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Experimental checking and justification of pyrochemical origin plutonium dioxide application for pellet MOX-fuel fabrication

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Experimental checking and justification of pyrochemical origin plutonium dioxide application for pellet MOX-fuel fabrication

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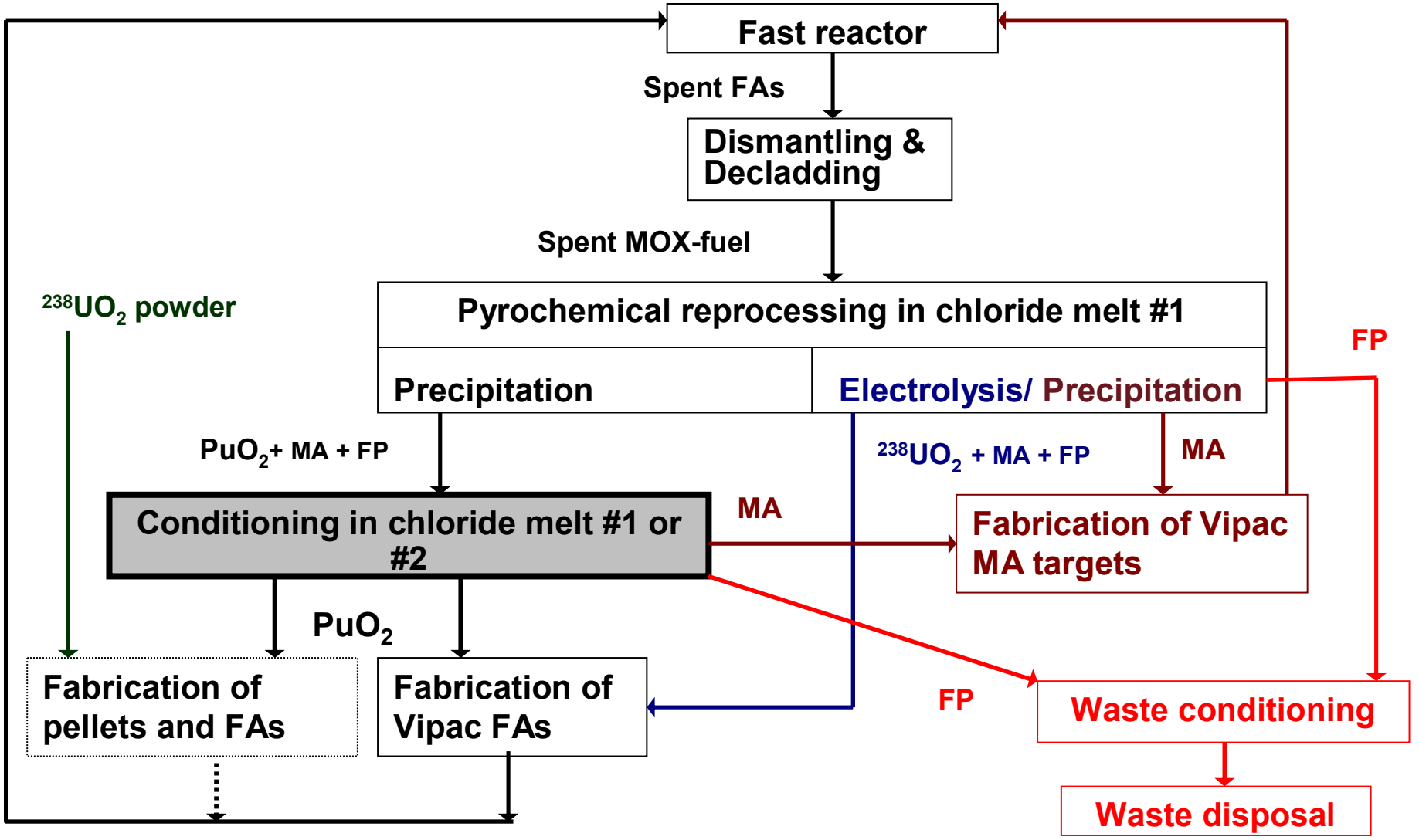
One of conceptions for on-site fast reactor closed fuel cycle



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Request to powders for fabrication of pellet and Vipac MOX-fuel

Characteristics	**Pellets***	**Vipac****	**Profile Vipac****
O/Pu	1.95-2.00	1.95-2.00	1.95-2.00
Particle size, μm	≤88	≤100	20-100
Bulk density, g/cm^3	1,5-2.5	≥2.3	≥2.3
Specific surface, m^2/g	5-30	no special request	no special request
Fluidity, g/s	no special request	no special request	no special request

*NE Standards NE E13-1T, Ceramic Grade Plutonium Dioxide, US DOE Nuclear Energy Programs, Washington, 1981.
Standard Specification for Nuclear Grade Plutonium Dioxide Powder, Sinterable, ASTM, C 757 – 90. Annual Book of ASTM Standards, V. 1201. .
**Osipenko A.G., Poglyad S.S., Skiba O.V. et al. Influence of precipitation conditions on gralunometric composition of plutonium dioxide // Bulletin of USTU-UPI, 2004, p.132.

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Reactions in chloride melt under bubbling of gas mixture

In bulk melt

$$Pu^{3+} + \tfrac{1}{2}\, Cl_2(gas) \leftrightarrow Pu^{4+} + Cl^-$$

$$Pu^{4+} + O_2(gas) + 2Cl^- \leftrightarrow PuO_2^{2+} + Cl_2(gas)$$

$$PuO_2^{2+} + Cl^- \leftrightarrow PuO_2^{+} + \tfrac{1}{2}\, Cl_2(gas)$$

$$PuO_2^{+} + Cl^- \leftrightarrow PuO_2(s) + \tfrac{1}{2}\, Cl_2(gas)$$

$$PuO_2(s) + Cl_2(gas) \leftrightarrow PuO^{2+} + 2Cl^- + \tfrac{1}{2}\, O_2(gas)$$

$$PuO_2(s) \leftrightarrow Pu^{4+} + O^{2-}$$

$$\tfrac{1}{2}\, O_2(gas) + 2\, Cl^- \leftrightarrow O^{2-} + Cl_2(gas)$$

In surface of carbon containment and devices

$$PuO_2^{2+} + C + Cl_2(gas) \leftrightarrow Pu^{4+} + CO_2(gas) + 2\, Cl^-$$

$$C + 2O^{2-} + 2Cl_2(gas) \leftrightarrow CO_2(gas) + 4\, Cl^-$$

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Main factors effected to particle growth condition

- critical size of nucleus of crystal
- nucleus of crystal amount
- rate of feed supply (gas or other oxidant)

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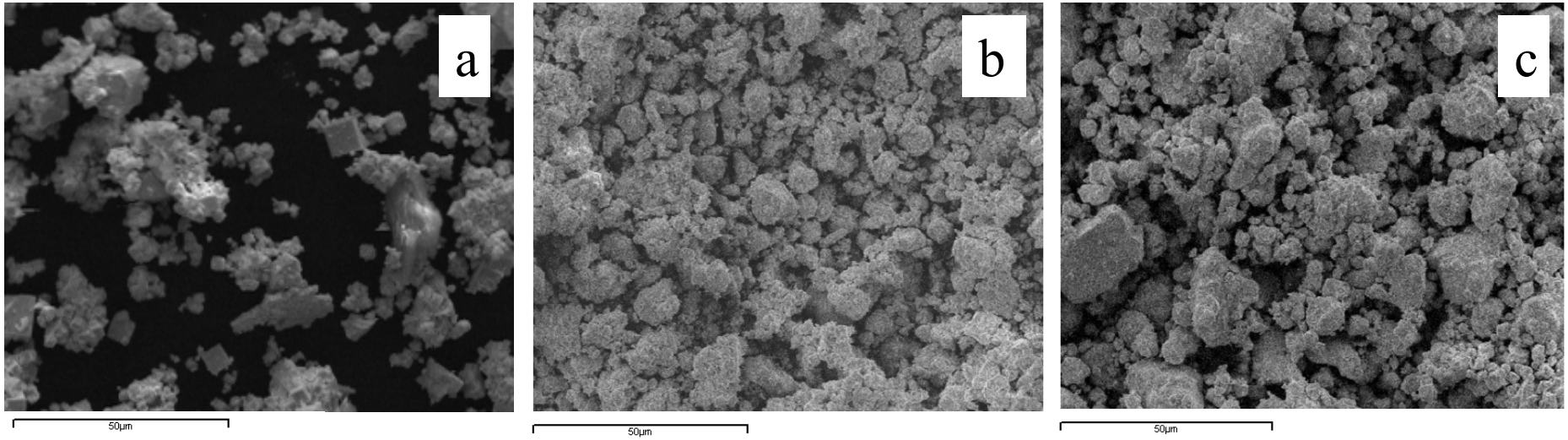
Influence of solvent



PuO_2 particle image:

a) NaCl-2CsCl, T=550°C;
b) 3LiCl-2KCl, T=450°C;
c) 0,575LiCl-0,165KCl-0,26CsCl, T=450°C

Specific interphase surface	0.26 cm^{-1}
$P^{1/2}(O_2)/P(Cl_2)$	99

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Influence of solvent

	Melt	NaCl-2CsCl	3LiCl-2KCl	0,575LiCl-0,165KCl-0,26CsCl
Conditions of powder production	T, ^oC	550	450	450
	$P^{1/2}(O_2)/P(Cl_2)$	99		
	Specific interphase “gas-liquid”, cm^{-1}	0.26		
Powder properties	Lattice spacing, Å	5,3745 ± 0,0005	5,3804 ±0,0005	5,3745±0,0005
	Size of coherent dispersion area, nm	139,2 ± 23,6	41,9 ± 2,6	31,7 ± 2,1
	Fluidity, g/s	22	no	no
	Specific surface, m^2/g	3.8 ± 0.6	12.5 ± 0.8	16.5 ± 1.1
	Bulk density, g/cm^3	4.4	3.7	3.4
	-20μm, wt%	32	12	15
	+20-100 μm, wt%	54	88	66

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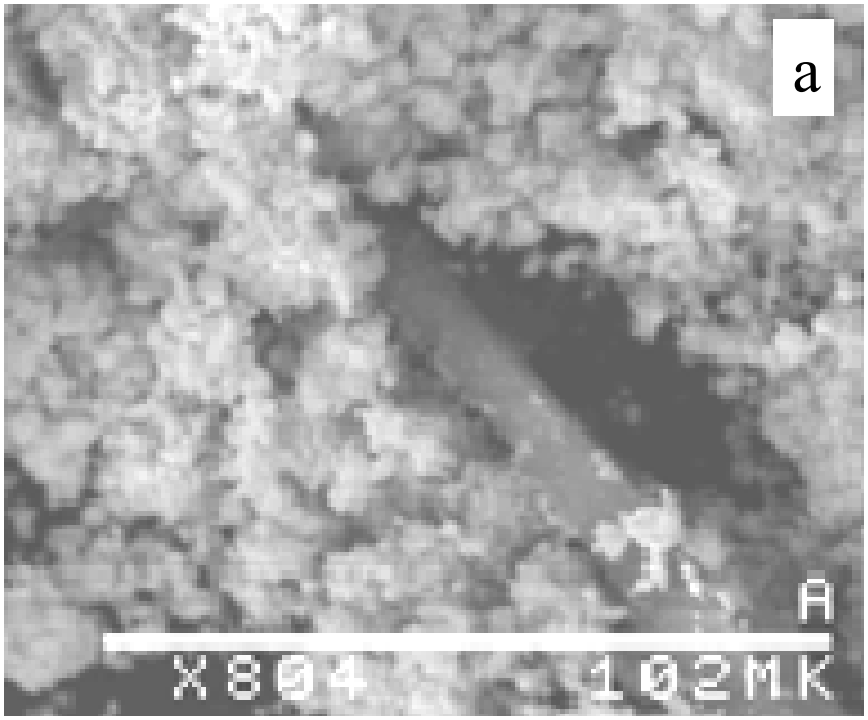
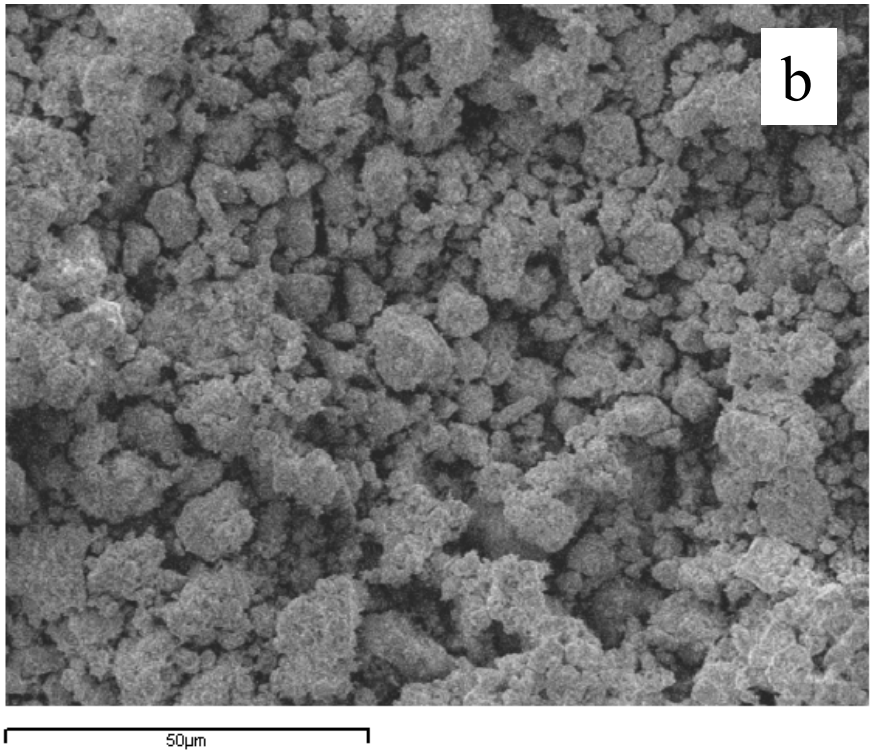
Comparison with powder from oxalate





Particle image : a) UO_2 from oxalate, T=750°C;
b) PuO_2 from 3LiCl-2KCl, T=450°C;

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Fabrication of MOX and PuO_2 pellets

Composition of molding powder, wt%	**Pellet density, g/cm^3**
100 UO_2 industrial (from oxalate)	10.4
97 UO_2 +3 PuO_2 (from 3LiCl-2KCl)	10.6
80 UO_2 +20 PuO_2 (from LiCl-KCl-CsCl)	10.8
20 UO_2 +80 PuO_2 (from 3LiCl-2KCl)	10.6
100 PuO_2 (from LiCl-KCl-CsCl)	10.3

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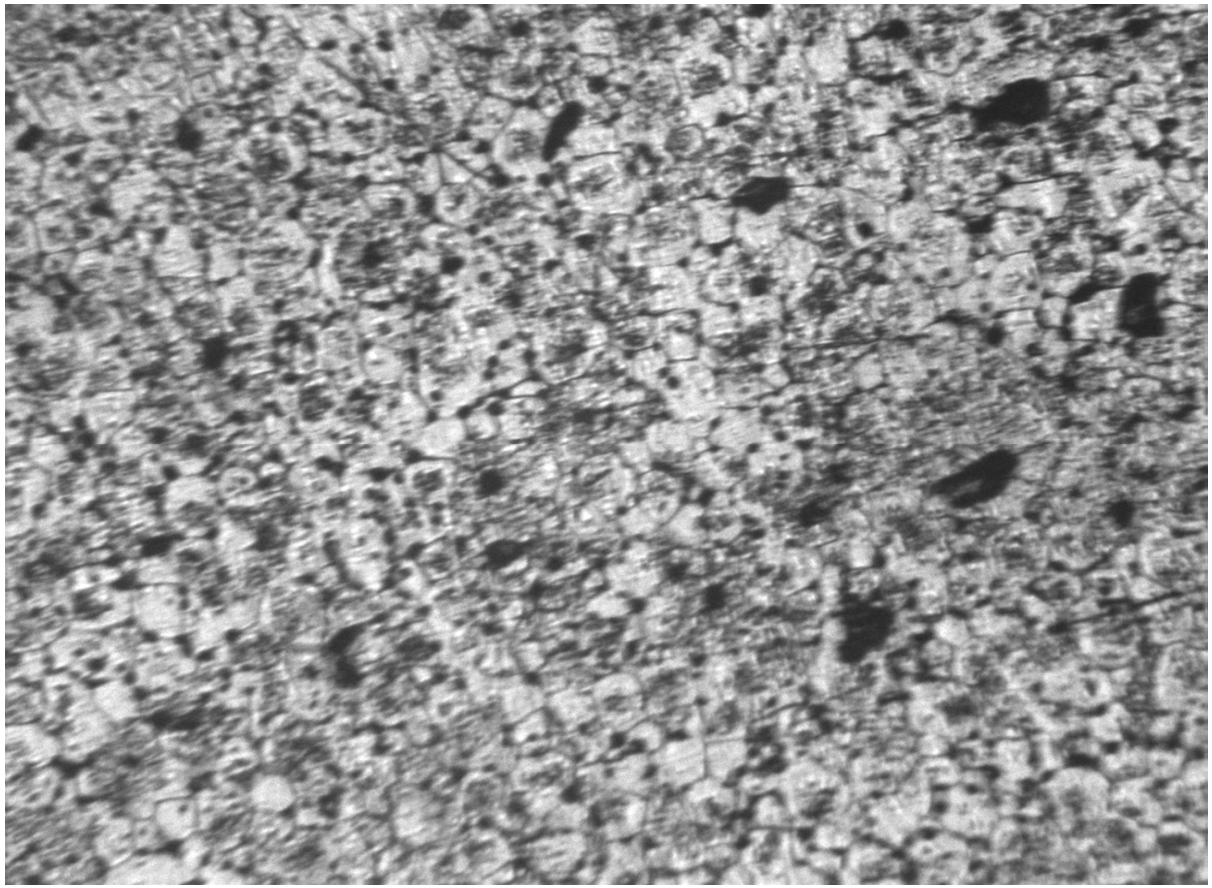
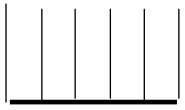
Microstructure of pickled pellet ($80UO_2+20PuO_2$)





100µm

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Distribution of U and Pu on pellet

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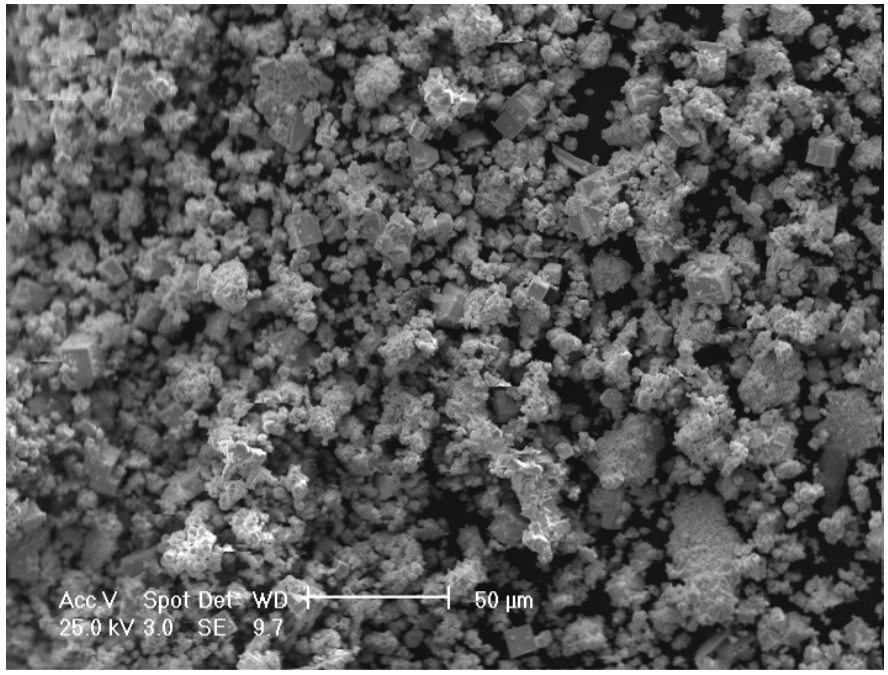
Influence of O_2/Cl_2 ratio

$P^{1/2}(O_2)/P(Cl_2)$= 2.5



$P^{1/2}(O_2)/P(Cl_2)$= 99

Melt	**NaCl-2CsCl**
Temperature	**550°C**
Specific interphase surface	**0.26**

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Influence of O_2/Cl_2 ratio

Conditions of powder production	**Melt**	NaCl-2CsCl	
	T, °C	550	
	Specific interphase "gas-liquid", cm^{-1}	0.26	
	$P^{1/2}(O_2)/P(Cl_2)$	99	2.5
Powder properties	**Fluidity, g/s**	22	16.2
	Specific surface, m^2/g	3.8 ± 0.6	0.03 ± 0.005
	Bulk density, g/cm^3	4.4	4.2/5.0
	-20μm, wt%	32	3
	+20-100 μm, wt%	54	97

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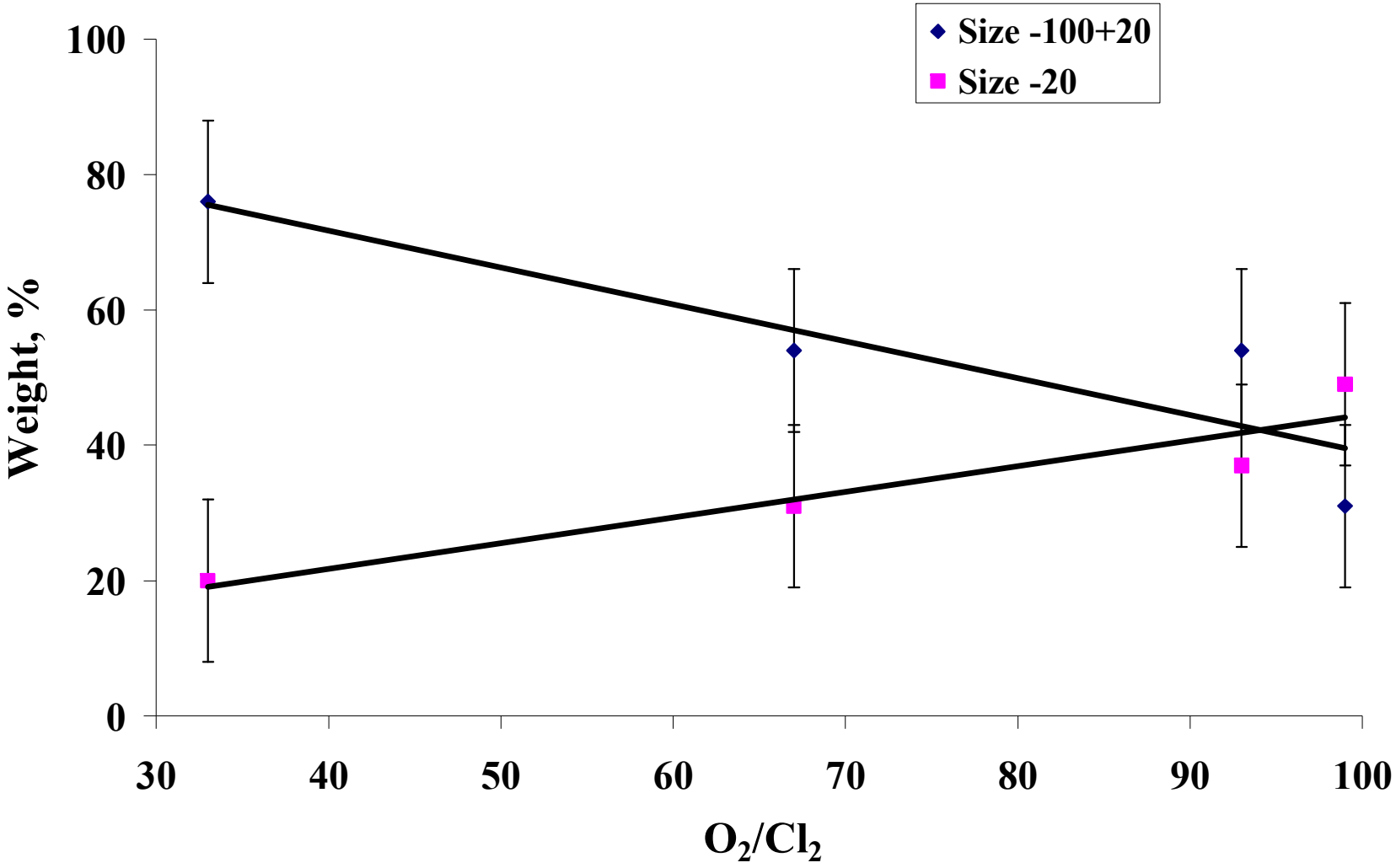
Influence of ratio O_2/Cl_2
Dependence of the particles weight on their size



Specific interphase	0.26 cm^{-1}
Temperature	550°C

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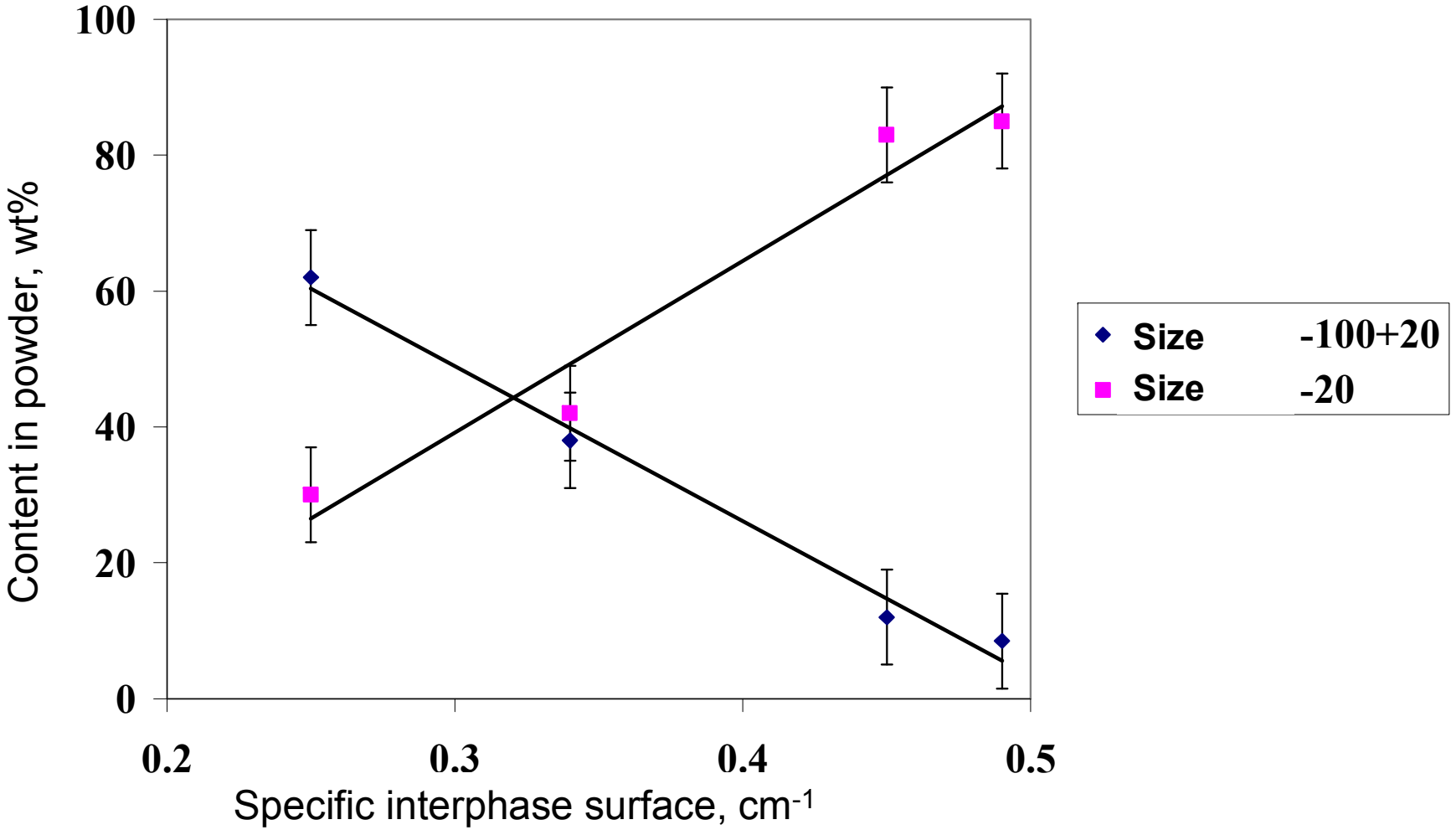
Effect of specific surphase on granulometric composition



Temperature	550°C
$P^{1/2}(O_2)/P(Cl_2)$	99

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Conclusions

- Pyrochemical processes can be used for production of plutonium dioxide powders suitable for manufacturing of MOX or PuO_2 pellet

- The effect of solvent, ratio O_2/Cl_2, specific interphase on morphology of plutonium dioxide precipitated from molten chloride was studied.

- Variation of these parameters makes it possible to widely vary properties of plutonium dioxide powder for MOX fuel (vibro or pellet)

Thank you for attention!

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