Laboratory
SOL-GEL

Synthesis of uranium carbides doped with metal oxides using ICHTJ methods for modeling carbide fuels doped with minor actinides

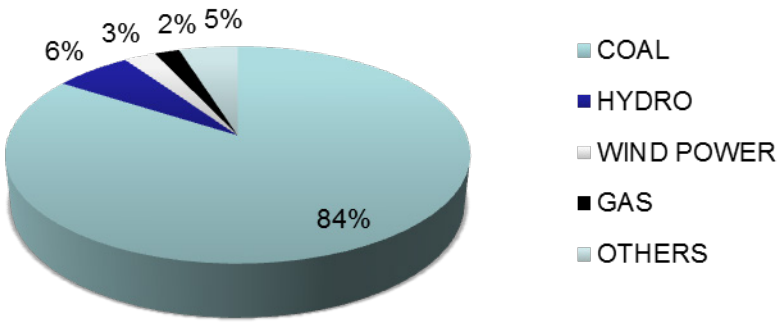
Marcin Brykala, Andrzej Deptula, Marcin Rogowski, Tomasz Smolinski, Tadeusz Olczak, Wieslawa Lada, Danuta Wawszczak

Institute of Nuclear Chemistry and Technology (INCT),
16 Dorodna Str., 03-195 Warsaw, Poland,
m.brykala@ichtj.waw.pl

Nuclear Energy in Poland

Laboratory SOL-GEL

The main sources of energy in Poland



Source: Energy Regulatorry Office

13 January 2009 - Polish Goverment signed:

„Program of development of nuclear energy in Poland"

(...)

IV Phase: 2016 - 2020: building and start-up first Nuclear Power Plant in Poland

Present Days

3 potential localization - geological analysis

INNOWACYJNA GOSPODARKA
NARODOWA STRATEGIA SPÓJNOŚCI

UNIA EUROPEJSKA
EUROPEJSKI FUNDUSZ
ROZWOJU REGIONALNEGO

Centre for Radiochemistry & Nuclear Chemistry

Laboratory
SOL-GEL

- 8 isotope laboratories II (to 10 GBq)
- 3 isotope laboratories III
- 4 chemical laboratories
- synthesis laboratory
- 8-10 analytical laboratories

New analytical equipment:

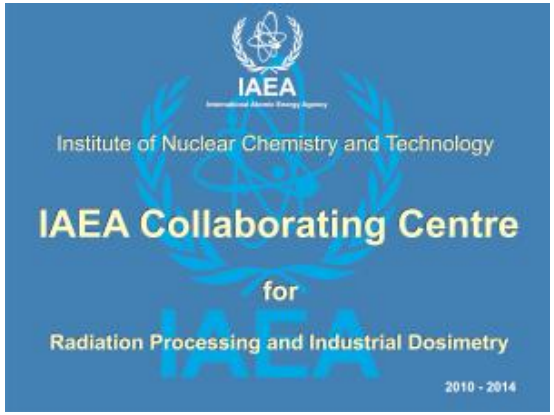
- spectrometers α, β and γ
- mass spectrometer
- X-ray spectrometer
- UV-VIS spectrometer
- Raman spectrometer
- TG-DTA analyzer
- glowboxes
- hot cell with manipulator
- VHT furnance
- dosimetry equipment

Institute of Nuclear Chemistry and Technology (INCT)

Laboratory
SOL-GEL

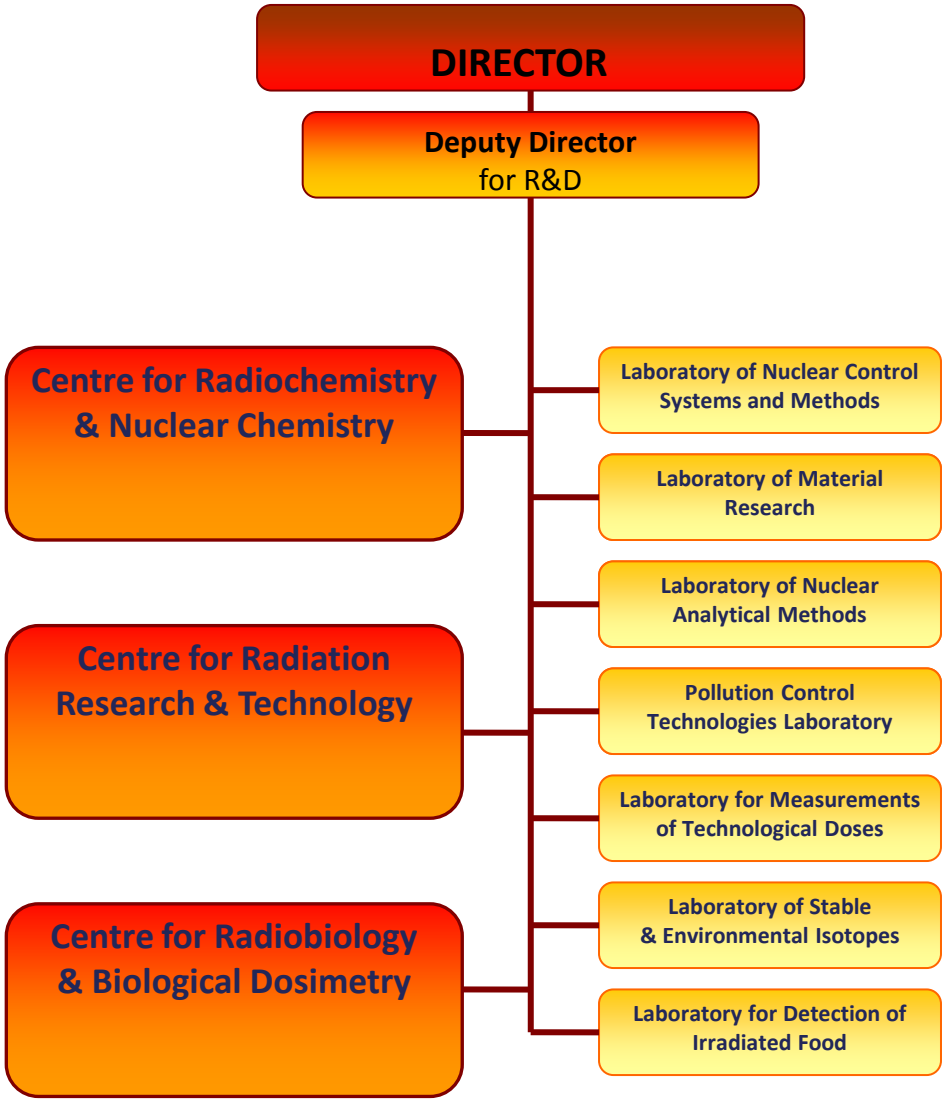
ICHTJ was a chemical division of Institute for Nuclear Research (IBJ) established in **1955** and is an **independent organization since 1983**. The basic research is focused on:

- radiochemistry,
- chemistry of isotopes,
- physical chemistry of separation processes,
- synthesis of advanced ceramic materials,
- radiation chemistry,
- radiopharmaceutical chemistry,
- cellular radiobiology.



ICHTJ is an advanced centre in radiation chemistry and technology, material and process engineering with the application of nuclear methods, radioanalytical techniques, design and production of instruments based on nuclear techniques, and in environmental research. The **ICHTJ was nominated Collaborating Centre on Radiation Processing and Industrial Dosimetry by IAEA for years 2010-2014**.

Laboratory
SOL-GEL



Staff

Total: 250

23 Prof.

50 PhDs.

80 MSs.

International PhD Studies

Laboratory
SOL-GEL

Inauguration - 1994

Number of participants – around 70

Actually – 26 students
(8 new in 2012)

Foreign students from China, France, Italy, Iraq, Egypt and Vietnam

PhD students graduated:
Warsaw University, Warsaw Technical University, Wrocław Technical University, Wrocław University, Poznań University, Podlaski University (Siedlce), Jan Długosz Academy (Częstochowa), Jagielonian University (Kraków), UMSC Lublin, Silesian Technical University, Białystok University

International PhD Studies

Laboratory SOL-GEL

PhD thesis focused on

- chemical aspects of nuclear energetic,
- fundamental problems of nuclear chemistry,
- application of nuclear techniques in industry, ecology and protection of historical heritage,
- radiopharmaceutical chemistry.

International cooperation of PhD studies

- IAEA fellowships
- Program Educators
- training programs – workshops, summer schools eg. TALISMAN
- EU Marie Currie Programs Transfer of Knowledge

Projects

Laboratory
SOL-GEL

This work is a part of studies of Polish Governmental Project "Technology Supporting Development of Safe Nuclear Power," (SP/J/4/143 321/11), part "Development of Techniques and Technologies Supporting Management of Spent Nuclear Fuel and Radioactive Waste".

Outline

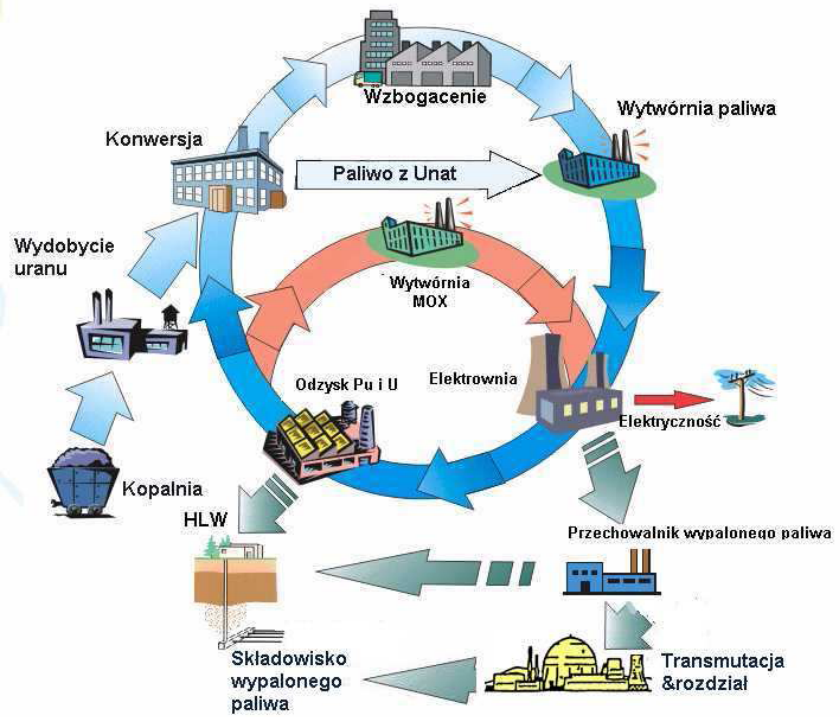
Laboratory
SOL-GEL

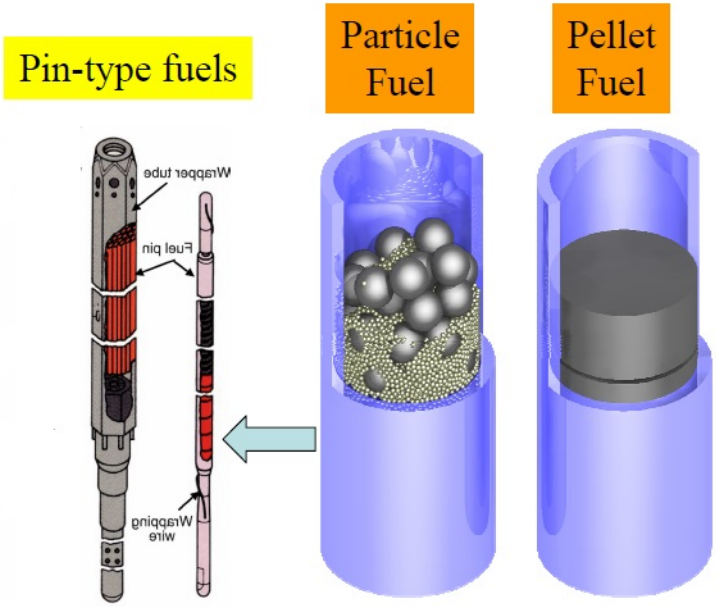
1. The main aim of work;
2. Short introduction – carbide nuclear fuel;
3. Complex Sol-Gel Process (CSGP);
4. Actualy results of synthesis of $U_{1-x}(Nd_x)C$ by CSGP:
   - ICHTJ Process;
   - Double Extraction Process;
   - Internal Gelation;
5. Summary.

The main aim of the work

Laboratory
SOL-GEL

1. Elaborated of method synthesis of precursors of carbides nuclear fuels e.g. uranium carbide, also with posibilities of doped by other elements, like minor actinides.
– Nd – surogate of americium (III) – ^{241}Am.





2. Synthesis of uranium carbide in different shapes:
- irregular particles,
- spherical particles (Ø < 100 μm),
- kernels (Ø > 400 μm).

Uranium Carbide as Nuclear Fuel

Laboratory SOL-GEL

Fuels for Nuclear Reactors IV Generations

Reactor Type	Acronym	Neutron Spectrum	Temp (°C)	Fuel	Fuel Cycle	Size (MWe)
Gas-Cooled Fast Reactor	**GFR**	Fast	850	UO_2, UN, UC	closed, on site	288
Lead-Cooled Fast Reactor	**LFR**	Fast	550-800	UO_2, UN, UC	closed, regional	50-150
Molten Salt Reactors	**MSR**	Epithermal	700-800	UF_4 in salt	closed	1000
Sodium-Cooled Fast Reactors	**SFR**	Fast	550	UO_2, UN, UC	closed	150-500
Supercritical-Cooled Fast Reactors	**SCWR**	Thermal or Fast	510-550	UO_2	open, thermal	1500
Very High-Temperature Gas Reactors	**VHTR**	Thermal	1000	UO_2	open	250-600

U.S.D.O.E., "The U.S. Generation IV Fast Reactor Strategy," U.S. Department of Energy Office of Nuclear Energy 2006.

U.S.D.O.E., "A Technology Roadmap for Generation IV Nuclear Energy Systems," U.S. Department of Energy Research Advisory Committee 2002.

Fuel	$(U,Pu)O_2$	$(U,Pu)C$	$(U,Pu)N$	UPuZr
Density ($g.cm^{-3}$)	11.0	13.6	14.3	15.6
Density of fissile atoms ($g.cm^{-3}$)	9.7	12.9	13.5	14
Melting Point Liquidus (°C) Solidus (°C)	 2775 2740	 2480 2325	 2780 2720	 1160
Thermal conductivity (1000°C, $W.m^{-1}.K^{-1}$)	2.9	19.6	19.8	35
Thermal expansion between 20°C and 1000°C (10^{-6}/°C)	12.6	12.4	10.0	16.5
Water compatibility	+ +	-	-	- - -
Sodium compatibility	-	+	+	+

Compilation by courtesy of Jérémy Caruso, 2010.

Industrial synthesis of uranium carbide

$$U + CH_4 \xrightarrow{625\text{-}900°C} UC + 2H_2$$

$$U + C \xrightarrow{2100°C} UC$$

$$U_3O_8 + 11C \xrightarrow{1800°C} 3UC + 8CO$$

$$UO_2 + 3C \xrightarrow{1500\text{-}1750°C} UC + 2CO$$

Advantages:

- high thermal conductivity;
- high density of fissile materials;
- radiation resistance;
- high temperature resistance;

Disadvantages:

- higher swelling ratio: reactive with water;
- less experience on the cycle of the fuel and radiation research;

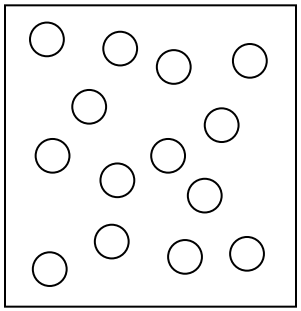
Complex Sol-Gel Process (CSGP)

Proces has been patented - Polish Patent No 172618, June 1997

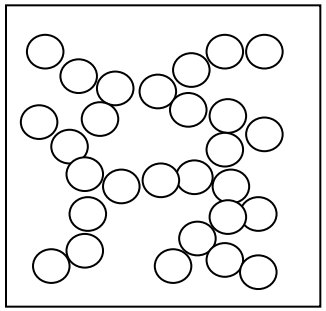
Complex Sol-Gel Process (CSGP)

Laboratory SOL-GEL

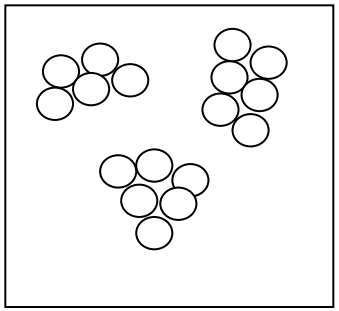
- preparation of starting metal salts solution;
- addition of ascorbic acid;
- formation of complex sol solution;
- partial hydrolysis by addition of ammonia aq.;
- evaporation to desired viscosity;
- drying and final thermal treatment.



sol



gel



final product

Prepared with CSGP (1):

Laboratory
SOL-GEL

- **YBCO, BSCCO** families - high temperature superconductors
- **$Ca_{10}(PO_4)_6(OH)_2$** - hydroxyapatite - bioceramics materials
- **$LiMn_2O_4$, $LiNi_{0.5}Co_{0.5}O_2$** - positive electrode materials in high-energy-density lithium and lithium-ion batteries
- **Li_2TiO_3** - unique Tritium breeding blanket for Fusion Reactors
- **$LiCoO_2$, $LiMg_{0.05}Co_{0.95}O_2$** – thin films on porous Ni/NiO cathodes for MCFC
- **TiO_2, $(Ba,Sr,Ca)TiO_3$** – powders, thin films, microspheres
- **$KY(WO_4)_2$, $KY(WO_4)_2$ + 1% mol Yb** – laser crystals
- **TiO_2-WO_3, ZrO_2-WO_3, ZrO_2-SiO_2-WO_3** – materials for W-188/Re-188 generator columns

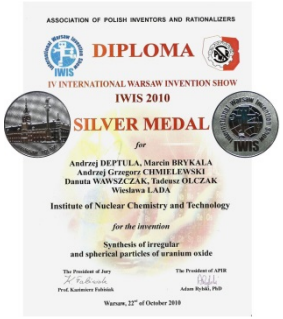
- 11 Polish Patents (5 Pending)
- 27 Awards

Prepared with CSGP (2):

Laboratory
SOL-GEL

Nuclear Applications

- **UO_2, UC particles, powders** – precursors of nuclear fuels;
- **ThO_2 particles, powders** – precursors fertile nuclear fuels;
- **$U_{1-x}MA_xO_2$ particles, powders** - matrix for transmutation of Minor Actinides (MA) – $x_{max} = 0,4$;
- **$Zr_{1-x}MA_xO_2$ particles, powders** – inert matrix for transmutation of Minor Actinides (MA) – $x_{max} = 0,2$;
- **TiO_2 based Synroc -** ceramic matrix for immobilization radioactive elements
- **SiO_2 glasses -** matrix for immobilization radioactive waste


ASSOCIATION OF POLISH INVENTORS AND RATIONALIZERS
DIPLOMA
IV INTERNATIONAL WARSAW INVENTION SHOW
IWIS 2010
SILVER MEDAL
for
Andrzej DEPTULA, Marcin BRYKALA
Andrzej Grzegorz CHMIELEWSKI
Danuta WAWSZCZAK, Tadeusz OLCZAK
Wiesława LADA
Institute of Nuclear Chemistry and Technology
for the invention
Synthesis of irregular
and spherical particles of uranium oxide
The President of Jury
Prof. Kazimierz Fabisiak
The President of APIR
Adam Rybak, PhD
Warsaw, 22nd of October 2010

- 2 Belarus Patents
- 12 Pendings (Poland, EU, Ukraine, Russia)
- 6 Awards

DIPLOMA
Eureka!
THE BELGIAN AND INTERNATIONAL TRADE FAIR
FOR TECHNOLOGICAL INNOVATION
A. Deptula, H. Brykala, W. Lada, D.
Wawszczak, Tadeusz Olczak, A. G. Chmielewski
Institute of Nuclear Chemistry & Technology
Synthesis of irregular and spherical particles of
uranium oxide
Silver medal
THE PRESIDENT OF
THE INTERNATIONAL JURY
THE PRESIDENT
Brussels, 20th November 2010

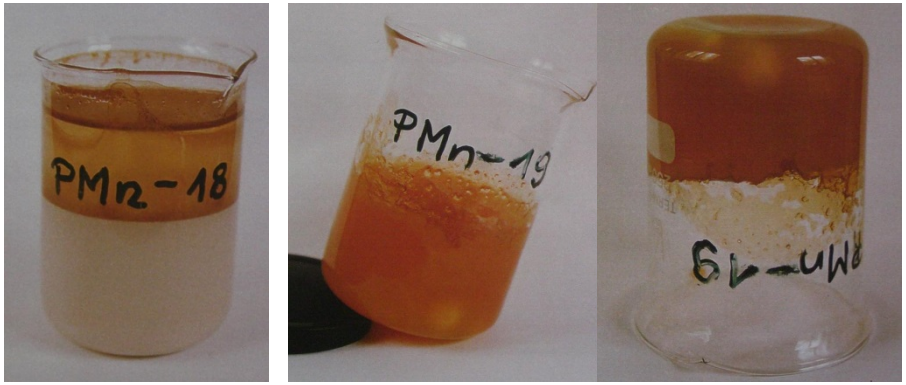
Characterization - Advantages:

Laboratory
SOL-GEL

+ a high degree of amorphicity of the starting gels joined with homogeneous distribution of the components;

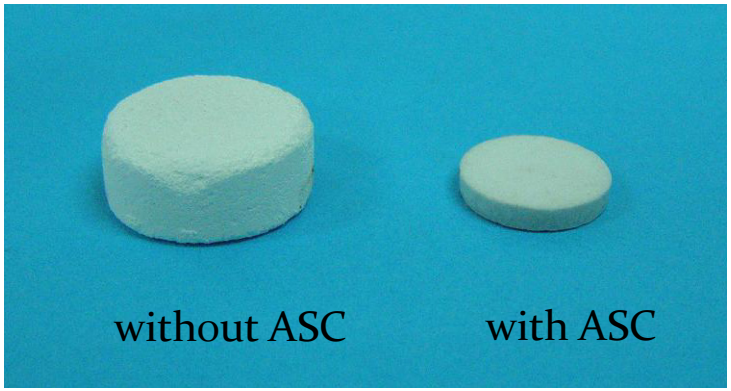
+ strong bonds in the network of the gels retarding premature crystallization of individual components;

+ high wettability of sols to metallic supports;



without ASC with ASC

Complex sols of compounds Li-Mn (without and with addition of ASC) with ammonia.



YAG ($Y_3Al_5O_{12}$) sintered in 1750°C/ 6h (ITME)

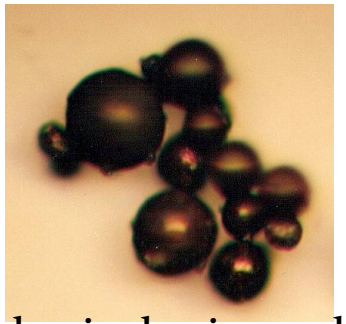
+ high adherence of the coatings after the thermal treatment, to metal substrates;

+ high sinterability of materials;

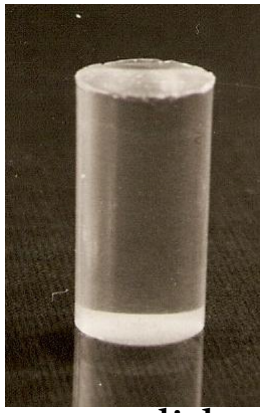
Characterization - Advantages:

Laboratory SOL-GEL

+ various shapes of CSGP products



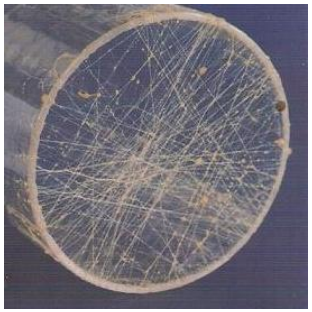
spherical microspheres



monoliths

irregular shaped powders

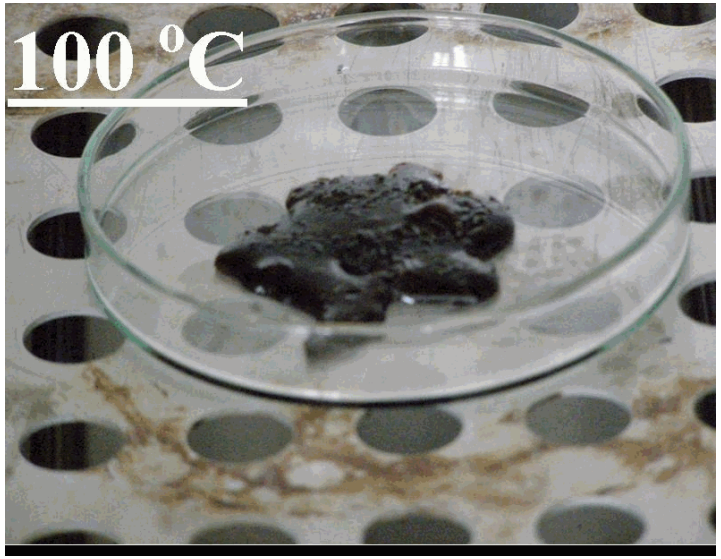
coatings



fibers

Characterization - Disadvantages:

Laboratory SOL-GEL



- sometimes foaming;

- sometimes formation of the carbonates;

+/- possibility of metallic cation reduction by organic additives;

Laboratory
SOL-GEL

Synthesis of uranium carbides doped by metal oxide by Complex Sol-Gel Processes (CSGP)

I. Preparation of ascorbate - uranyl sols solution (with ASC, C, Nd and NH_4OH.);
II. Gelation of complex sols to gels in various shapes;
III. Thermal treatment of gels to uranium-neodymium carbide.

The genesis of this work:

Synthesis of uranium dioxides particles, doped with MA surrogates by Complex Sol-Gel Process (CSGP)

This work was part of the Seventh Framework Programme, and project is called **A**ctinide re**C**ycling by **SEP**aration and **T**ransmutation, in shortcut ACSEPT (No project FP7-CP-2007-211267)

Preparation of uranyl sols solutions

Laboratory
SOL-GEL

uranyl-neodymium nitrate
Nd:U=1-20%

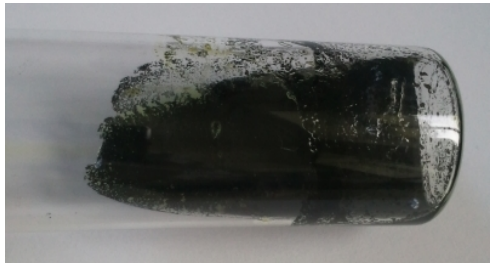
ascorbic acid (ASC) → blending
$MR_{ASC/U}$= 1

amorphous carbon → dispersion
$MR_{C/U}$= 0,5-3

ammonium hydroxide → pre-neutralization
pH~ 4-5

ascorbate-uranyl sol + carbon
[ASC-U(Nd) + C]

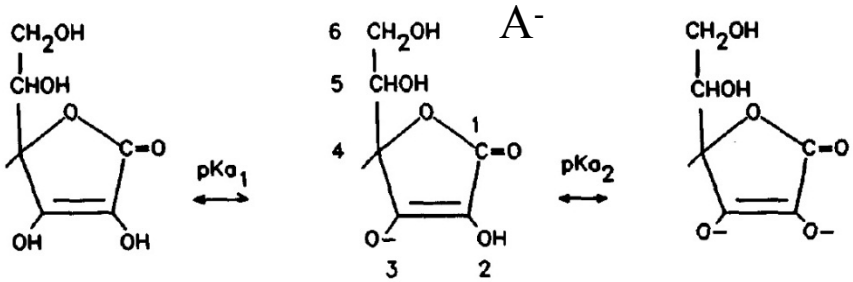
sol U-ASC + C



sol U + C

Reactions:

Deprotonation:



C(3) pK1 = 4,04 (25ºC) and C(2) pK2 = 11,34 (25ºC)

Complexation:

$$\mathbf{UO_2^{2+} + HA_{aq} \rightarrow UO_2A^+}$$

- MR ASC/U=1
  - stable to pH ~ 4-4.5
  - for pH>6 formation of $[UO_2A(OH)_2]NH_4$
- MR ASC/U=2 formation of $[UO_2A_2]$
- MR ASC/U=3 formation of $[UO_2A_3]^-$

Preparation of gels in various shapes

Laboratory SOL-GEL

irregular agglomerates

ascorbate-uranyl (+ C) sol solution

↓

evaporation of water

↓

drying

↓

grinding

↓

ascorbate-uranyl (+ C) gel

Preparation of gels in various shapes

Laboratory SOL-GEL

ICHTJ Process

spherical particles (Ø below 100μm)

ascorbate-uranyl (+ C) sol solution

↓

formation of sol's drops in dewatered 2-ethylhexanol with SPAN-80

↓

gelation by extraction of water with 2EH

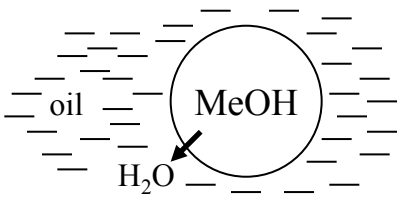
↓

filtration and washing with acetone

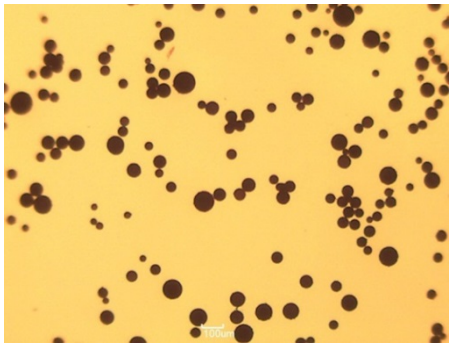
↓

spherical ascorbate-uranyl(+ C) gels

Water Extraction



(ORNL Process)

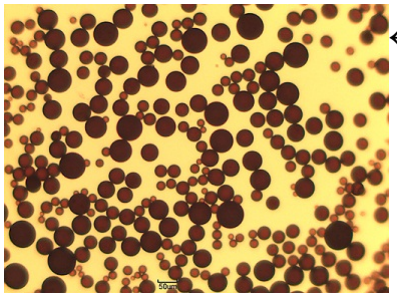


ICHTJ Process

Laboratory
SOL-GEL

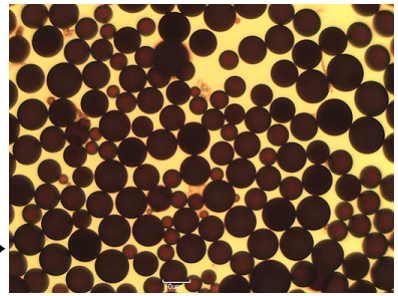
Characterization of ICHTJ Process

- dose rate;
- Ø syringe;



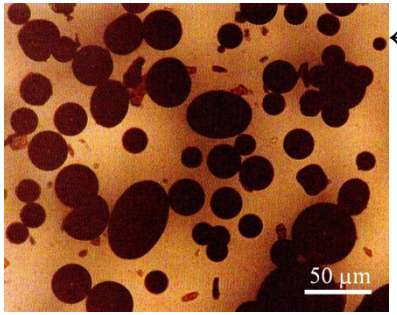
← 0,1 ml/min

0,7 ml/min →



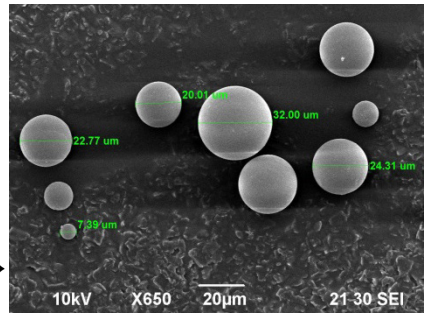
uranyl-ascorbate gel

- mixing speed;
- type of mixer;

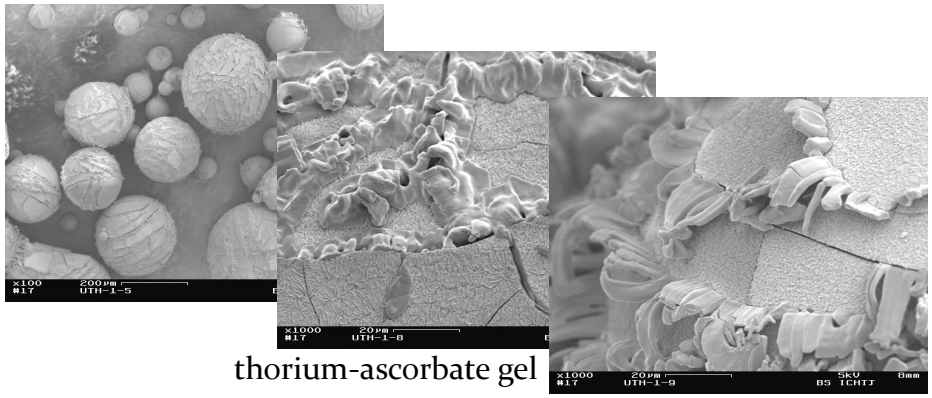


← 600 obr/min

1000 obr/min →



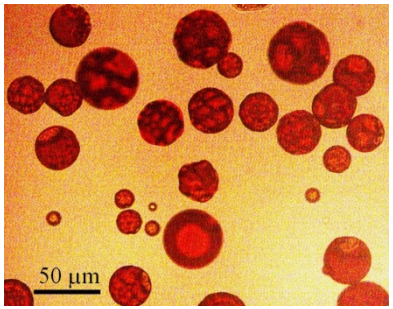
- size of spherical particles;



thorium-ascorbate gel

ICHTJ Process

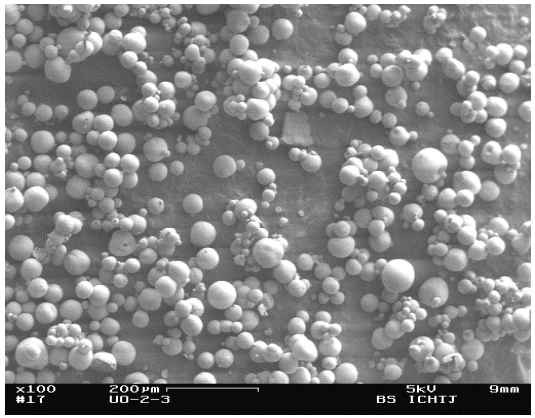
Laboratory
SOL-GEL



without NH_4OH

- **pH;**
- **viscosity;**

pH > 4,5 (see pH=8.29)



- volume and yield of 2EH and SPAN-80;

Problem with uranyl nitrate ??

Laboratory
SOL-GEL

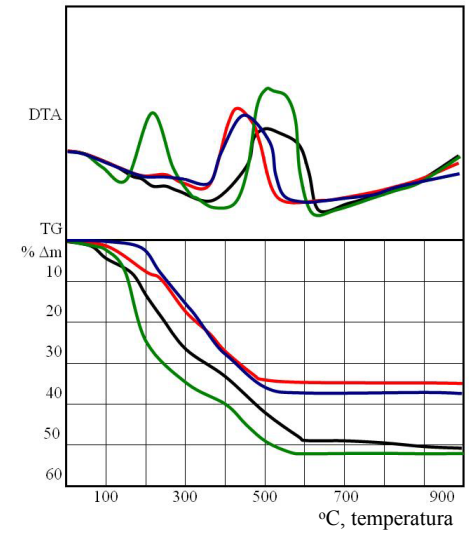
uranyl nitrate

ascorbic acid (ASC) → blending
MR ASC/U = 2

ammonium hydroxide → pre-neutralization
up to pH 4-6

ascorbate-uranyl sol solutions

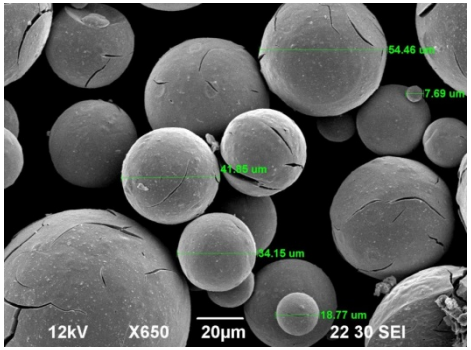
Thermal analysis (TG, DTA)



- from uranium trioxide (microspheres)
- from uranium trioxide (agglomerates)
- from ADU (microspheres)
- from uranyl nitrate (microspheres)

During of thermal treatment

Decomposition of ammonium nitrate
170°C - 250°C



Preparation of gels in various shapes

Laboratory SOL-GEL

Double Extraction Process

uranyl nitrate
$UO_2(NO_3)_2 \cdot 6H_2O$

mixing

ASC + C

ammonia aq

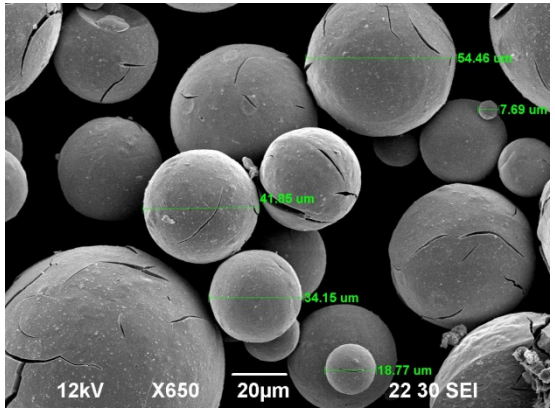
ascorbate – uranyl sol

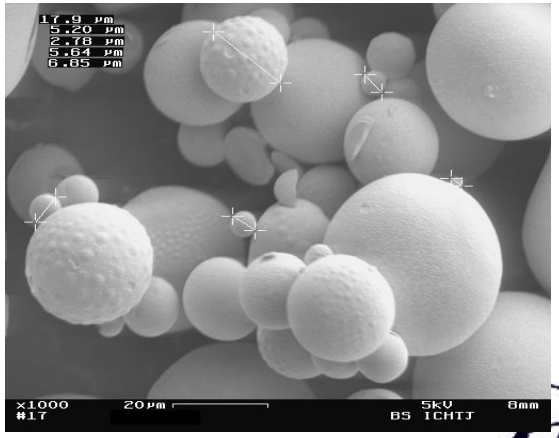
formation of sol's drops in dewatered 2-ethylhexanol with SPAN-80 (2EH)

addition of 2v/o Primene JMT ($C_{18}H_{37}N_2$)

gelation by extraction of water with 2EH and nitrate with Primene JMT

ascorbate – uranyl gel
(spherical particles with ø >100μm)



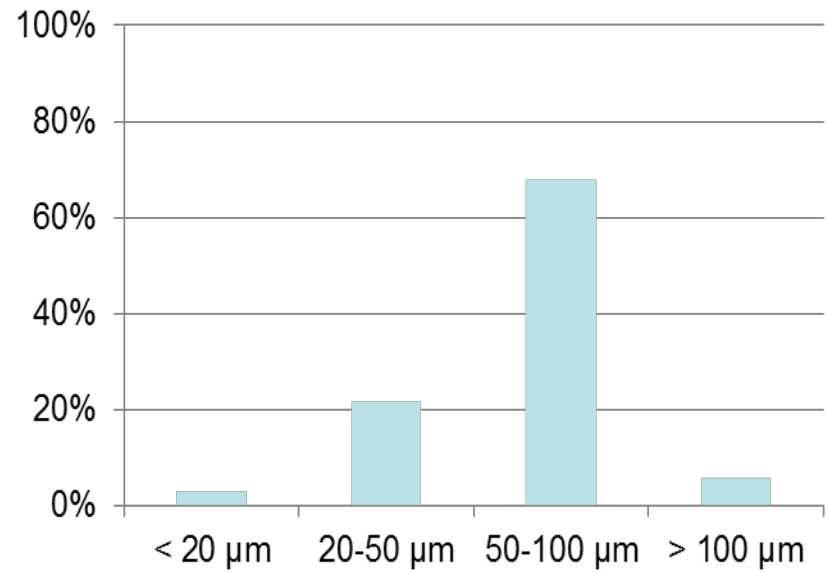


Optimal Gelation Process

Laboratory
SOL-GEL

Parameters of gelation process	
MR sol/2EH	1:70
gelation mixture	2-ethylohxanol + SPAN-80 + Primene JMT
diameter of syringe	0.4-0.5 mm
dose rate	0.2-0.5 ml/min
mixing speed	800 rpm
gelation time	1h

Particle Size Analysis



Preparation of gels in various shapes

Laboratory
SOL-GEL

kernels (Ø above 400µm)

Internal Gelation (KEMA Process)

ascorbate-uranyl (+ C) sol solution

HMTA → Mixing

↓

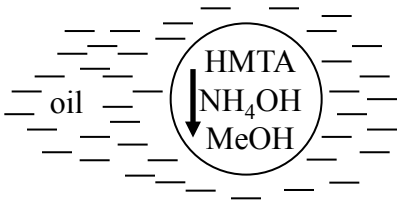
formation of sol's drops in hot silicon oil

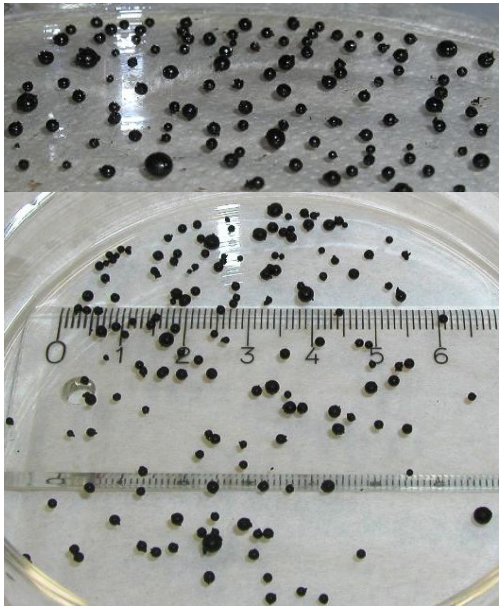
↓

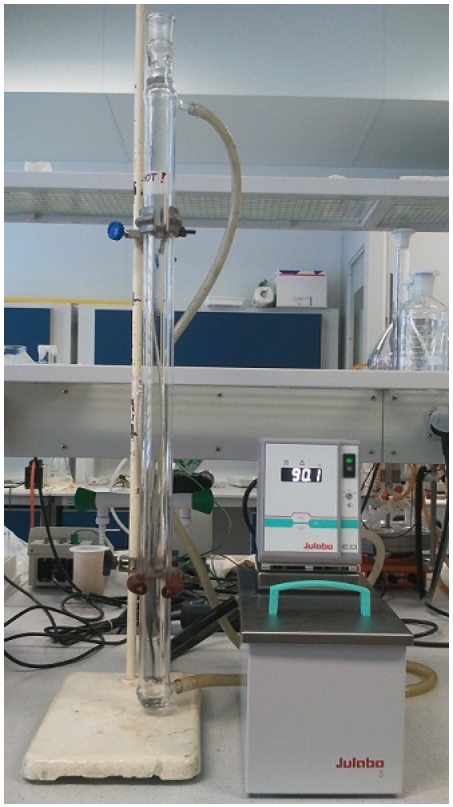
filtration and washing with petroleum ether, dryling on air

↓

spherical ascorbate-uranyl (+ C) gels



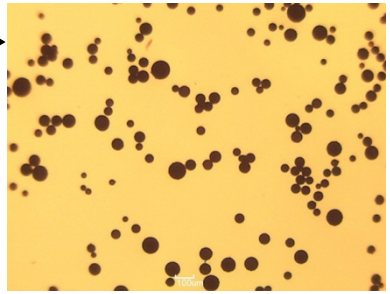




Thermal treatment

Laboratory
SOL-GEL

spherical ascorbate-uranyl (+ C) gels

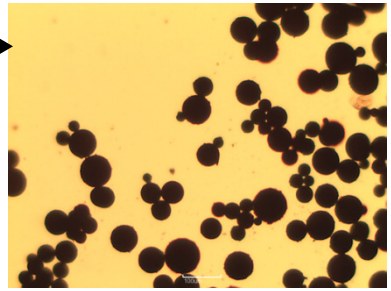


↓

drying in vacuum (250°C/2h)

↓

thermal decomposition (gas atmosphere N_2+H_2) of gels to homogeneous mixture $UO_{2.x}$-C 2°C/900°C/2h



↓

carbothermic reaction T=1800°C in vacuum

↓

spherical $U_{1-x}(Nd_x)C$

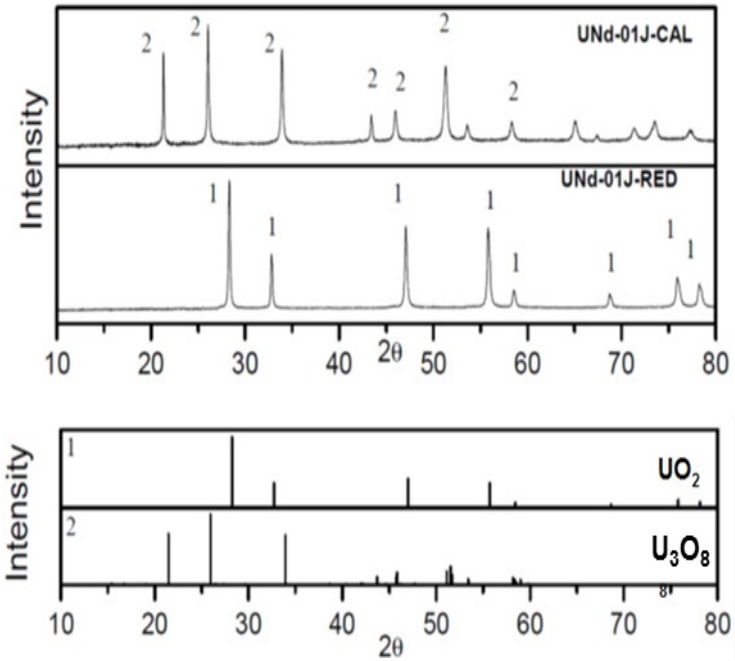
Hightemperature of vacuum furnance
Nabertherm type VHT

The works are still going !!!

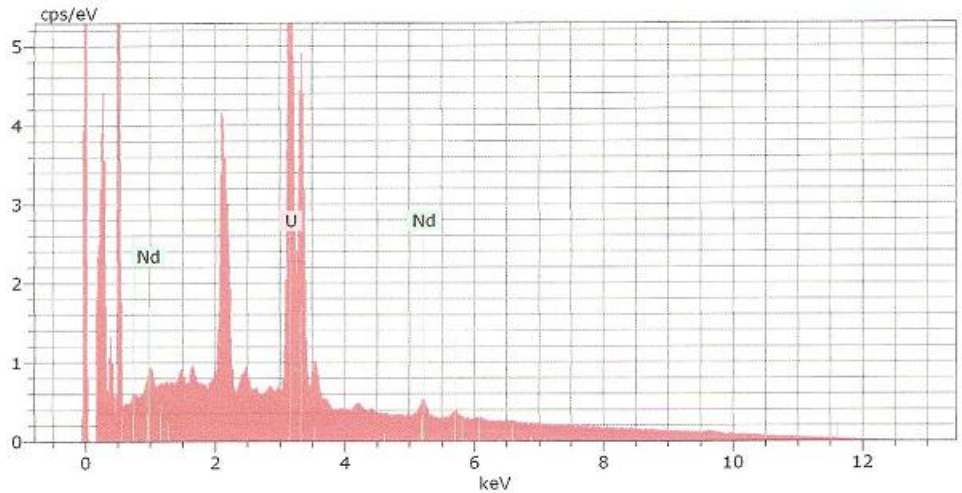
What we expect ???

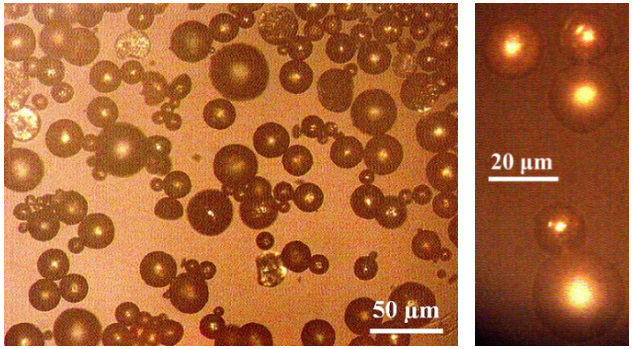
Laboratory
SOL-GEL

Thermal treatment of ASC-$U_{0.9}(Nd_{0.1})$ gels with reduction to $U_{0.9}Nd_{0.1}O_2$



X-ray spectrometry – EDS with Quantax 400 (Bruker, Germany)





Summary

Laboratory
SOL-GEL

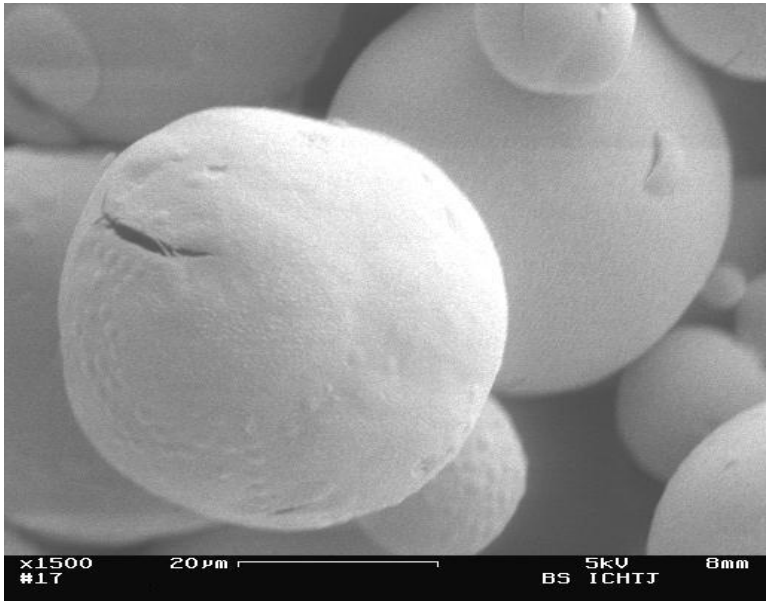
1. Complex Sol-Gel Process can be successfully applied to a preparation of homogeneous sols using complexation with ascorbic acid of various uranyl substrates (uranium trioxide, ammonium poliuranates, uranyl nitrate) containing carbon;

2. Gels contain of carbon have been obtained in shapes:
   - irregular agglomerates;
   - medium sized microspheres (diameter <100 μm);
   - kernels (diameter > 400 μm).

3. Special procedures for non-destructive thermal treatment of spherical gels to carbides are necessary.

4. The combination methods – CSGP with different gelation process - is characterized by high versatility for use to the synthesis of differents types of spherical ceramic nuclear fuel.

Spherical particles of ASC-U(Nd)-C with Vitaminium C



Thank you for your attention !!!!