CHEMISTRY INVOLVING DEPLETED UO_2 IN THE PROPOSED YUCCA MOUNTAIN HIGH-LEVEL WASTE REPOSITORY

A PRESENTATION to the NWTRB

by

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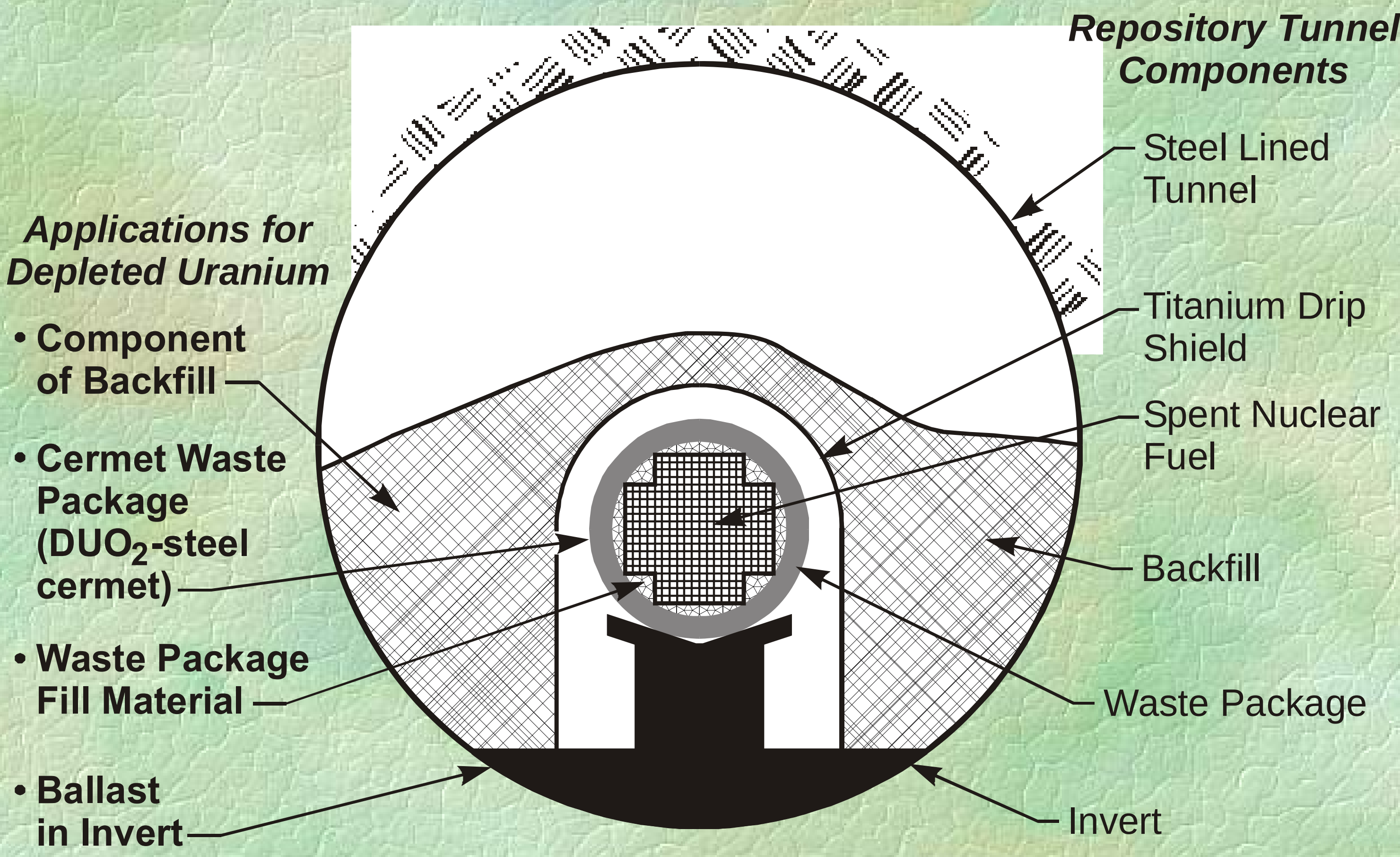
BASED ON RUSSIAN DATA OBTAINED WITH ISTC FUNDING

May 15, 2007

POTENTIAL DUO_2 APPLICATIONS IN A GEOLOGIC REPOSITORY



INTRODUCTORY OBSERVATIONS

POTENTIAL SOURCE OF DEPLETED UO_2

- 700,000 Te OF UF_6 IN 14 Te CYLINDERS AT PADUCAH, KY AND PORTSMOUTH, OH
- UF_6 CONVERSION PLANTS BEING BUILT AT BOTH SITES (~80% U_3O_8)*
- RELATIVELY MINOR CHANGES REQUIRED TO PRODUCE UO_2
- *Re-enrichment is a possibility

PRIMARY FACTORS IN RADIOACTIVITY RELEASE

- INGRESS OF WATER
- FAILURE OF DRIP SHIELDS
- BREACH OF WASTE PACKAGES
- BREACH OF FUEL RODS/WASTE CANISTER
- DISSOLUTION OF FUEL PELLETS/GLASS
- WATER TRANSPORT OF RADIOACTIVITY
- ENGINEERED AND NATURAL BARRIERS FAIL
- CHEMISTRY IN DRIFT, UZ, AND SZ

CHEMICALLY IMPORTANT REPOSITORY ATTRIBUTES FOR DUO_2 APPLICATIONS

- WATER: AMOUNT AND COMPOSITION
- AIR (OXYGEN AND CO_2)
- TEMPERATURE
- RADIATION
- MATERIALS OF CONSTRUCTION

IMPORTANCE OF AIR

- BAROMETRIC PUMPING, DIFFUSION AND WATER WILL PROVIDE A SOURCE OF AIR (O_2, CO_2, N_2) IN THE LONG TERM
- THE REPOSITORY WILL HAVE AN AVERAGE OXIDIZING ENVIRONMENT
- THERE WILL BE LOCAL REDUCING CONDITIONS [DUE TO METALS (ESPECIALLY IRON) AND RADIATION]

IMPORTANCE OF TEMPERATURE

- WATER INGRESS IS TEMPERATURE-DEPENDENT (ABOVE BOILING POINT)
- DUO_2 SOLUBILITY IS TEMPERATURE-DEPENDENT
- RADIONUCLIDE SORPTION IS TEMPERATURE-DEPENDENT
- CORROSION IS TEMPERATURE-DEPENDENT
- CHEMICAL REACTIONS/KINETICS ARE TEMPERATURE-DEPENDENT

DISCUSSION OF RUSSIAN DATA

DATA COURTESY OF T.V. KAZAKOVSKAYA (VNIIEF, RUSSIA) AND E.V. ZAHAROVA (IPC, RUSSIA)

URANIUM (UO_2) DISCUSSION

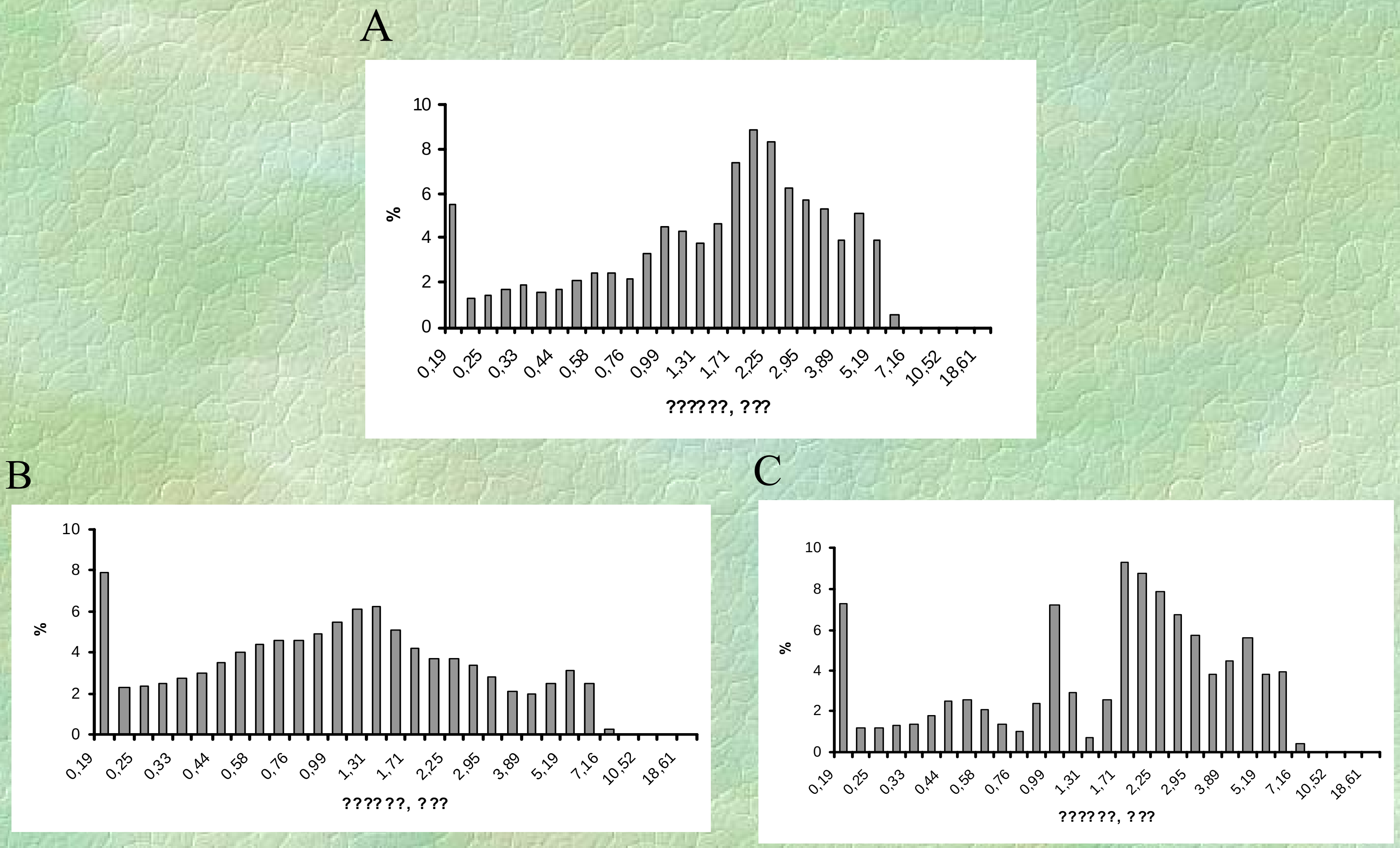
J-13 WELL WATER COMPOSITION

	mMOLES/L
Na^+	1.96
Mg^{2+}	0.075
Ca^{2+}	0.29
SiO_2	1.07
K^{1+}	0. 136
Cs^{1+}	0. 105
Cl^-	0.18
NO_3^-	0.16
SO_4^{2-}	0.19
F^-	0.11
CO_2^{2-}	Approx. 2.81 (total)

- Everything Else < 50 µg/L

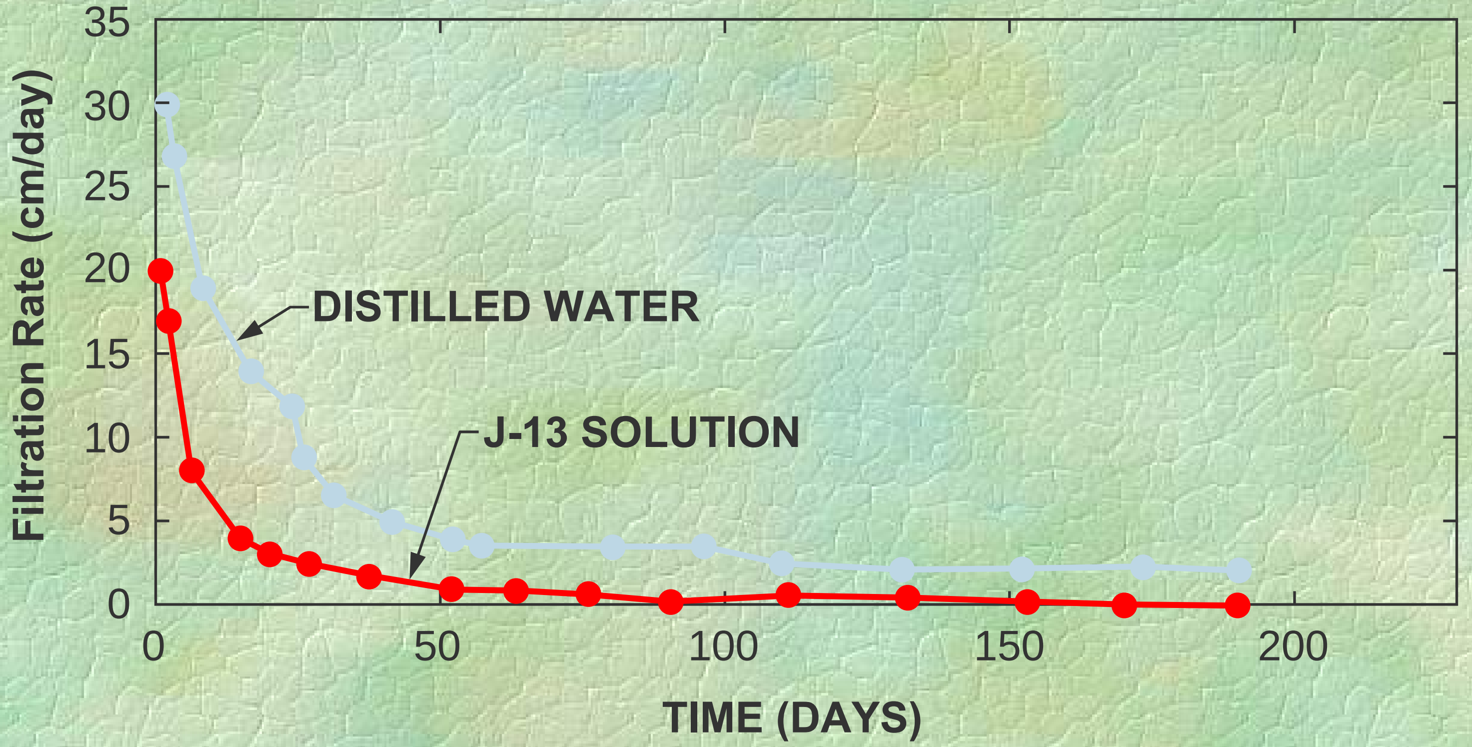
DUO2 SAMPLES STUDIED

SAMPLE	AVG. SIZE	PREP'N. TEMP.
DUO2 - 1	1.5 MICRON	650º C
DUO2 - 2	1.9 MICRON	700º C
DUO2 - 3	2.1 MICRON	800º C



PARTICLE SIZE DISTRIBUTION IN MICRONS FOR DUO_2-1 (A), DUO_2-2 (B), DUO_2-3 (C)

RELATIVELY THIN LAYERS OF UO_2 BECOME IMPERMEABLE TO WATER



DUO2 SOLUBILITY MEASUREMENT CONDITIONS

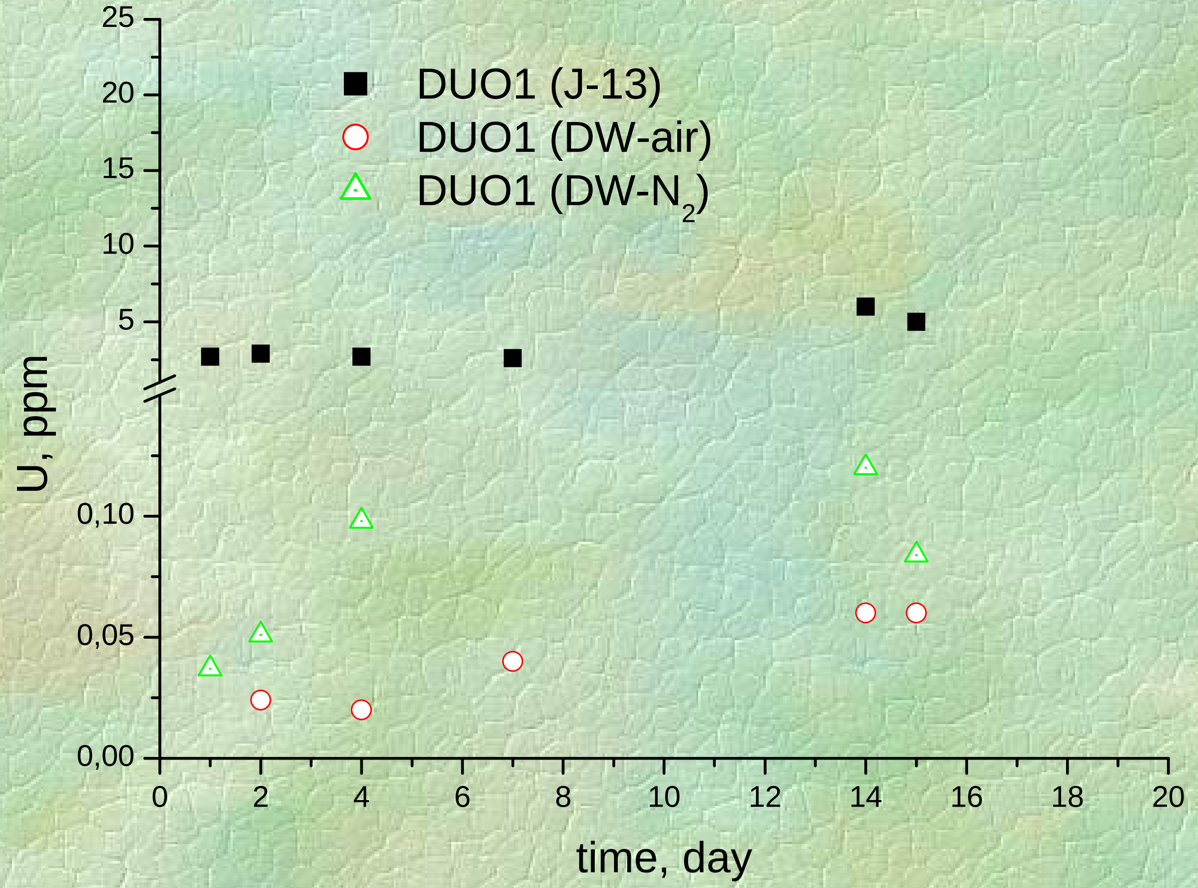
PHASE RATIO: 0.002 g/ml

DISTILLED WATER (DW) AND J-13 SOLUTION

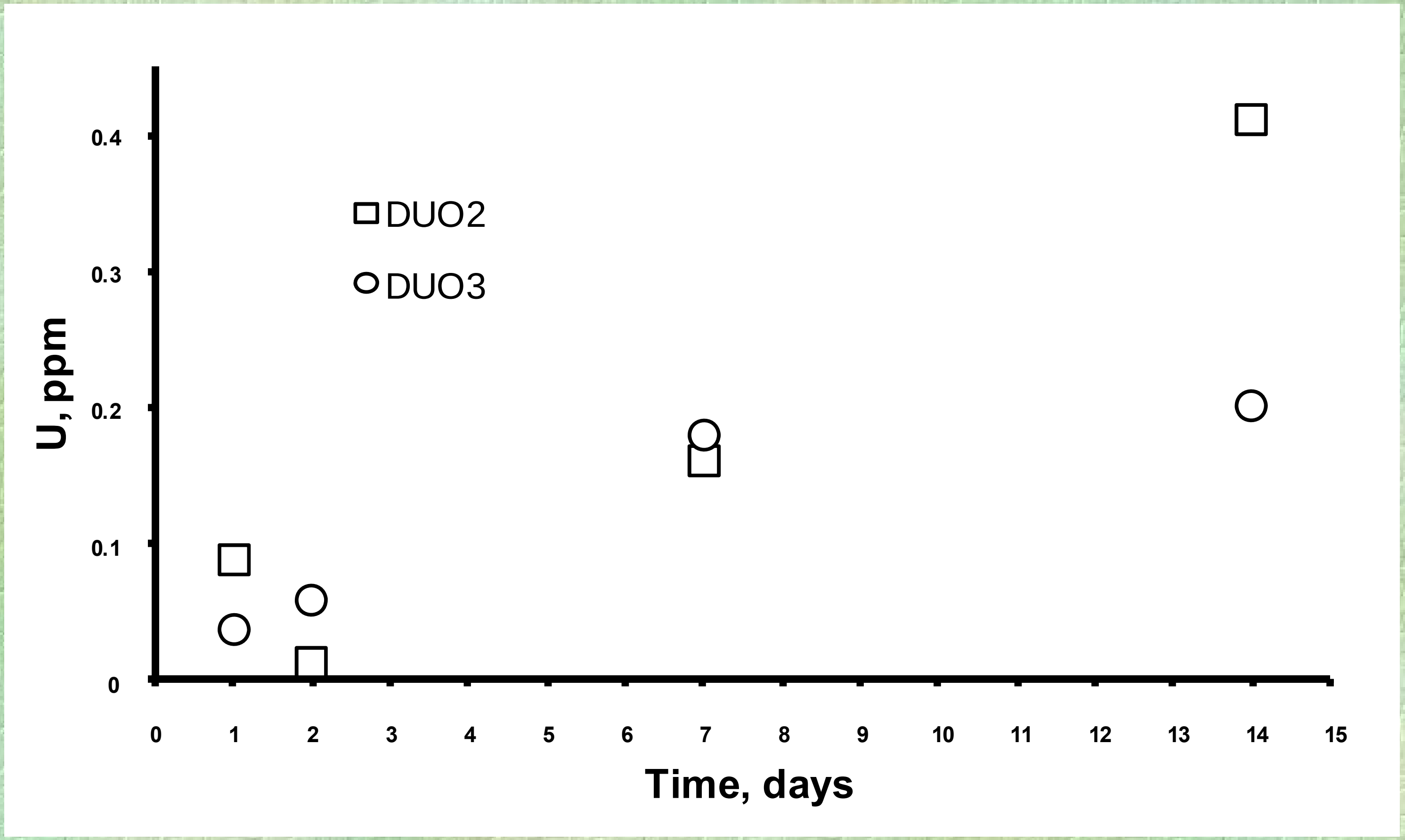
5, 50 AND 170 nm PORE FILTERS

DW pH = 6.4

J-13 SOLUTION pH > 7



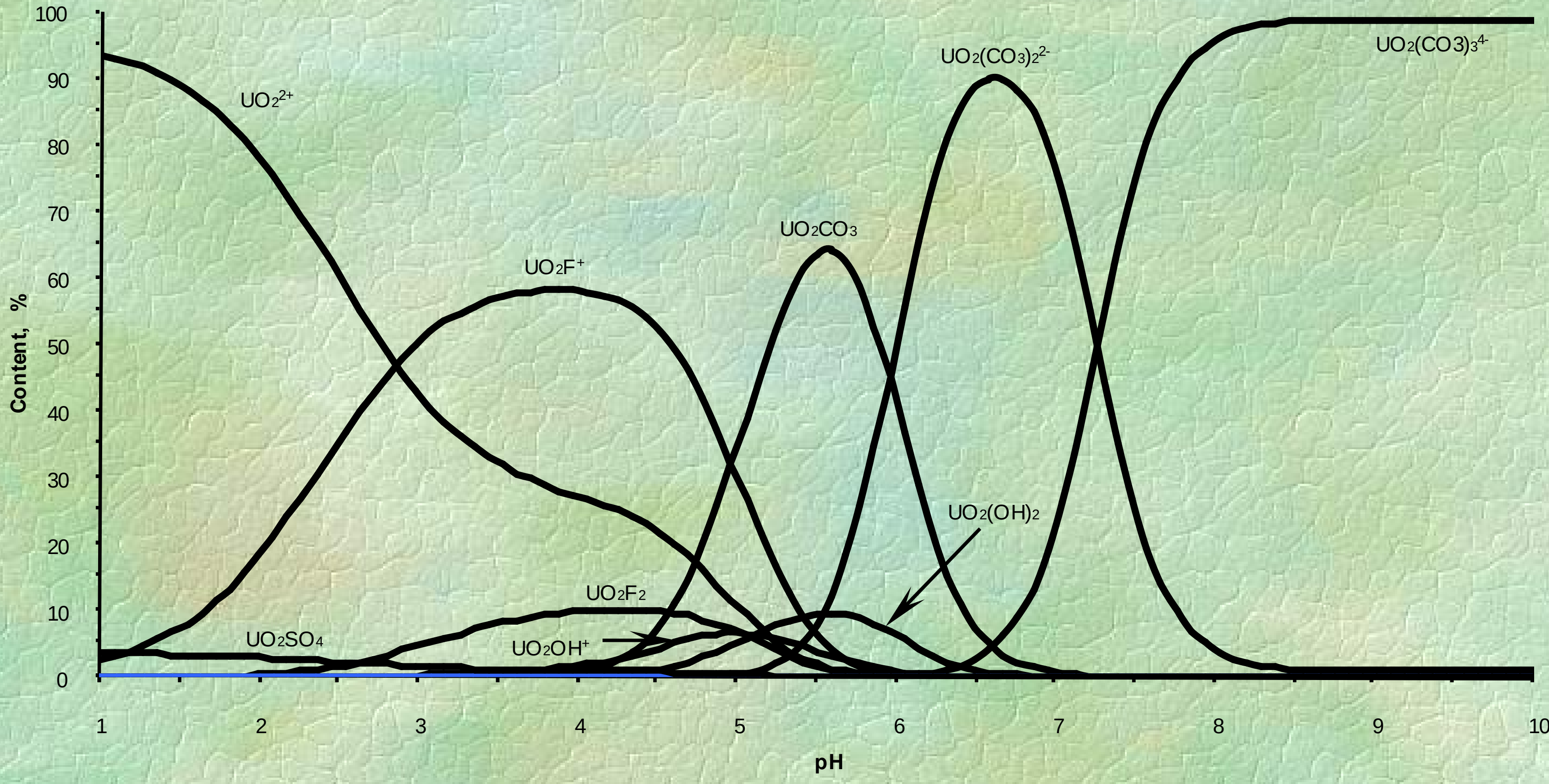
SOLUBILITY KINETICS OF DUO_2-1 IN J-13 WATER (pH=7.0) AND DEIONIZED WATER (pH=6.4)



SOLUBILITY KINETICS OF DUO2-2 AND DUO2-3 IN J-13 WATER (pH = 7.0)

EQUILIBRIUM URANIUM CONTENT IN J-13 WATER AFTER FILTRATION

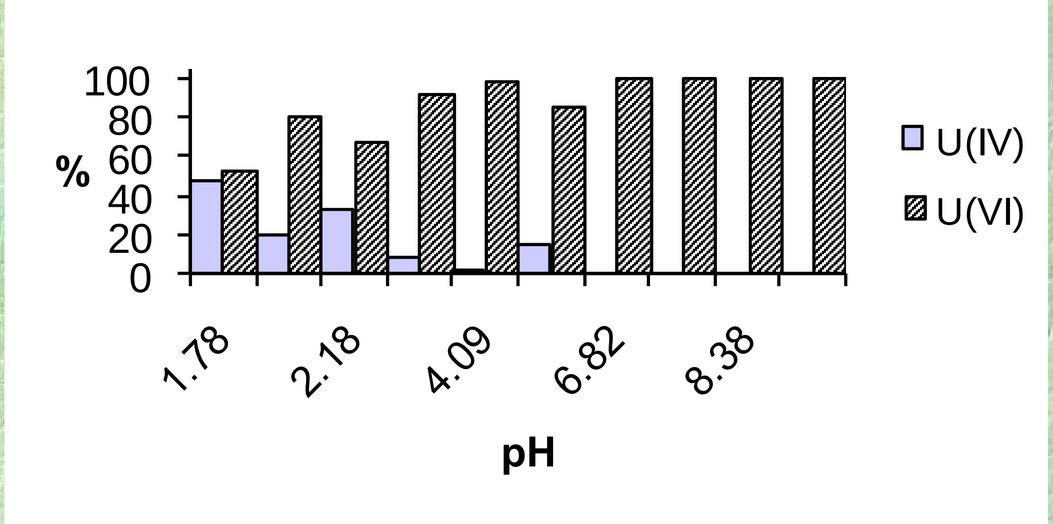
SAMPLE	URANIUM CONTENT, PPM		
	170 -nm FILTER	50 -nm FILTER	5 -nm FILTER
DUO_2-1	10.0	4.7	0.5
DUO_2-2	2.3	0.8	0.4
DUO_2-3	1.0	0.2	0.3



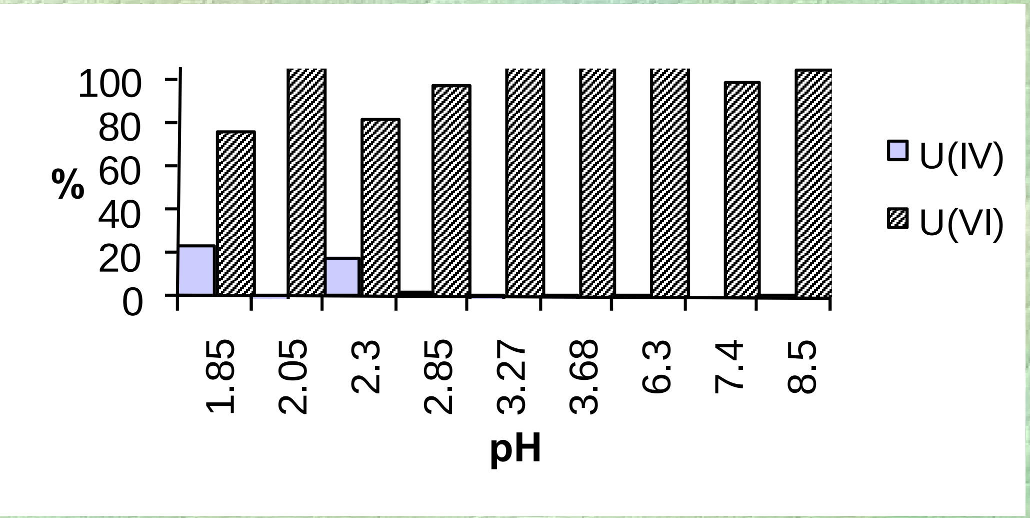
DISTRIBUTION OF U(VI) FORMS IN J-13 WATER AT VARIOUS pHs (THERMODYNAMIC CALCULATIONS)

pH DEPENDENCE OF URANIUM SPECIATION ON THE SURFACE OF UO_2

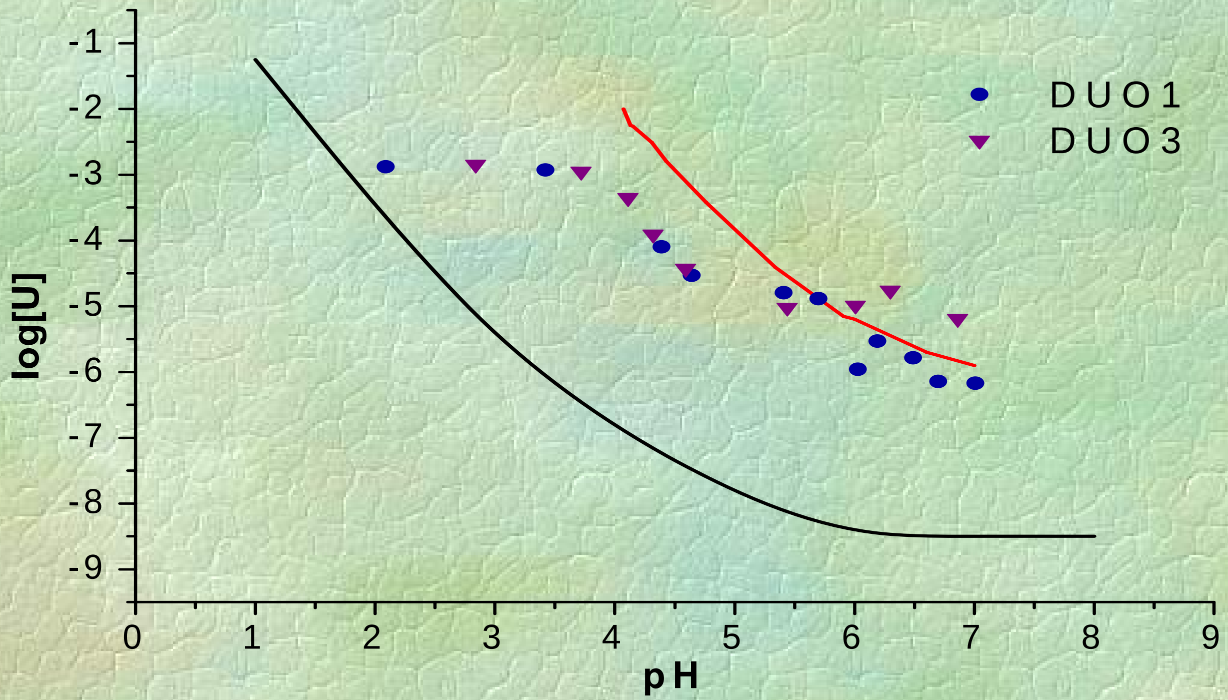
pH	U(IV), %	U(VI), %
2.54	60	40
4.35	53	47
7.04	46	54



A



Distribution of U valence forms in solution versus pH:
TOP – DUO2-1; BOTTOM – DUO2-3

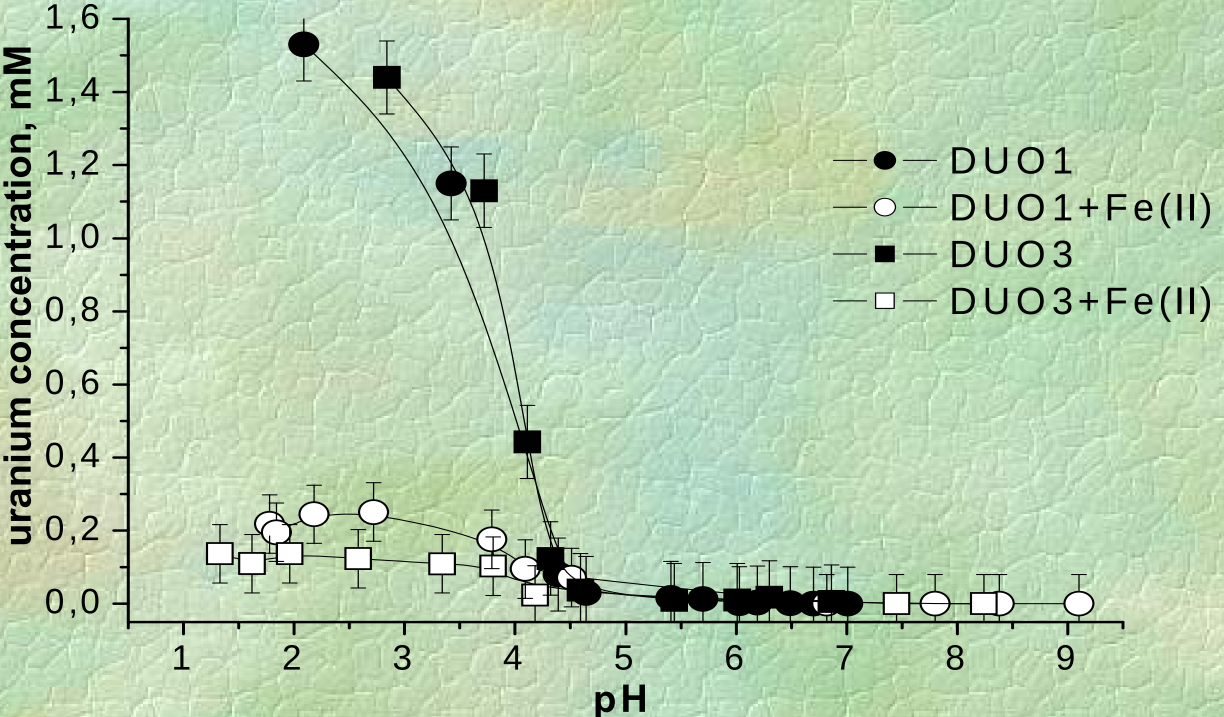


THEORETICAL AND EXPERIMENTAL DATA ON DUO2-1 AND DUO2-2 SOLUBILITY.

DOTS – EXPERIMENTAL DATA

BLACK LINE- THEORETICAL SOLUBILITY OF U(IV)

RED LINE – THEORETICAL SOLUBILITY OF U(VI)



SOLUBILITY OF DUO1 AND DUO3 VERSUS pH IN THE PRESENCE OF REDUCING AGENTS

NEPTUNIUM DISCUSSION

SEE ALSO

CHEMICAL SPECIATION OF NEPTUNIUM IN SPENT FUEL

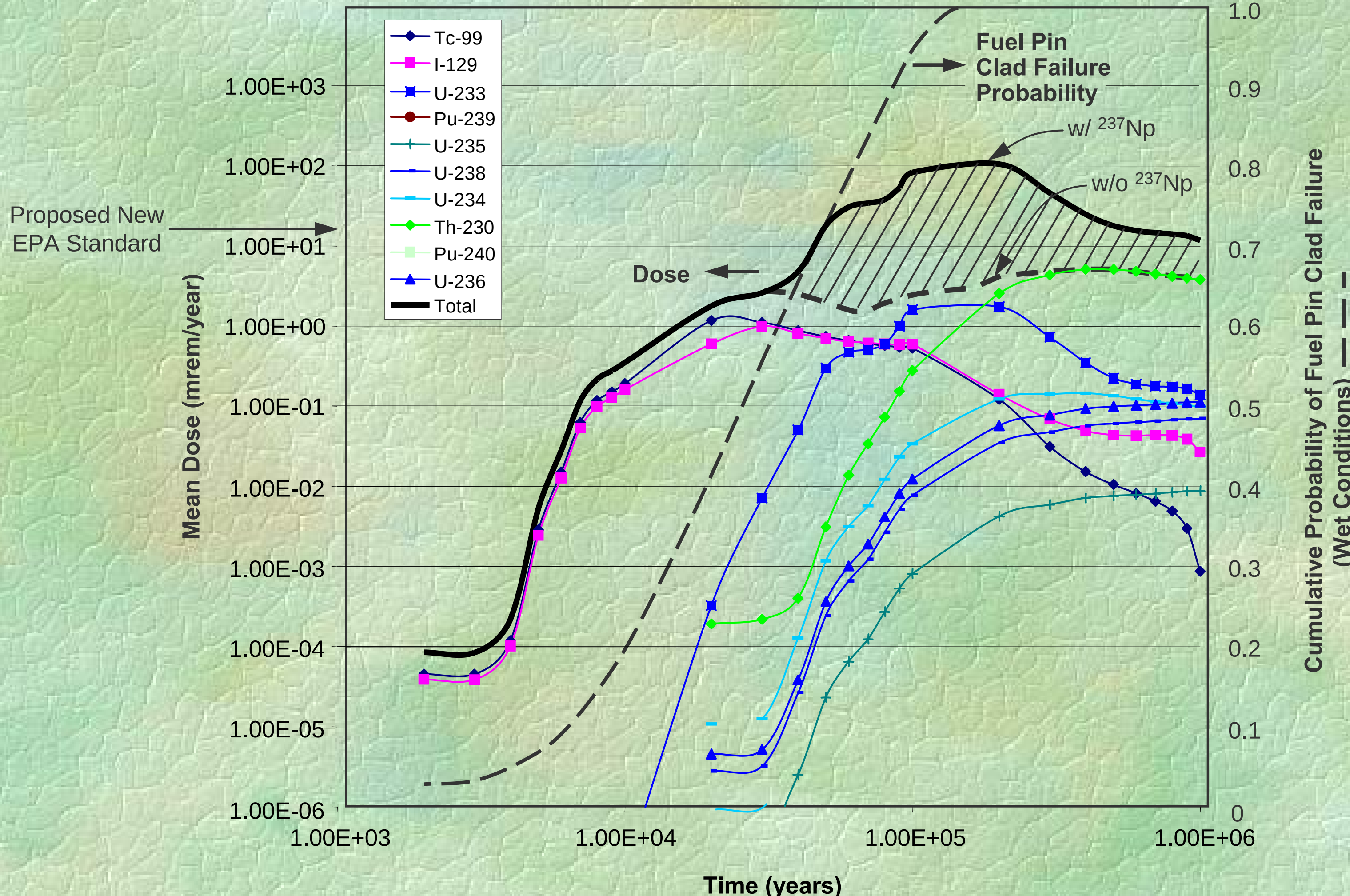
DE-FG03-99SF21903

1ST ANNUAL REPORT AUGUST 1999 TO AUGUST 2000

NUCLEAR ENGINEERING DEPARTMENT

MIT

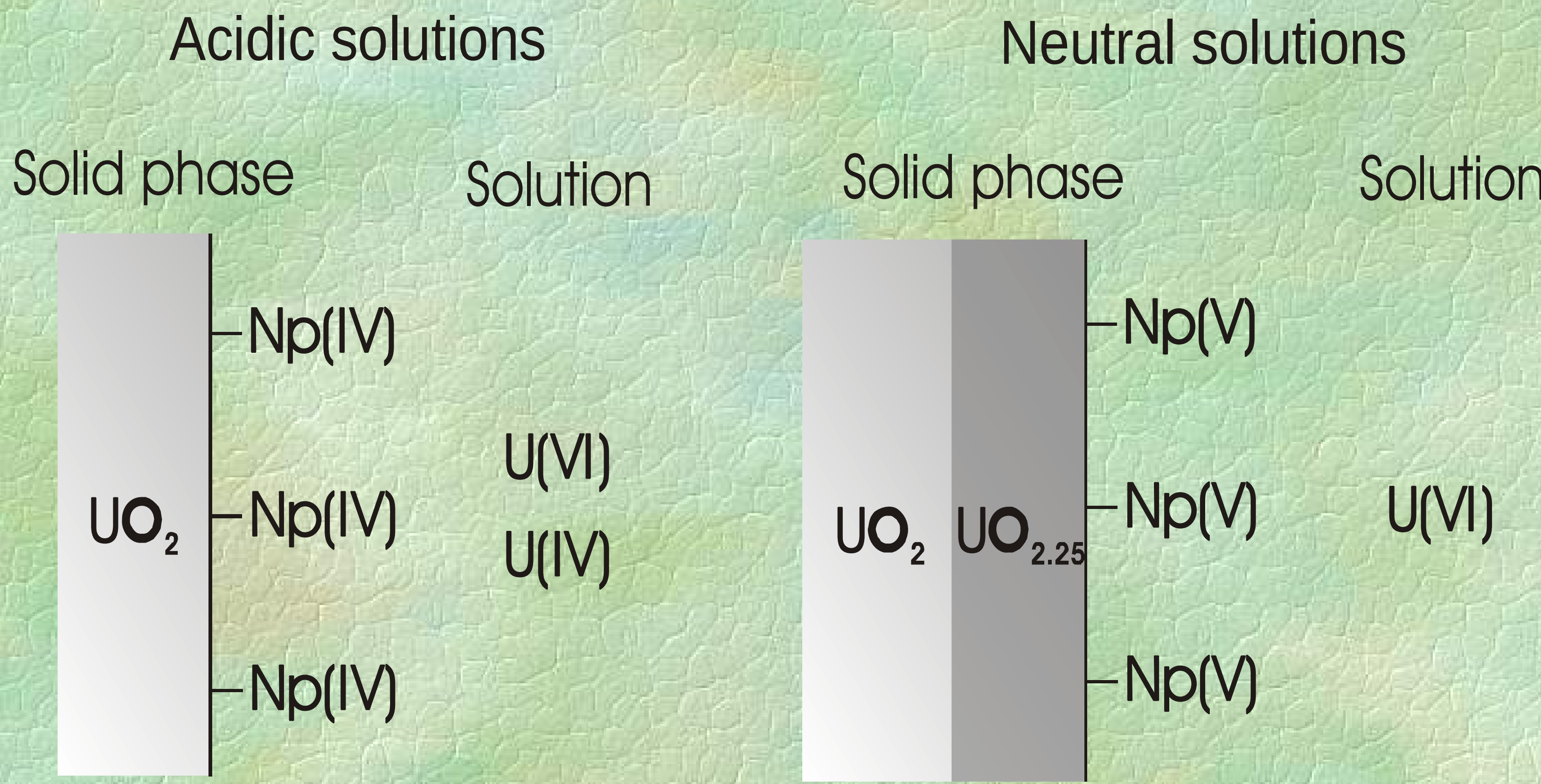
THE CONTRIBUTION OF ^{237}NP TO TOTAL SITE BOUNDARY CALCULATIONS (Taken from J. Kessler, EPRI)



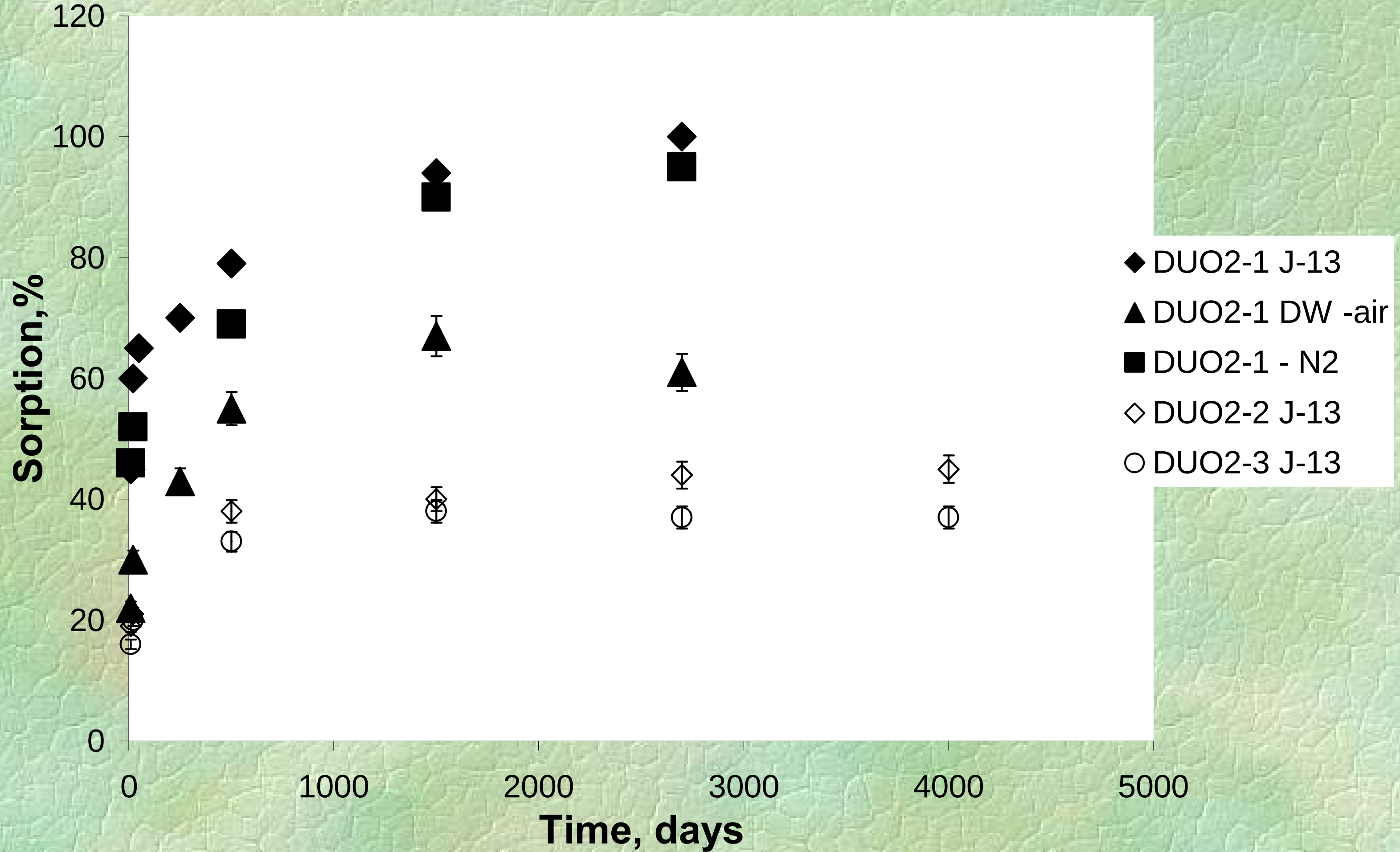
05-016R3

NEPTUNIUM SPECIATION AS A FUNCTION OF pH

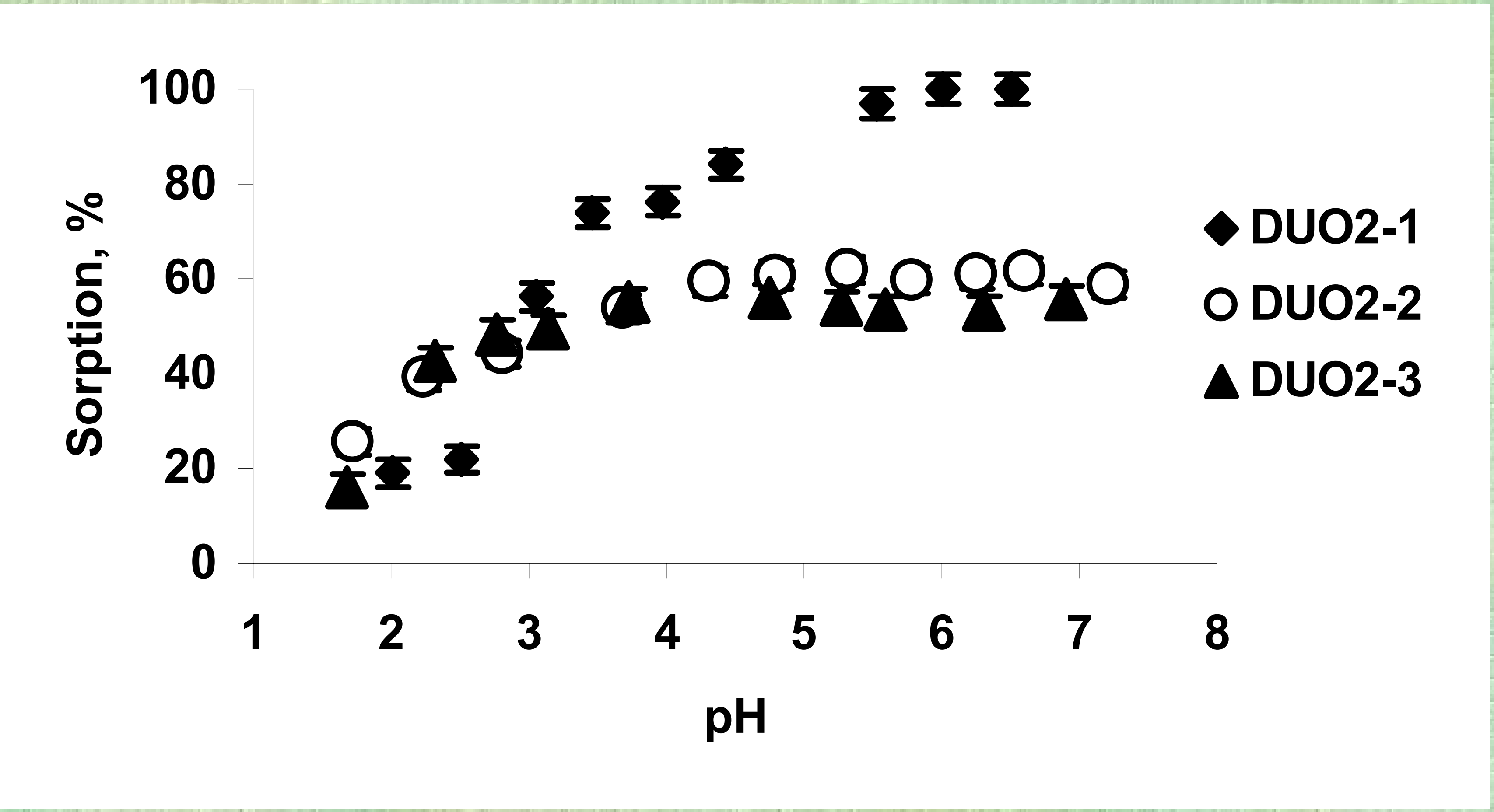
pH	Np(IV) %	Np(V) %
1.85	24	76
3.03	6	94
5.73	0	100
6.16	0	100



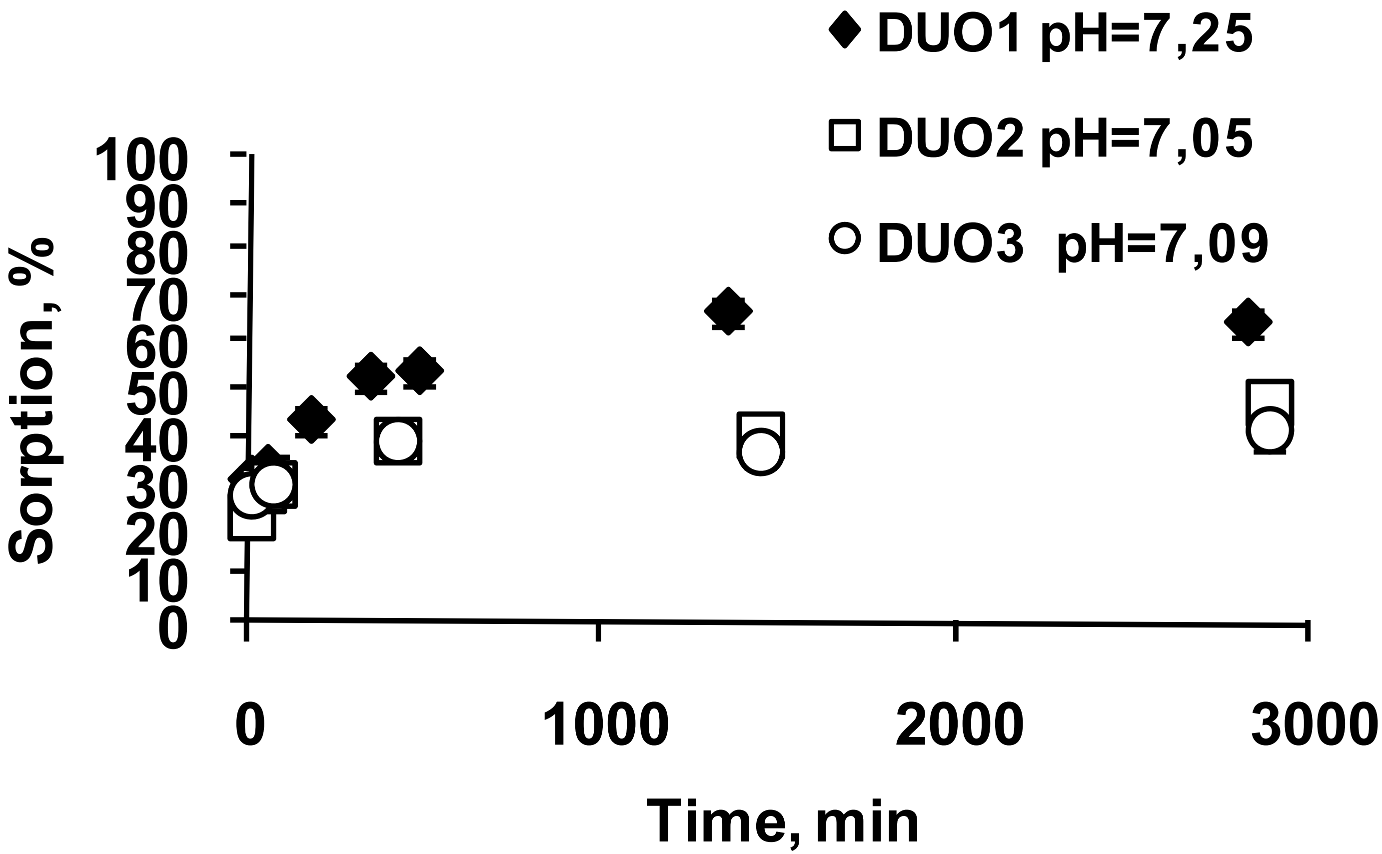
SCHEMATIC OF SPECIATION OF Np ON URANIUM SURFACES



SORPTION OF NP(V) ONTO VARIOUS DUO2 SAMPLES VERSUS TIME



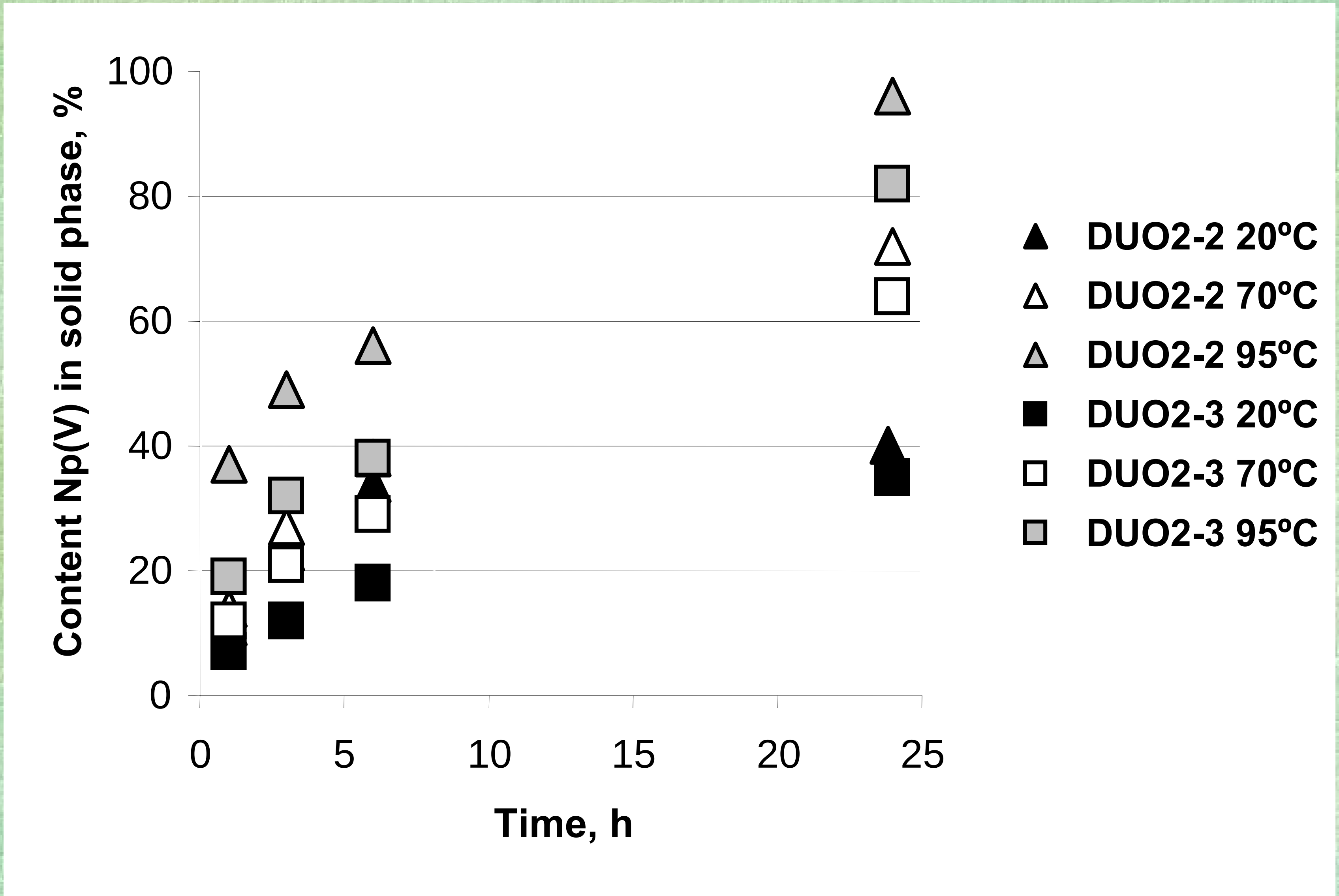
Np(V) SORPTION FROM DE-IONIZED WATER ONTO DUO2 SURFACES VERSUS pH (NITROGEN ATMOSPHERE)



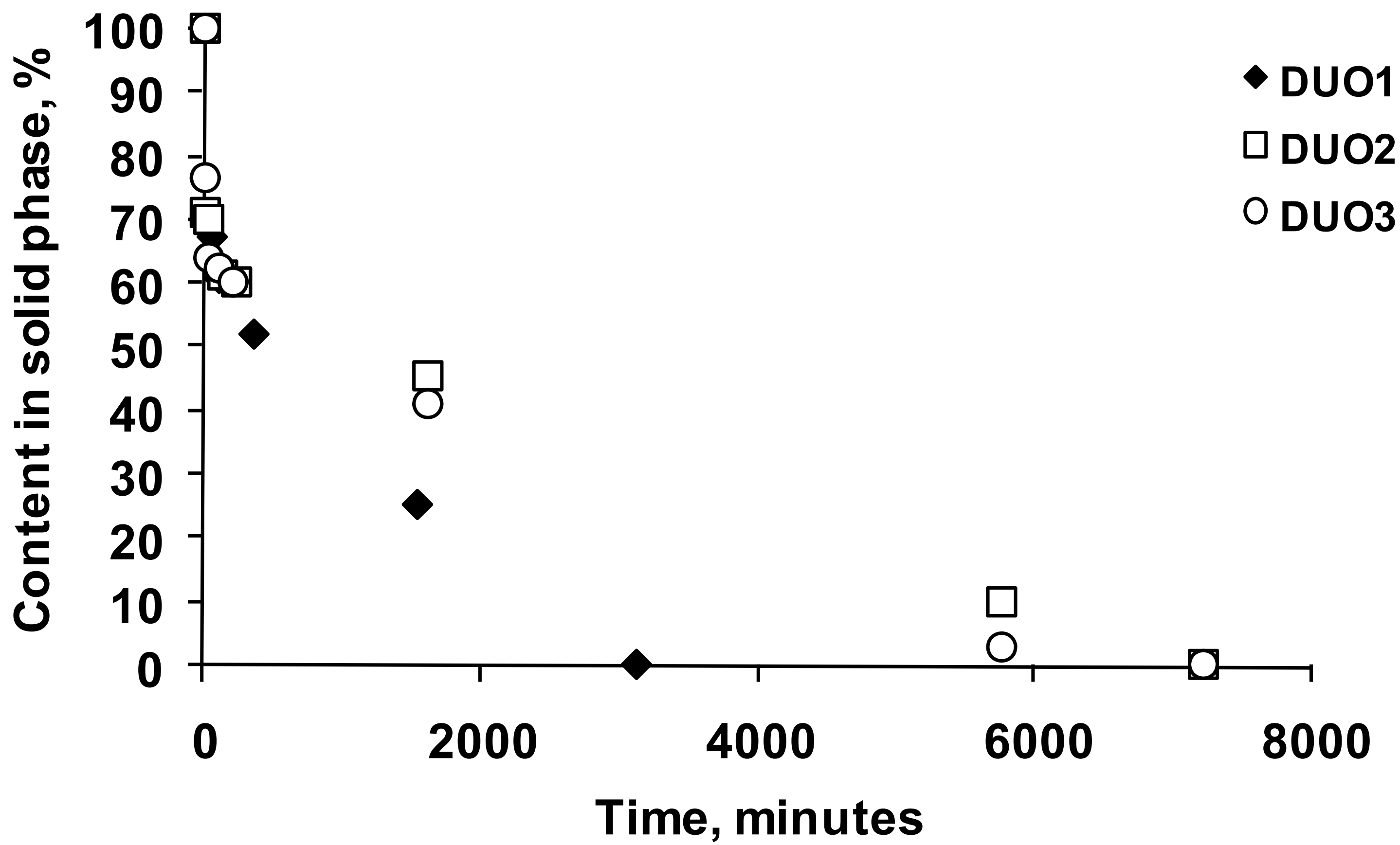
Np(V)SORPTION IN J-13 WATER ONTO DUO_2-1, DUO_2-2, DUO_2-3

SORPTION OF Np(V) IN EQUILIBRIUM SYSTEM URANIUM DIOXIDE – WATER SOLUTION.

SAMPLE	pH	MEDIUM	SORPTION %
DUO_2-1	6.02	DEIONIZED WATER (N_2)	100±3
DUO_2-1	6.05	DEIONIZED WATER (AIR)	100±3
DUO_2-1	7.25	J-13 WATER	65±3
DUO_2-2	6.75	DEIONIZED WATER (N_2)	59±3
DUO_2-2	7.05	J-13 WATER	48±3
DUO_2-3	6.59	DEIONIZED WATER (N_2)	56±3
DUO_2-3	7.09	J-13WATER	41±3



NP(V) SORPTION FROM J-13 SOLUTION ONTO DUO_2-2 AND DUO_2-3 VERSUS TIME AND TEMPERATURE



Np(V) DESORPTION FROM DUO2 SURFACE BY 0.01M HCL

TECHNETIUM DISCUSSION

TECHNETIUM SORPTION

1. TcO_4^- IS THE STABLE Tc SPECIES UNDER YM (OXIDIZING) CONDITIONS
2. TcO_4^- IS HIGHLY MOBILE IN WATER
3. AN ABUNDANCE OF IRON IN YM MAY PROVIDE A REDUCING ENVIRONMENT LOCALLY TO PRODUCE Tc(IV)

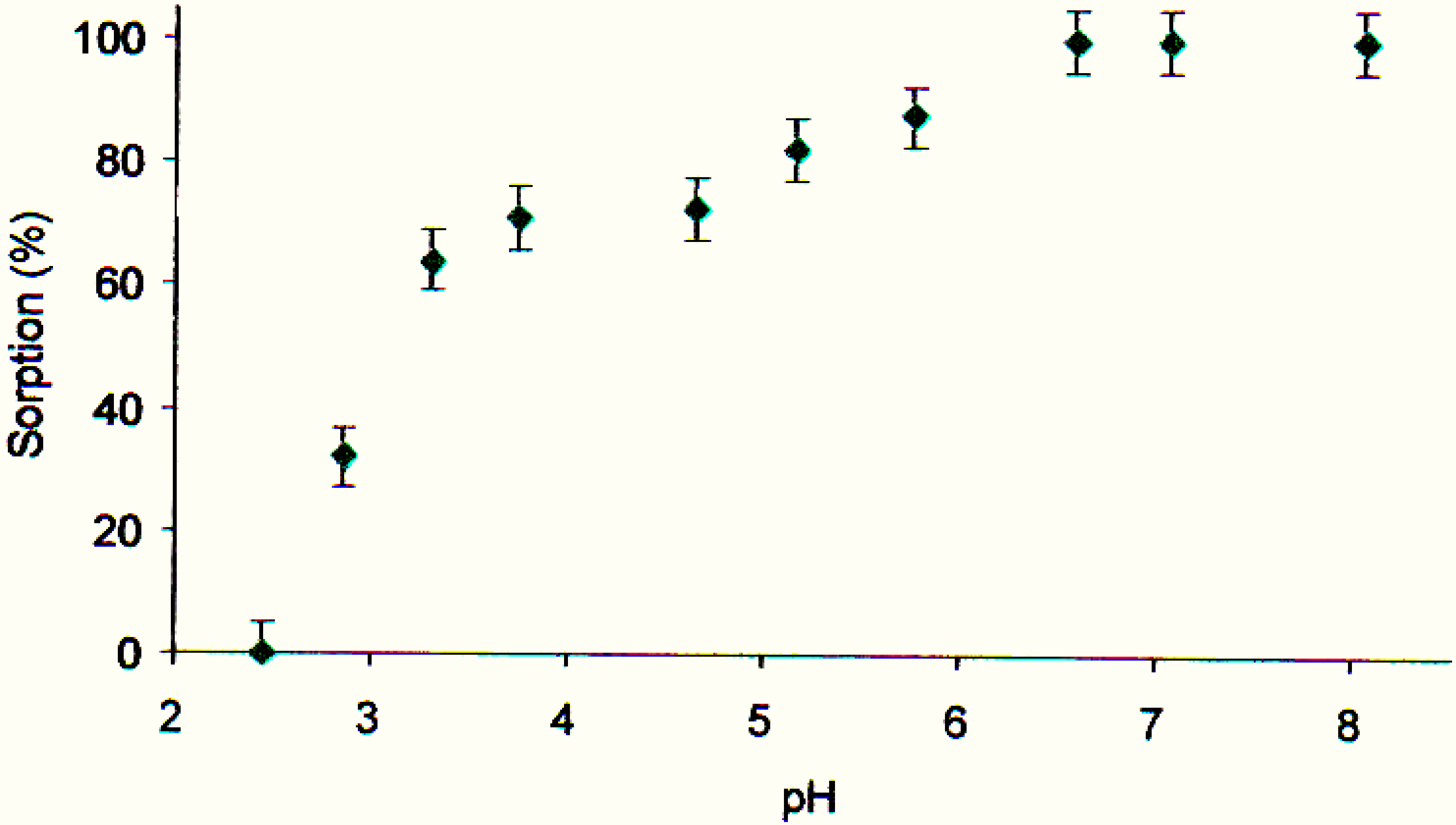
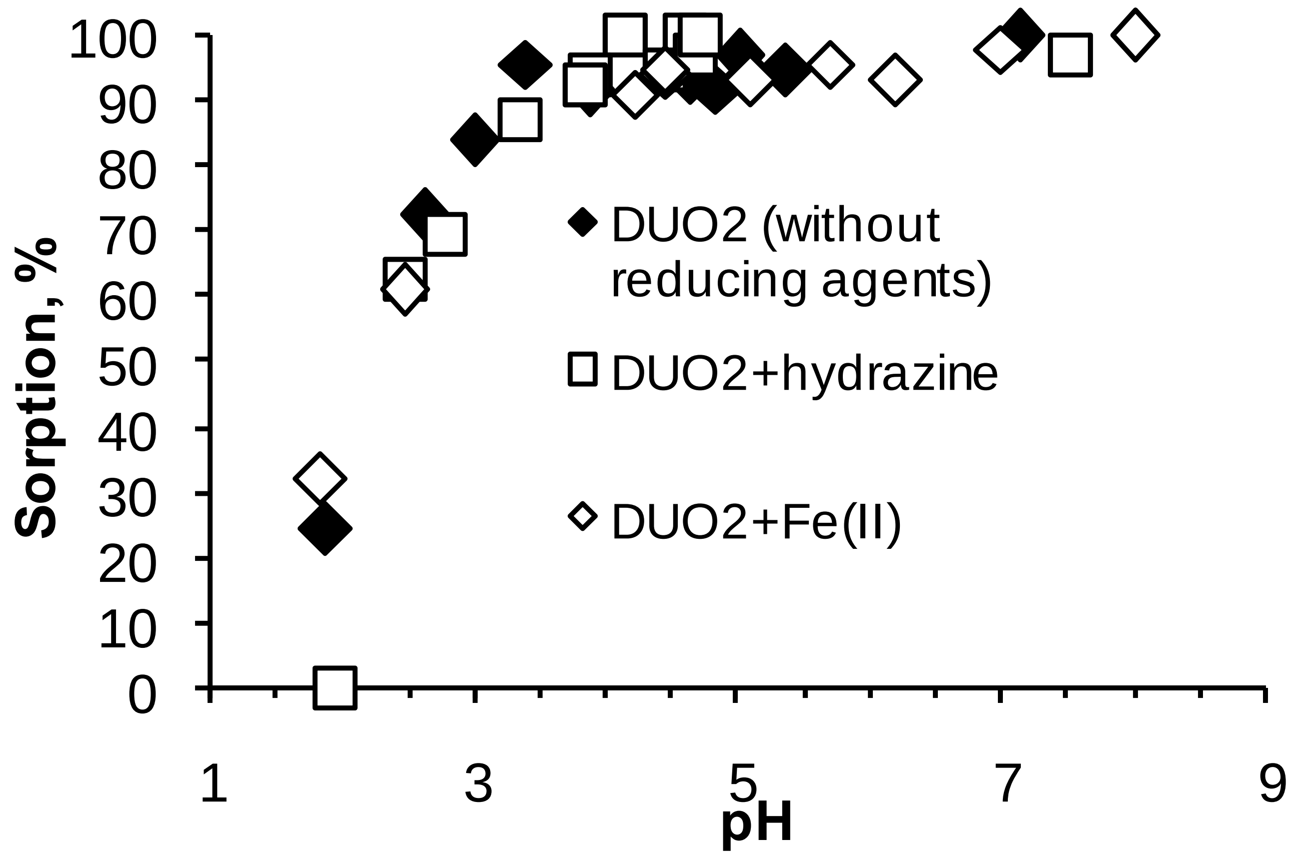


Fig. 5. Tc(IV) sorption onto DUO2 surface vs. pH (in a nitrogen atmosphere).



Tc(IV) SORPTION ONTO DUO2-1 VERSUS pH

Tc(IV) SORPTION FROM DW UNDER NITROGEN

SORPTION ON DUO_2 – 1

PHASE RATIO: 0.05 g/ml

SORPTION INCREASES AS pH INCREASES

AT pH >7 SORPTION IS ~100%

FUTURE WORK IS PLANNED ON SORPTION ON U_3O_8

THE END