different types of vessels. Both entities are very much interested in the system being developed by the Institute of Nuclear Chemistry and Technology, Warsaw, Poland, based on electron beam technology for marine diesel off gases treatment - which is related to the project TANGO 2 financed by the National Centre for Research and Development. Due to IMO regulation this type of installations has to be installed on the ships operating in ECA areas which include Baltic Sea and North Sea. The big advantage of the system is simultaneous removal of SO<sub>x</sub> and NO<sub>x</sub>.

Moreover, in the framework of project "Development of hybrid electron accelerator system for the treatment of marine diesel exhaust gases" foreseen after Tango 2 project realization and implementation stage, in cooperation with consortium led by Riga University, Riga Shipyard will support the onshore tests regarding accelerator integration with flue gas system on one of their off gases sources installed at Riga Shipyard, which is a needed as a step to convert the system for offshore use at the ship.

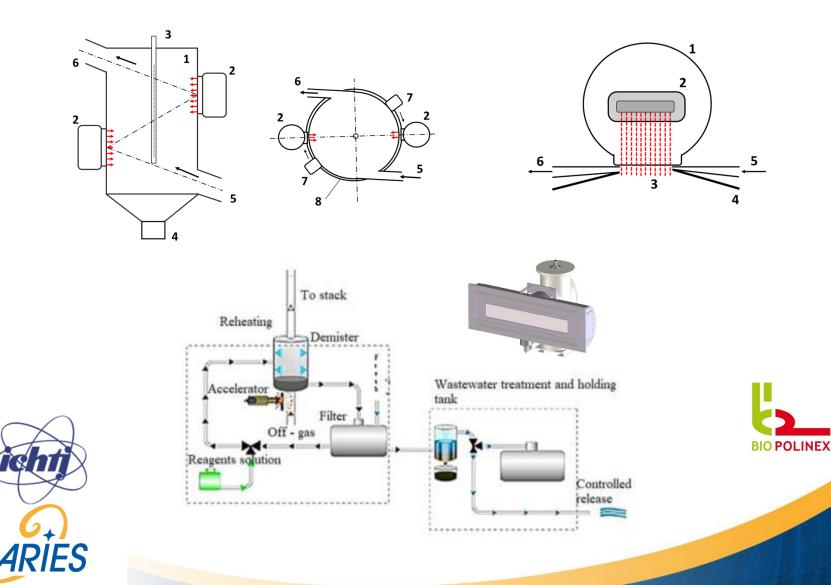
The optimization results obtained by INCT at their laboratory rig and onshore tests performed at shipyard will lead to development and upscaling of the technical installation, which after positive economic and technical evaluation, will be offered to the ship owners and installed by shipyards.



Director of the RTU Center of High Energy Physics and Accelerator Technologies Professor, Dr.Sc.Ing. Toms TORIMS



# New solutions of process chamber





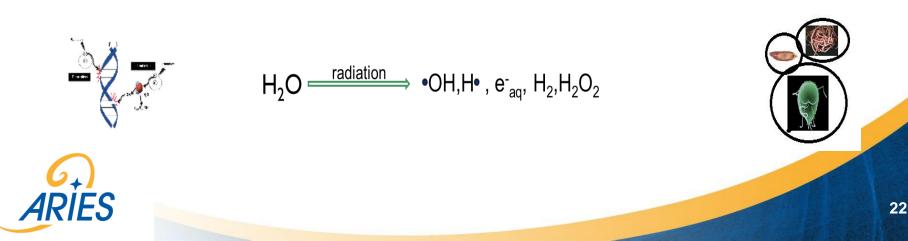
### Sludge EB Disinfection (Partly IAEA project)



# **Sludge Disinfection**

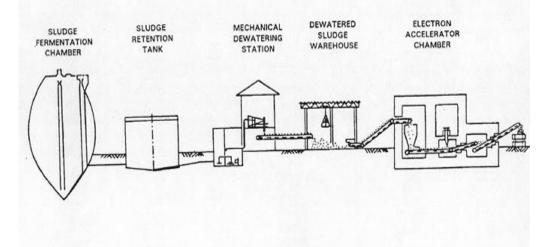


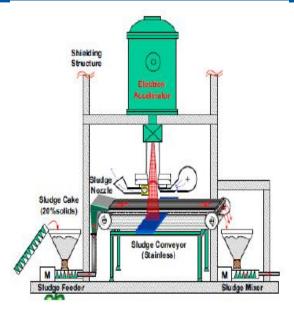
- The sludge of municipal wastewater origin is biologically contaminated by viruses, bacteria and eggs of parasites.
- Anaerobic fermentation can reduce number of pathogenic microorganisms but can't eliminate them completely.
- Dissinfection process must be applied.
- Under irradiation the decomposition of pollutants and elimination of microorganisms in water undergo due to reaction of water radiolysis products.



#### **Pilot experiments**







Bacteria	Dose [kGy] <sup>1</sup> )			
	0	5.0	6.0	7.0
Total bacteria content (in 1 ml)	1.1x10 <sup>9</sup>	2.7x10 <sup>7</sup>	6.5x10 <sup>6</sup>	1.1x10 <sup>5</sup>
Spore-forming bacteria (in 1 ml)	4.1x10 <sup>6</sup>	1.4x10 <sup>5</sup>	9.3x10 <sup>4</sup>	-
Coliform counts	10-5	10-5	10-3	10-2
Clostridium perfringens counts	10-4	10-4	10-3	10-2
6,)				
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Living eggs [	number/kg dry	matter ]
---------------	---------------	----------

Dose [kGy]	Ascaris sp. (A)	Trichuris sp. (T)	Toxocara sp. (T)	Total (ATT)
0	90	90	60	240
5.0	30	0	0	30
6.0	0	0	0	0
7.0	0	0	0	0

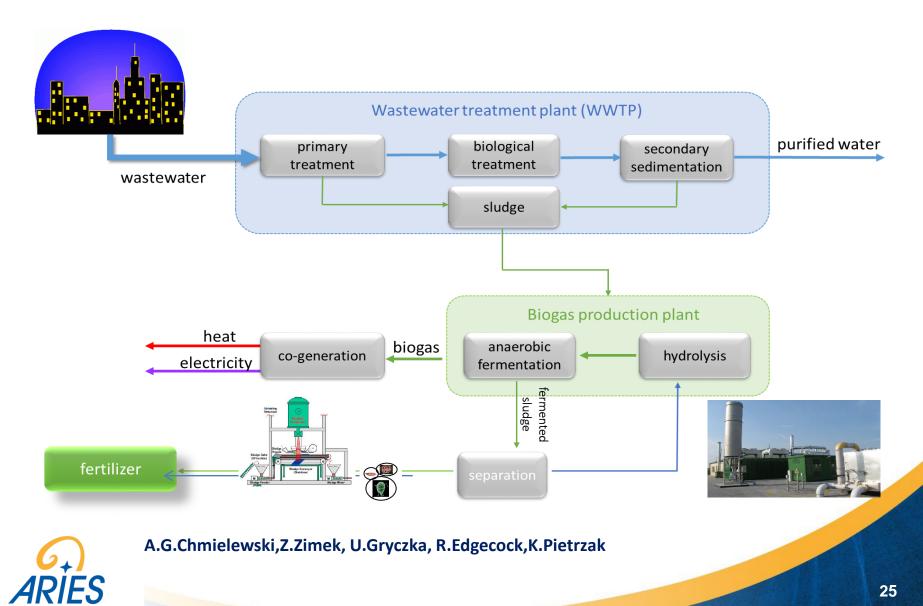
### Biogas plants – INCT experience



Participation in the design and start-up of biogas plants with capacity of 1.2 MW in Koczergi and Międzyrzec etc.



We need new solutions to preserve the environment - zero energy sludge hygenization plant!





# EB treatment of wastewater from Solvay process





### Treatment of wastewater from Solvay process

#### Problem:

 Great Solvay process disadvantage – generating of huge amounts of waste: 10m<sup>3</sup> of concentrated chloride solution and 1,7 ton of sludge per 1 ton of product – soda ash



M.Sc, eng. Marcin Sudlitz

Proposed solution:

- Sludges from proces can be used as a fertilizer – one condition: low chlorides concentration level
- Ionising radiation can be used to enchance removing chlorines from sludges obtained in process
- Irradiation cause flocculation of solid particles in suspensions increasing speed of sedimentation



Solvay wastebeds in Janikowo





# Irradiation of wastewater from Solvay process

Usefullness of processing Solvay waste using ionising radiation

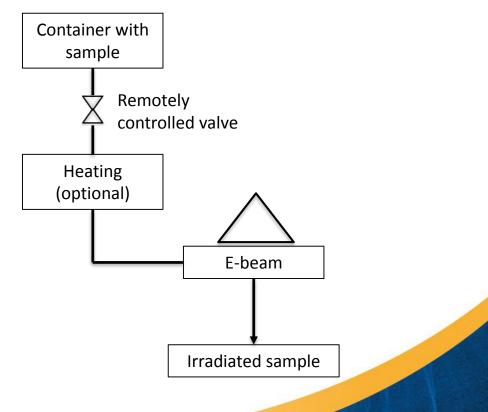
Experiments using crude brine shown distinct change in sedimentation speed of suspension obtained in brine purification process. To irradiate samples <sup>60</sup>Co source

was used. Speed of sedimentation of suspension received in crude brine purification process 1200 1000 Sludge volume [cm<sup>3</sup>] 800 600 - 2.5 kGv O kGv 400 200 0 0 20 40 <sup>60</sup> Time [min.] 100 120 140

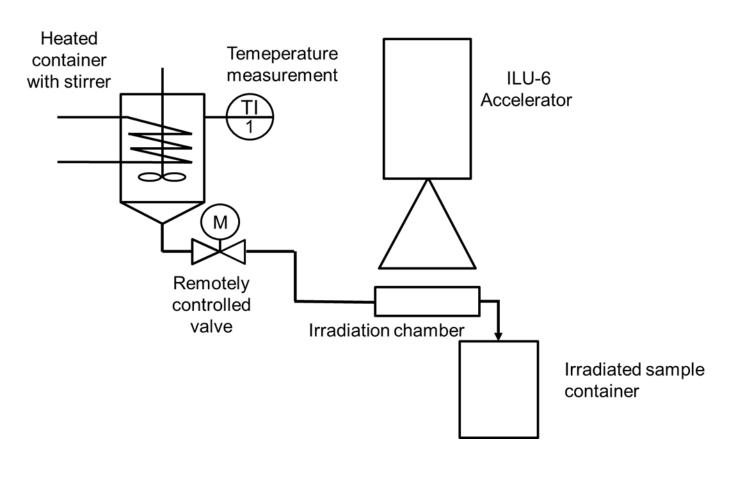
Speed of sedimentaion of irradiated brine purification suspension compared to a speed of sedimentation of non-irradiated sample. Experiment made in cooperation with Msc., P. Iwański and Msc., A. Najmrodzki from UMK, Toruń.



Small scale (about 5 dm<sup>3</sup>) installation to irradiate suspension obtained in solvay proces is in preparation. It will allow to flow irradiation of samples using electron beam.



# Laboratory scale installation for flow irradiation coupled to a ILU-6 electron accelerator









Contract with Soda Industry

Measurements of speed of sedimentation, zeta potential and microscopic observations

- using raw brine
- using postdistillation sludge

Electron accelerator and Cobalt-60 source will be used.





# Electron beam for preservation of water damaged paper (partly IAEA project)





#### Electron beam for preservation of water damaged paper

Chief scientific Investigator (IAEA)

Dagmara Chmielewska-Śmietanko •



A very good alternative to EtO fumigation (treatment of huge quantities of paper-based objects in a short time, any harmful residues)

Different kids of paper (office, Whatman)

- Comparison of two drying protocols natural air drying and lyophilization
- Dose 5 kGy (safe for paper, effective even for high level of bioburden)
- Investigation of influence of drying method, irradiation and aging on the optical, mechanical, chemical and thermal properties of the paper







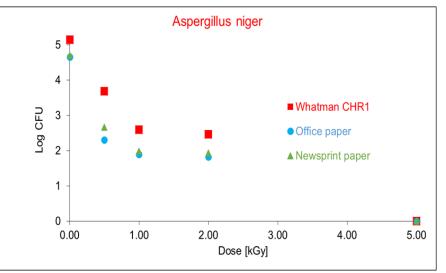


#### Electron beam for preservation of water damaged paper

A very good alternative to EtO fumigation (treatment of huge quantities of paperbased objects in a short time, any harmful residues)

#### Investigation:

- Ofiice paper moisture content:75% RH
- Comparison of two drying protocols natural air drying and freeze-drying
- Dose 5 kGy (safe for paper, effective even for high level of bioburden)



 Investigation of influence of drying method, irradiation and aging on the optical, mechanical, chemical and thermal properties of the paper according to

the relevant standards.



#### **Results:**

- Application of the freeze-drying before EB irradiation is more gentle for waterdamaged paper than application of natural air drying
- Application of natural air drying before EB irradiation has a lager effect on the tensile strength, pH and colour parameters of the office paper than application freeze-drying before EB treatment
- The calculated value of the total colour difference ΔE<sub>00</sub> for the office paper freezedried and natural air dried and irradiated with EB was lower than 1, which confirmed that for these samples colour difference can not be noticed by the observer (in comparison to the control sample)

#### Further works:

- Conduct aging and/or post irradiation long term storage effect on the properties of the materials.
- Comparison of EB treatment with EtO treatment





# DESINFECTION OF ORNAMENTAL FLOWERS BULBS LOW ENERGY EB



#### Application of low energy electron beam in elimination of plant pathogens from ornamental bulbs

- Elimination of the plant pathogens from the surface of flower bulbs:
  - to inhibit the development of the disease,
  - to reduce spread of the pathogens,
  - to prevent the loss of the plants.
  - Application of the electron beam having energy below 300 keV:
    - limited penetration of the electron beam,
    - alternative to chemical methods.



Chief scientific Investigator (IAEA) Urszula Gryczka



Different flower bulbs



Fusarium oxysporum infested flower bulb



# Application of low energy electron beam in elimination of plant pathogens

Elimination of the plant pathogens from the surface of flower bulbs:

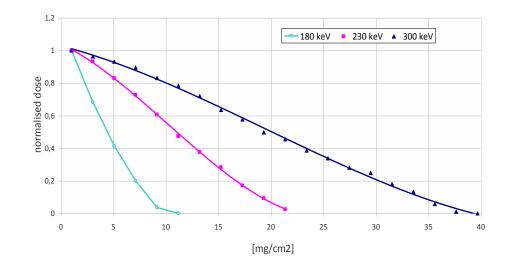
- to inhibit the development of the disease,
- to reduce spread of the pathogens,
  - to prevent the loss of the plants.

### Irradiation:

- Accelerator ILU-6
- Energy of electrons 180-300 keV
- Tulip bulbs were used for experiments



Penetration ability of electron beam



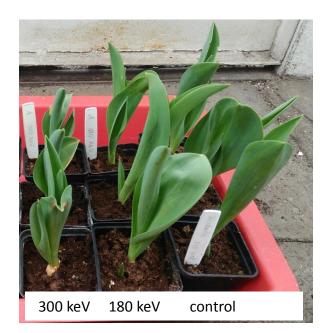


# Application of low energy electron beam in elimination of plant pathogens from ornamental bulbs

Experiments: Influence of electrons energy on growth of tulip bulbs

- Irradiation of tulip bulbs using electron beam of energy:
  - 180 keV growth was not affected by irradiation
  - 300 keV slowed growth, visible darkening on leaves





The programme of work to be performed includes:

- Irradiation of tulip bulbs harvested after flowering, to eliminate pathogens and prevent its spread during storage.
- Evaluation of the effectiveness of low energy electron beam in elimination of *Fusiarium oxysporum* from ornamental bulbs. Determination of the surface dose needed for pathogens elimination.
- Determination of the germination properties of treated bulbs.





# **POLYMER EB PROCESSING**



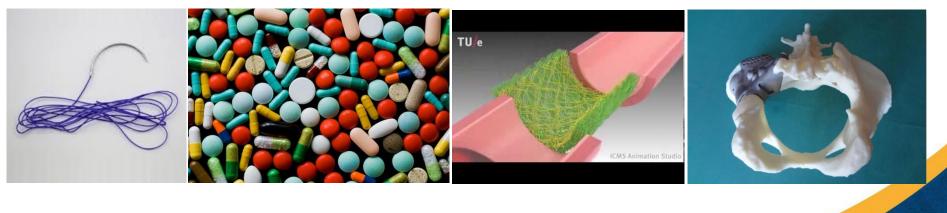
Effect of electron beam irradiation on properties of polymer materials for biomedical applications

Biomedical Applications of Biodegradable Polymers:

- microspheres and microcapsules,
- nanospheres and nanofibers for controlled release drug delivery systems,
- bones implants,
- scaffolds for tissue engineering,
- resorbable surgical sutures.



### Magdalena Rzepna







### EFFECT OF IONIZING RADIATION ON THE PROPERTIES OF PBAT

### Magdalena Rzepna, Grażyna Przybytniak, Jarosław Sadło

Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw m.rzepna@ichtj.waw.pl

Biodegradable polymeric materials are currently being investigated by numerous scientific centers. The studies are focused on the new generation of materials on the plastics market and, like traditional polymers, can be used in a variety of applications. Replacing plastics with biodegradable polymers is a response to the growing problem of post-consumer waste pollution, lack of storage space, and long-term degradation [1]. Their growing use is not only related to biodegradability, but also to their specific properties that allow new applications in the areas such as medicine, pharmacology and biomedical engineering [2,3].

The goal of the study was the evaluation of the influence of ionizing radiation on the physicochemical properties of biodegradable aliphatic-aromatic polyesters on the example of Ecoflex - a BASF commercial product made from 1,4-butanediol, adipic acid and terephthalic acid. For this purpose, the samples were exposed to high-energy electron beams produced in the Electronika 10/10 accelerator in the dose range of 10-200 kGy. At regular intervals, series of studies were conducted to determine the changes in physicochemical properties after irradiation.

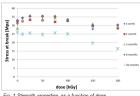
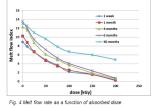
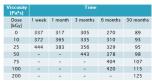


Fig. 1 Strength properties as a function of dose.





"-" viscosity value aut of range of the apparatus



European Union's Horizon 2020 Research and Innovation programme under Grant Agreement No 730871 and the Polis Science and Higher Education, project 3697/H2020/2017/2



The obtained results indicate the clear impact of radiation processes on the mechanical and thermal properties of the samples for the studied dose range. The macroscopic consequences of the processes involve crosslinking, chain scission and oxidation that influence significantly physicochemical features. The material exhibits almost of linear relationship between both the volume of hydrogen emitted and the volume of oxygen consumed as a function of absorbed dose. The crosslinking process is confirmed by decreasing melt flow index and increasing viscosity in molten state as a function of dose. Degradation of the material occurs during long-term storage process, which confirms the deterioration of mechanical properties, increase melt flow index and viscosity reduction after 30 months storage.

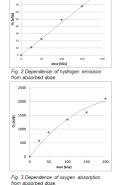
- [2] G.E. Luckachan, C.K.S. Pillai, Journal of Polymers and the Environment (2011), 19, pp. 637–676 (3) V. Ojipa, S.S. Ray, Progress in Polymer Science, (2013), 38, pp 1543–1589 (4) T. Seguchi, Nuclear Instruments and Methads in Physics Research Section B, 185, 1-4, pp. 43-49

The mechanical properties (Fig. 1) were determined using the universal strength machine, Instron 5565, according to PN-81/C-89034. The maximum stress at break for the control sample was 31 MPa. For the samples irradiated with doses lower than 50 kGv, mechanical properties were improved due to partial crosslinking of the samples.

Gas chromatography was used to determine the volume of hydrogen extracted (Fig. 2) and absorbed oxygen (Fig. 3) during irradiation. On this basis, radiation yields were estimated. Radiation yield determines the amount of chemical particles or groups that are generated or destroyed per unit of energy absorbed. The oxygen uptake efficiency G (-O2) is 0.7  $\mu mol$  / J, and G (H\_2) = 0.02  $\mu mol/J$  and the value is almost 10 times lower than for PE, what confirms the protective effect of the aromatic domains [4].

Viscosity and melt flow index were determined to investigate the rheological properties of the molten material. The table presents the results of viscosity tests made according to ISO 11-33. Viscosity increases with increasing radiation dose and decreases with time of sample storage. On the other hand, the melt flow index (Fig. 4) decreases with increasing radiation dose and increases with time

Electron paramegnetic resonance (EPR) experiments were conducted under cryogenic conditions because paramagnetic intermediates turned out to be unstable at ambient temperature (Fig. 5). The spectrum of irradiated PBAT recoded at liquid nitrogen temperature consists of dominant singlet and weak side absorptions, both sensitive to microwave power (P) changes. Traces of CH2-CH2- terminal radical are visible just at 77 K at microwave power of 10 µW in the form of weak quintet of hyperfine splitting 2.3 mT and g=2.0031. The intermediate is stable in the wide temperature range, up to 210K, when all detected paramagnetic species are converted to peroxyl radicals.



T....=77 H

P=10 uV

T....=210 K

P=10 uV

T\_\_\_=210 K

P=10 mW

335 340 Magnetic Field [mT] 345

Fig. 5 EPR spectra of PBAT

T.....=77 K



International Conference on Developments and Applications of Nuclear Technologies Kraków, 10–13 September 2017



41



"Radiation degradation and stability of PBAT - impact of aromatic and aliphatic ester segments,, M.Rzepna, G.Przybytniak, J.Sadło - accepted for publication

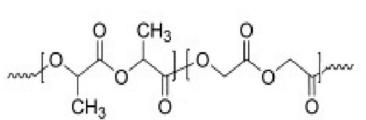
## Plans for 2018

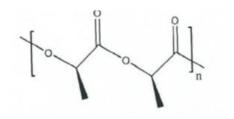
## **Tested materials**:

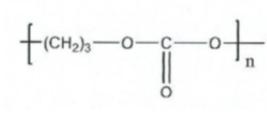
- PTMC
- copolyester PLLA 70% /TMC 30 %
- copolyester PLLA 30% /TMC 70 %
- PLLA

### Measurement methods:

- UV-Vis spectroscopy,
- EPR,
- DSC,
- TGA,
- mechanical tests,
- surface wettability,
- melt flow index,
- gas chromatography













## **Dissimination and promotion**







## Flue Gas Treatment using Industrial EB Accelerators - Status and Challenges

### Andrzej G. Chmielewski Institute of Nuclear Chemistry and Technology, Warsaw, Poland





# **DONE 2017**





- The meeting was attended by 40 people from 14 countries representing scientists working in this field, manufacturers and end users of this technology.
- With cooperation with International Atomic Energy Agency within project





### The Summer School " Advanced application of electron beam accelerators " 19-23 June 2017 in Warsaw.

- Topics: applications of the electron accelerators to the modification of polymers, environmental protection, the radiopharmaceuticals production and the food hygienization.
- The experimental part in Radiation Plant for Sterilization of Medical Devices, Laboratory of Radiation Modification of Polymers and Laboratory for Measurements of Technological Doses (INCT).
- A panel discussion on the possible applications, development perspectives and economic aspects of the technologies based on electron accelerators using.





The International Conference on Developments and Applications of Nuclear Technologies – NUTECH 2017 was held from September 10-13th in Krakow, Poland. Approximately 100 participants from 28 countries attended the conference







### Innovation for European Science and Society.





## **Radiation Sterilization School for Industry**





## **Radiation Processing of Polymers for Industry**





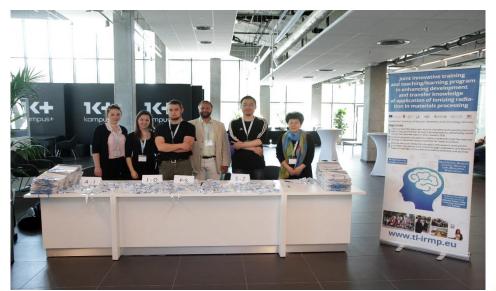


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## • Textbook " APPLICATIONS OF IONIZING RADIATION IN MATERIALS PROCESSING", Warsaw, Poland, 2017

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# **NEW TRENDS IN RADIATION** PROCESSING





International Conference on Developments and Applications of Nuclear Technologies Kraków, 10-13 September 2017



