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Re and Tc in cermet waste forms

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- Tc-99 in the Geosphere & biosphere
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Tc in the Periodic Table

VIB	VIIB
$^{42}Mo_{95.9}$ [Kr] $4d^5 5s^1$ +2...+6 (+4,+6)	$^{43}Tc_{97.9}$ [Kr] $4d^5 5s^2$ -1...+7 (+4,+7)
	$^{75}Re_{186.2}$ [Xe] $4f^{14} 5d^5 6s^2$ -1...+7 (+4,+7)

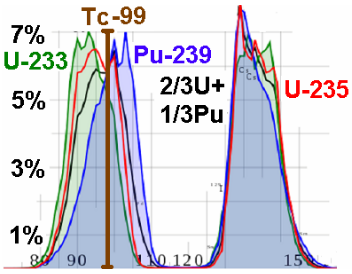
> 30 isotopes.

Most long-lived:
^{98}Tc ($4.2 \cdot 10^6$ y),
^{97}Tc ($2.6 \cdot 10^6$ y).

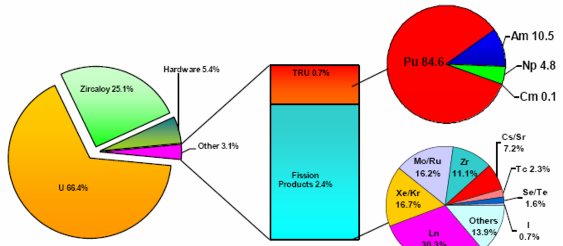
Most important:
^{99}Tc ($0.2 \cdot 10^6$ y),
^{99m}Tc (6 hours).

Re can be used as Tc imitator

Tc in the Nuclear Fuel Cycle



Yield of FPs at ^{233}U, ^{235}U, ^{239}Pu fission

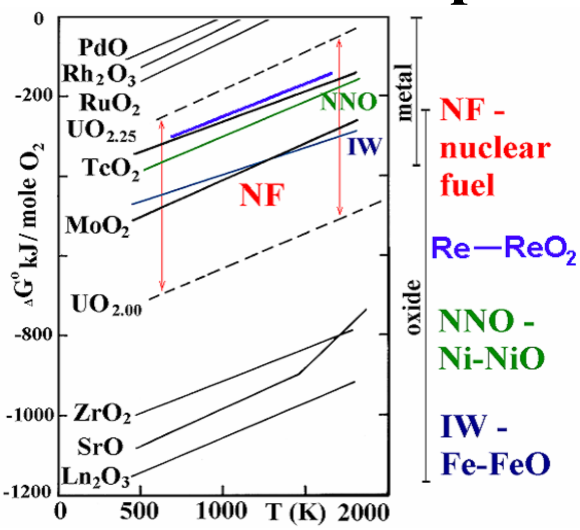


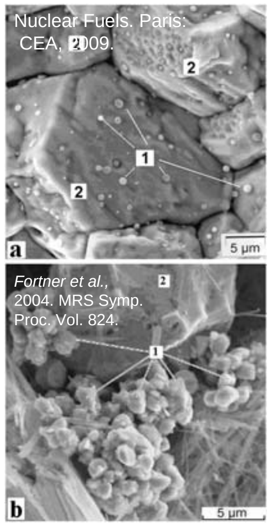
LWR SNF composition.
~ 3 wt.% ^{99}Tc in the FPs,
~1 kg (13 Ci) Tc / t SNF.

GWt reactor → >10 kg ^{99}Tc / y. Total ~5 t / y.

~250 ton of ^{99}Tc: 2/3 – SNF, 1/3 – pure ^{99}Tc.

Technetium in Spent Nuclear Fuel





Free energies of main FP oxides formation.

1 – (Mo,Ru,Rh,Pd,Tc) or ε-phase, 2 – UO_2.

Tc in the Geosphere & biosphere:

Natural Tc is found in U ores (Tc : U ~ 10^{-12}),

ΣU deposits ~ $30 \cdot 10^{12}$ grams (= **tens g of ^{99}Tc**).

Nuclear industry: **~250 t** of ^{99}Tc **(~ 4 MCi)**.

~10^5 Ci are discharged due to SNF reprocessing (**~2500 Ci = 0.2 ton Tc / y** – from a large plant).

~ 4000 Ci – from the all nuclear weapon tests.

~10 tons of Tc-99 in the biosphere.

0.005 – **0.5 Bq / L** (up to 0.001 ppb) in the waters of North and **Irish Sea** near La Hague and Sellafield SFRPs.

0.004 – **0.78 Bq / g** (**1.6 ppb**) in soils and in sediments of **the Techa river**

.

1 Ci = 74 g of ^{99}Tc, 1 Bq = 2 x 10^{-9} g.

Attention to Tc is explained by:

- Large half-life period of Tc-99
- High content in spent nuclear fuel
- Separation in PUREX / UREX, etc
- Stability of TcO_4^- in surface waters
- Good solubility of pertechnetates

⇓

Should be immobilized in stable forms

Summary of data on the Tc host phases corrosion in water.

Waste form (Tc, in wt.%)	Oxidation state of Tc	N_L Tc, $g / m^2 \cdot day$
Glasses (< 0.1)	$Tc^{7+} > Tc^{4+}$	$>10^{-2}$
Concretes (≤ 0.1)	Tc^{4+} or Tc^{7+}	10^{-3} (Tc^{4+}) – 1
Mg_2TiO_4 (10 – 40)	Tc^{4+}	$10^{-1} – 10^{-3}$
Spent NF (~0.1)	$Tc^{o} > Tc^{4+}$	10^{-3}
Synroc-C (~0.5)	Tc^{o}	$10^{-3} – 10^{-5}$
Alloys (2 – 80)	Tc^{o}	10^{-4}

Host phases for Tc^{4+} and Tc^{o}:

$^{[6]}Ti^{4+}$ (0.61) < $^{[6]}Tc^{4+}$ (0.65Å) < $^{[6]}Zr^{4+}$ (0.72)

↓

Tc^{4+}: *Spinel – $MgTiO_4$, Rutile – TiO_2*

Perovskite – $CaTiO_3$,

Pyrochlore – $Ln_2(Ti,Zr)_2O_7$

Tc^{o}: *Zr-, Fe-Zr-, SS-based alloy*

Routes for Tc-99 forms fabrication

Route	T, °C	Media	Matrix	Remarks
Low–T	**25 – 100**	Air	Concrete, CBPCs	$Tc^{4+/7+} < 0.1\%$ (P = 1 atm.)
Interme-diate–T	**200 – 400**	Air	Silica gel	$Tc^{4+} = 10$ wt.% (P = 1 atm.)
High–T	**800 – 1300**	Air, Ar, Vacuum	Glasses, Ceramics, Synroc	$Tc^{4+/7+} =$ 0.1 – 40 wt.% (P = 1–300 atm.)
Super–HT **(SHS)**	**> 1600**	Air, Ar, Vacuum	Alloys, **Cermets**	$Tc^{0} = 2 – 80\%$ (P = 1 atm.)

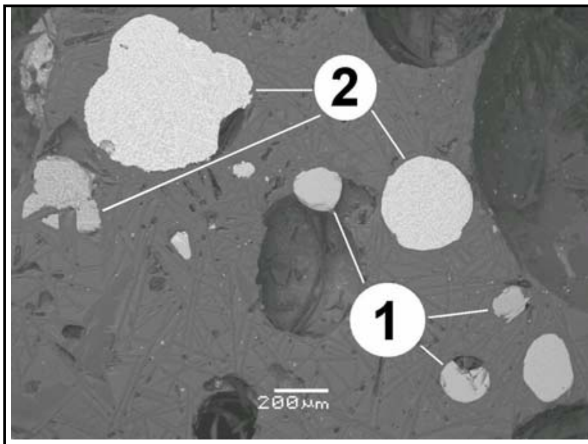
Volatility of Tc^{7+} (>100°), Tc^{4+} (>900°)!

Self-sustaining high-temperature synthesis (SHS) of Re (Tc) matrices

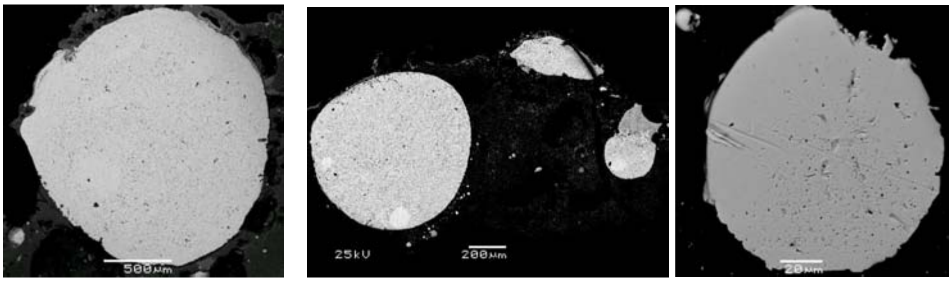
$$Al + 0.18 \cdot [Fe_2Cr_{0.6}Ni_{0.29}O_{4.34}] + 0.22 \cdot KReO_4 + x \cdot Al_2O_3 + 0.44 \cdot SiO_2 = 0.11 \cdot (K_2O \cdot Al_2O_3 \cdot 4SiO_2) + (0.39 + x) \cdot Al_2O_3 + \mathbf{0.18 \cdot [Fe_2Re_{1.22}Cr_{0.6}Ni_{0.29}] + Q}$$

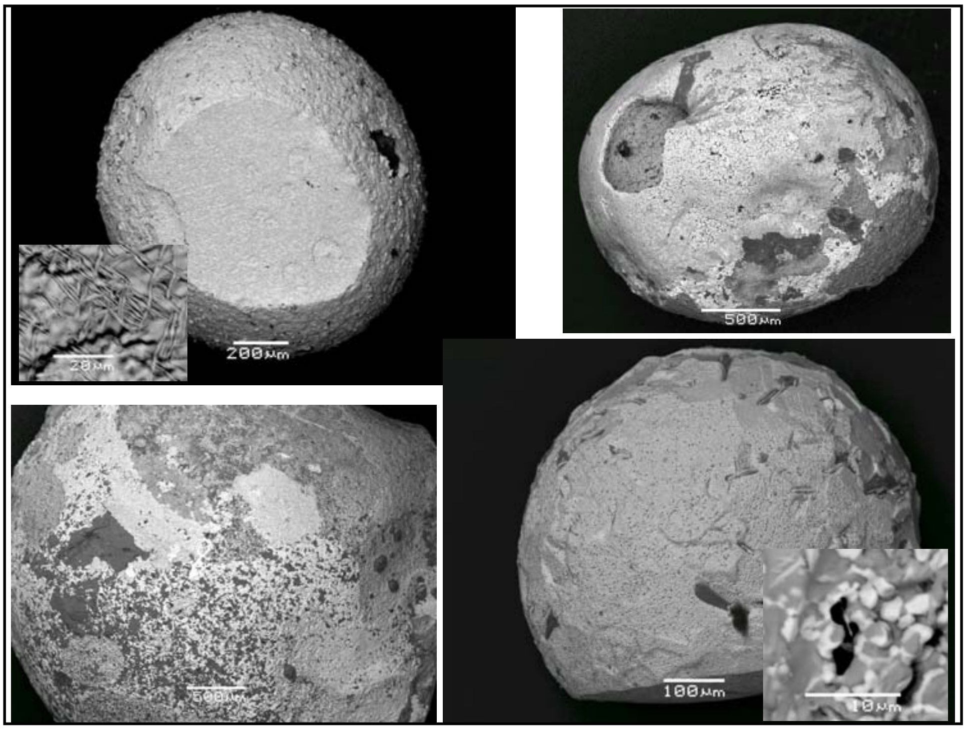
30 wt.% $KReO_4$ in batch (19 % Re in matrix)

Product: cermet = ceramic + alloy

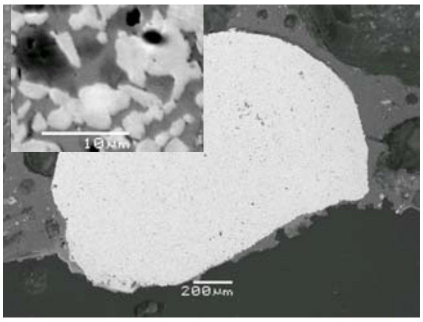


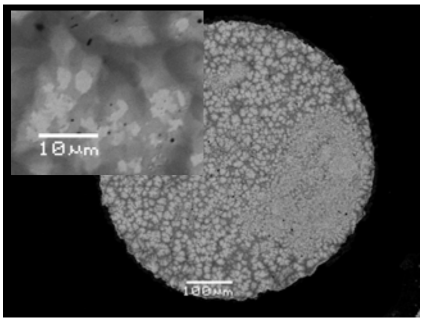
Alloy inclusions are varied **in size** (0.01 – 5 mm) and chemical **composition** (Fe : Re ratio)



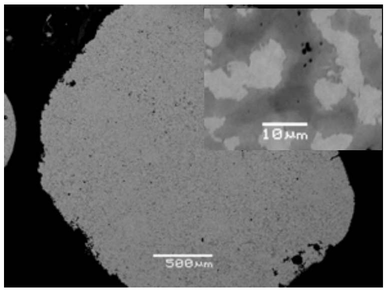


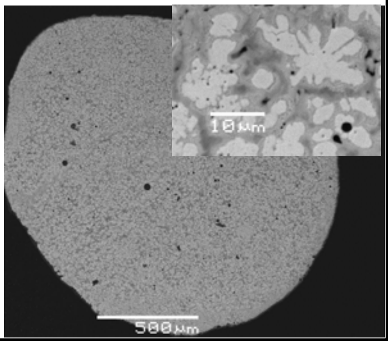
2-phase inclusions are most common:





<u>Light:</u>
35 Fe
57 Re
7 Ni
1 Cr
in at.%
<u>Grey:</u>
55 Fe
21 Re
21 Ni
3 Cr





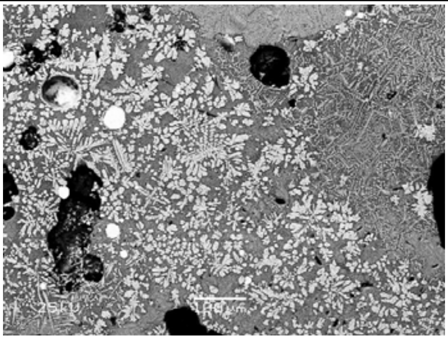
Forms for REE-An and Tc fractions

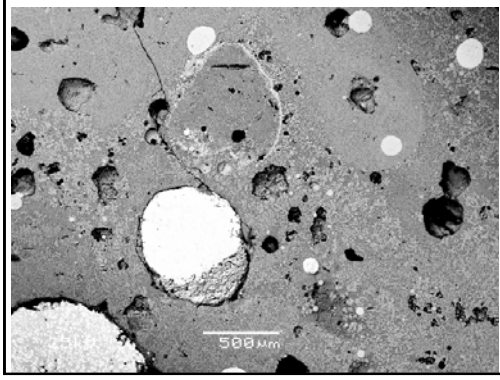
Al + oxides Fe, Cr, Ni + $KReO_4$ + REE_2O_3 + SiO_2 = ***<u>Fe,Cr,Ni,Re,Tc-alloy</u>*** *+ <u>REE-Al-garnet</u> + glass + Q*

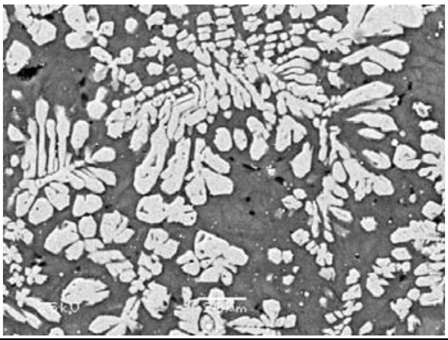
2) Ti + oxides Fe, Cr, Ni + $KReO_4$ + REE_2O_3 + SiO_2 + CaO = ***<u>Re-alloy</u>*** *+ <u>REE-Ti-pyrochlore</u> + glass + Q*

10-16 wt.% Re and 9-18 wt.% Sm (Nd)

Alloys + Garnet + Glass



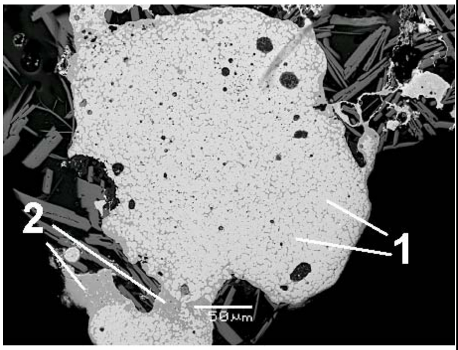


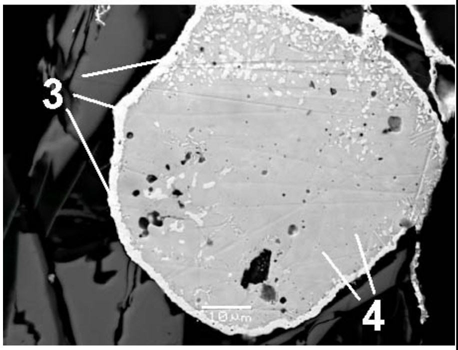


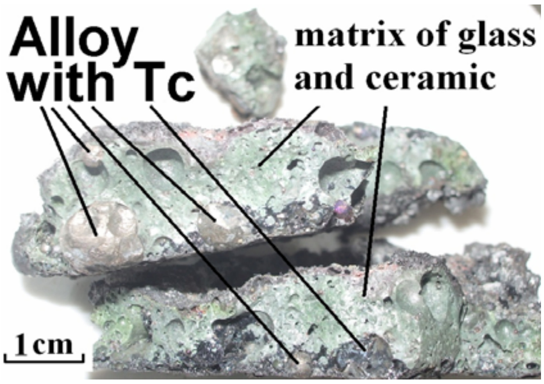
System: Steel-Re (Tc)

Alloy composition, at.%

Element	1	2	3	4
Re	47	15	67	31
Fe	35	55	17	48
Ni	6	17	16	17
Cr	12	7	-	4
Si	-	6	-	-
Phase	σ	γFe	ε	σ



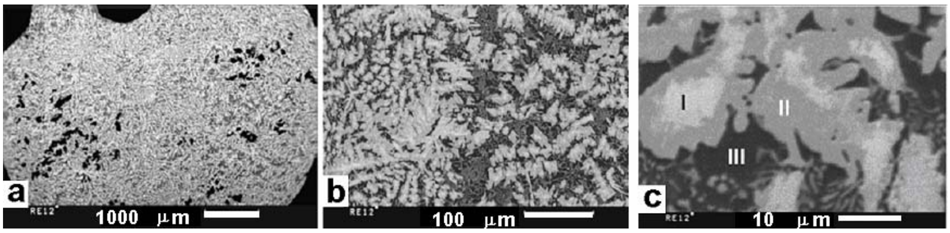




Batch contained 0.5 g $KTcO_4$ (Re : Tc ≈ 50).

Run was carried out in RI.

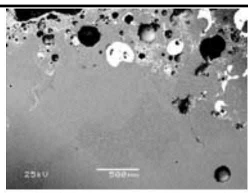
Evaporation of Tc during the SHS was not observed.

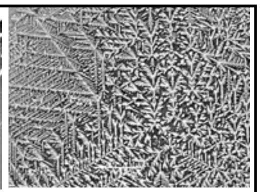


I, II – Alloy (**Tc ~0.5%**), III – (Fe,Ni)O (Tc < 0.05%).

System Mo - Re:

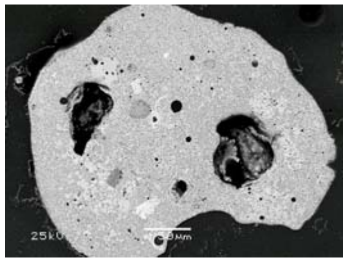
glass+alloy+garnet.

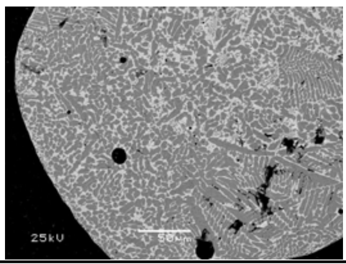


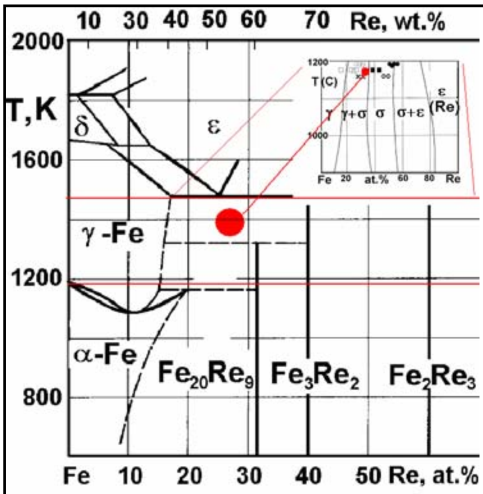


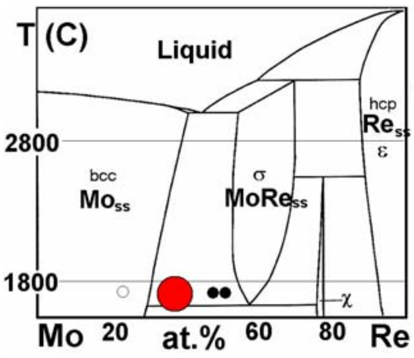
Alloys composition, at.%

Element	1	2	3 (minor)
Re	48	20	13
Mo	43	73	51
Si	7	4	34
Y	2	3	2
Phase	MoRe	Mo_{ss}	Mo_4ReSi_3









SS – Re:

Fcc (γ-Fe),

σ (Fe_3Re_2)

Mo–Re:

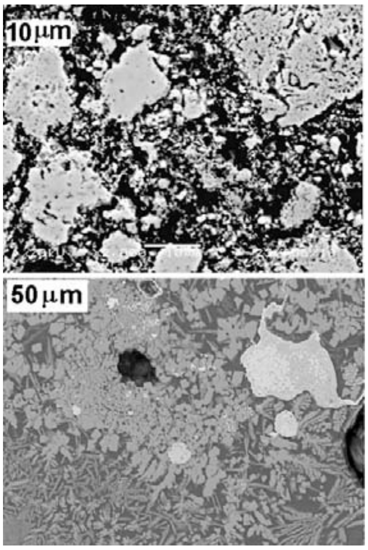
Bcc (Mo),

Fcc (MoRe)

Minor phases:

ε-phase (hcp), $(Mo_4Re)Si_3$

Titanate forms for REE-An and Tc



Single phase, 100 mg, $Nd_2Tc_2O_7$ pyrochlore. Sintering, Ar, 1150°C, 48 h *(Hartmann et al., 2011).*

Polyphase cermet, ~ 50 g, $(Sm,Y)_2Ti_2O_7$ pyrochlore+ (Fe,Re)-alloy+glass. SHS, air, ≥2000°C, mins *(our data).*

Low productivity of the methods!

Inductive melting in “cold” crucible – promizing route for Tc-alloy fabrication.

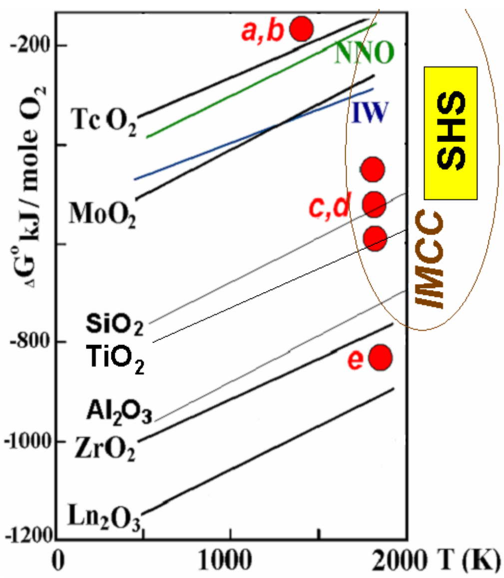
VNIIKhT. H = 3.5 m, d = 650 mm, up to 2500°C (Ar, air, vacuum). **50 kg / h of Fe-, Zr-, Nb-, U-alloy** (Gotovchikov et al.).

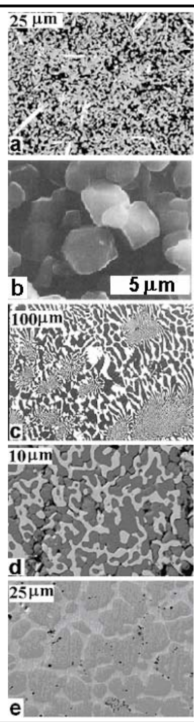
IMCC, SIA “Radon”: glasses, glass-ceramics, & ceramic waste forms (Stefanovsky et al.).

VNIINM. Ar: Steel, Zr-alloy, up to 50 kg / h (Pastushkov et al.).

Tc – as metal and melting in inert gas

Parameters of synthesis of Tc-containing matrices





$(Ti,\mathbf{Tc}^{4+})O_2$
ANSTO
(Carter et al., 2007)

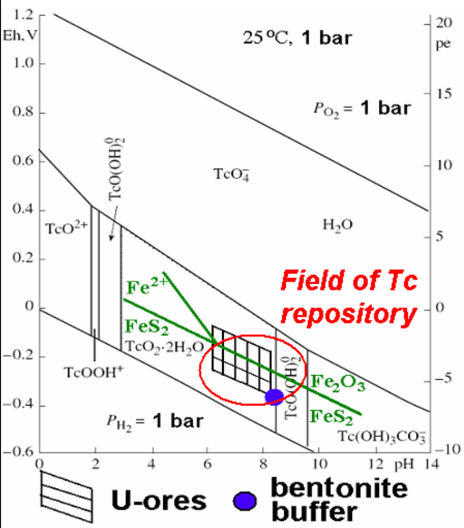
$Mg_2(Ti,\mathbf{Tc}^{4+})O_4$
PSU
(Khalil et al., 1983)

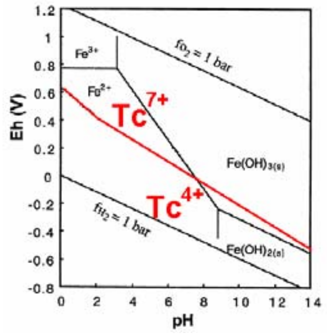
SS-15Zr+2%**Tc**
INL
(Frank et al., 2000)

ZrO_2 + **Tc**
UNLV

$ZrTc_2 + ZrTc_6$
UNLV
(Poineau et al., 2010)

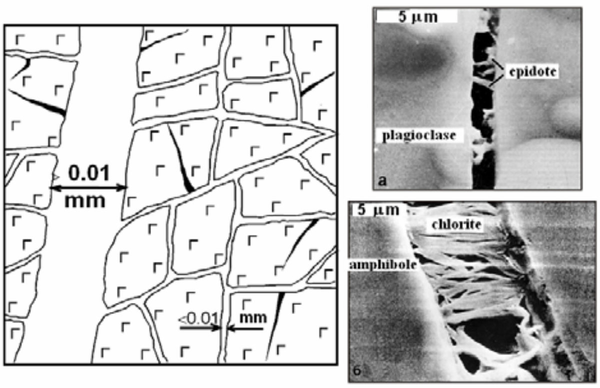
Conditions for Tc-99 disposal





$Tc^0 \Rightarrow TcO_2 \cdot 2H_2O$

Due to low solubility of $TcO_2 \cdot 2H_2O$ and Tc^{4+} high sorption (K_d ~1000 ml/g) – content of Tc in waters <10^{-9} M / l (~ 50 Bq / l).



Main minerals: Ca,Na-plagioclase, <u>olivine, pyroxene</u>, <u>amphibole</u>, quartz, <u>biotite</u>, <u>magnetite</u>, feldspar, <u>chlorite</u>, epidote, <u>sulfides</u>.

Crystalline rocks structure

Crystalline masifs of basic (basalt, gabbro) or intermediate (diorite, granodiorite, gneiss) rocks at depth of 300–500 m.

Rock – water interaction provides reducing (Eh < 0) and weakly alkaline (pH = 8–9) hydrogeochemical conditions.

Conclusions on management with ^{99}Tc-containing wastes:

1. Incorporation of ^{99}Tc in alloy and its disposal in weakly alkaline and reducing media (pH=7.5 – 9, Eh≤ 0), typical for waters at depths ≤ 500 m.

2. Industrial methods for synthesis of the ^{99}Tc forms can be developed: sintering, arc-melting, SHS, IMCC ?

Results are published in papers:

- Geology of Ore Deposits. 2009 (51) 259–274.
- Geochemistry International. 2010 (1) 1–14.
- Doklady Chemistry. 2010 (431) 71–75.
- Doklady Chemistry. 2010 (431) 102–108.
- Doklady Chemistry. 2010 (434) 214–218.
- Russian Chemical Journal. 2010 (LIV) 69–80.
- Geoecology. 2010 (3) 232–242.
- Geochemistry International. 2011 (10) 1–14.

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