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Deep Borehole Radionuclide Sequestration

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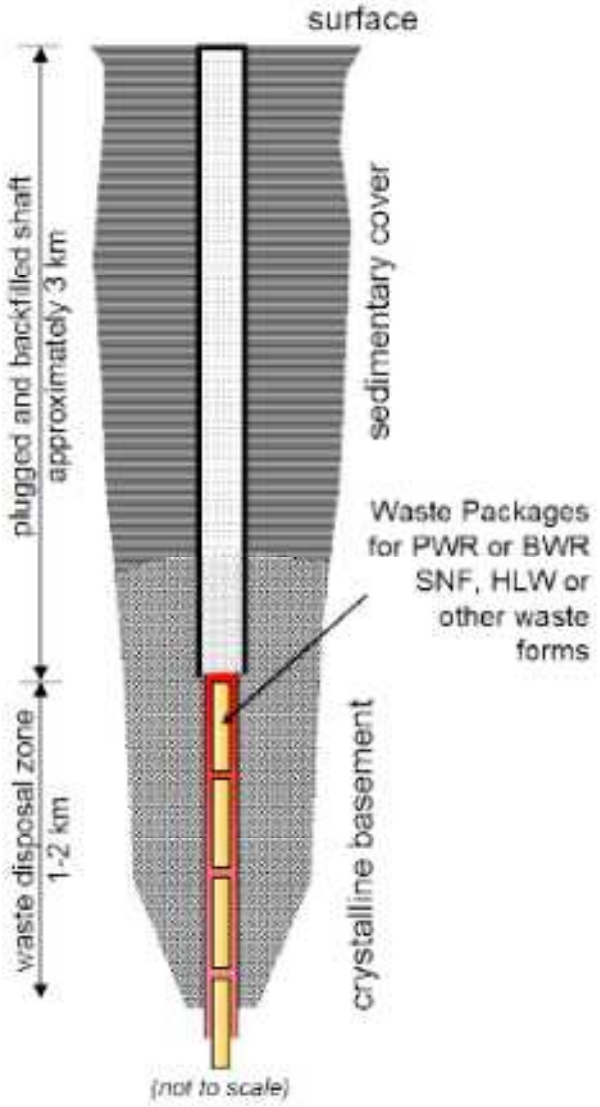
Deep Borehole Disposal Concept



[1]Deep Borehole k_ds (ml/g).

Element	$k_{d\ basement}$	$k_{d\ sediment}$	$k_{d\ bentonite}$
Am, [b]Ac, [b]Cm	50-5000	100-100,000	300-29,400
C	0-6	0-2000	5
Cs	50-400	10-10,000	120-1000
Np, [b]Pa	10-5000	10-1000	30-1000
Pu	10-5000	300-100,000	150-16,800
[c]Ra	4-30	5-3000	50-3000
Sr	4-30	5-3000	50-3000
[d]Tc	0-250	0-1000	0-250
Th	30-5000	800-60,000	63-23,500
U	4-5000	20-1700	90-1000
I	0-1	0-100	0-13

Mildly reducing conditions will persist so solubility of redox-sensitive U, Pu and Np is negligible, and most other radionuclides will sorb strongly.

^{129}I, therefore, becomes the long-term (T>10^{+6} years) dose driver.

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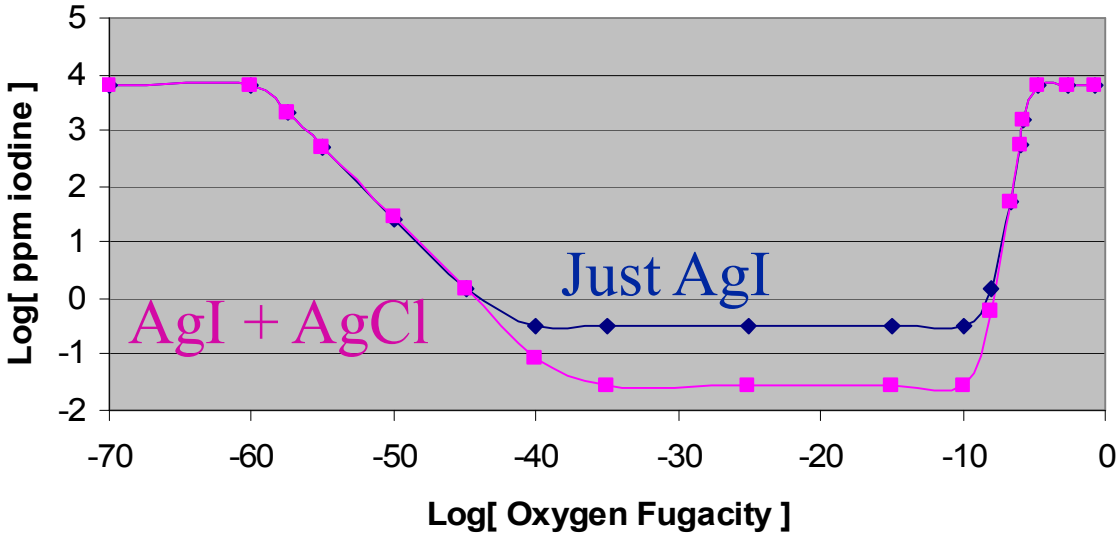
A seemingly obvious choice, AgI, will not actually restrict iodine mobility

AgI is nominally very, very insoluble: Ksp ≈ $10^{-16.1}$, but it is also redox sensitive: $2AgI + Fe \leftrightarrow 2Ag + Fe^{++} + 2I^-$.

O_2 Buffer	fO_2 (at pH 7)
$AgIO_3$ - AgI	$10^{-3.17}$
Ag metal - AgI	$10^{-40.62}$
$UO_2(OH)_2.H_2O$ - UO_2	$10^{-44.7}$
Fe_3O_4 - Fe_2O_3	$10^{-72.3}$

Multiple oxygen buffers present in a deep borehole disposal concept will reduce AgI to silver metal and release iodide ions.



←(Highest concentrations reflect amount of AgI in the model, not an upper solubility limit.)

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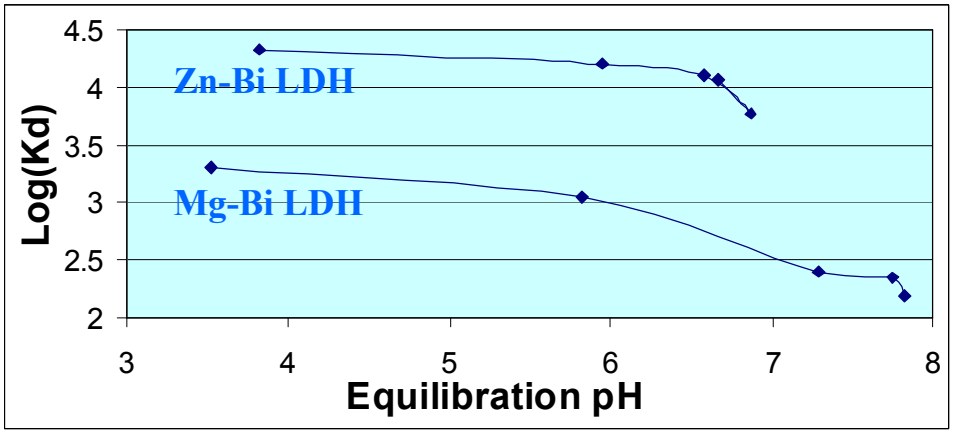
YMP and Hanford (LLW) related work suggests alternate materials can scavenge iodide

(Kd values in low ionic strength YMP- simulated groundwater)

Bi-O-I related materials are one choice.



Although different metals in the synthesis change the Kd (and crystallinity), they do not enter into the crystal structures.

(Kd I^- = 10^2-$10^{4.2}$, Kd IO_3^- = $10^{2.3}$-$10^{4.9}$

(Kd ReO_4^- = $10^{1.4}$-$10^{3.8}$, KdTcO_4^- = 10^0-$10^{2.5}$

Unusual hydrotalcites are a second choice.

	Log Kd I^-	Log Kd IO_3^-	Log Kd ReO_4^-	Log Kd TcO_4^-
$Mg_6Al_2(OH)_{18}$	1.60	0.52	0.887	-
$Co_6Al_2(OH)_{18}$	2.36	4.00	2.18	-
$Ni_6Al_2(OH)_{18}$	2.51	4.70	2.55	3.40
$Cu_6Al_2(OH)_{18}$	3.98	> 4.66	2.44	3.05
$Zn_6Al_2(OH)_{18}$	2.26	3.82	2.00	-
$Co_6Cr_2(OH)_{18}$	1.99	4.51	2.13	-
$Ni_6Cr_2(OH)_{18}$	2.63	> 4.66	2.55	3.22
$Cu_6Cr_2(OH)_{18}$	3.62	> 4.66	2.69	3.32

Bi-O-I is marginally better for I^- than hydrotalcites.

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Definition of Getter Test Conditions:

1. Ratio of total I to ^{129}I in spent fuel is about 1.3.
2. 82.4g ^{129}I in a PWR fuel assembly (YMP reference package).
3. 228 liters of fluid in the hole per PWR fuel assembly.
4. ~7% of the iodine is released without extensive oxidation of the fuel - which will not occur under reducing conditions.
5. $(82.4g) \times 1.3 \times 10^6 \times 0.07/(228 \times 10^3) =$ 32.9 ppm I
   (actual testing done with 20 ppm I to facilitate sample preparation)
6. Unlike the YMP environment tested historically, fluids in deep boreholes may be rather saline so interferences from common groundwater anions requires evaluation.
7. Because of the geothermal gradient the environment will stay warm (60^o -95^o C) after radiogenic heat has dissipated.

Step 1 is to evaluate the performance envelope of Bi-O-I getters in this environment.

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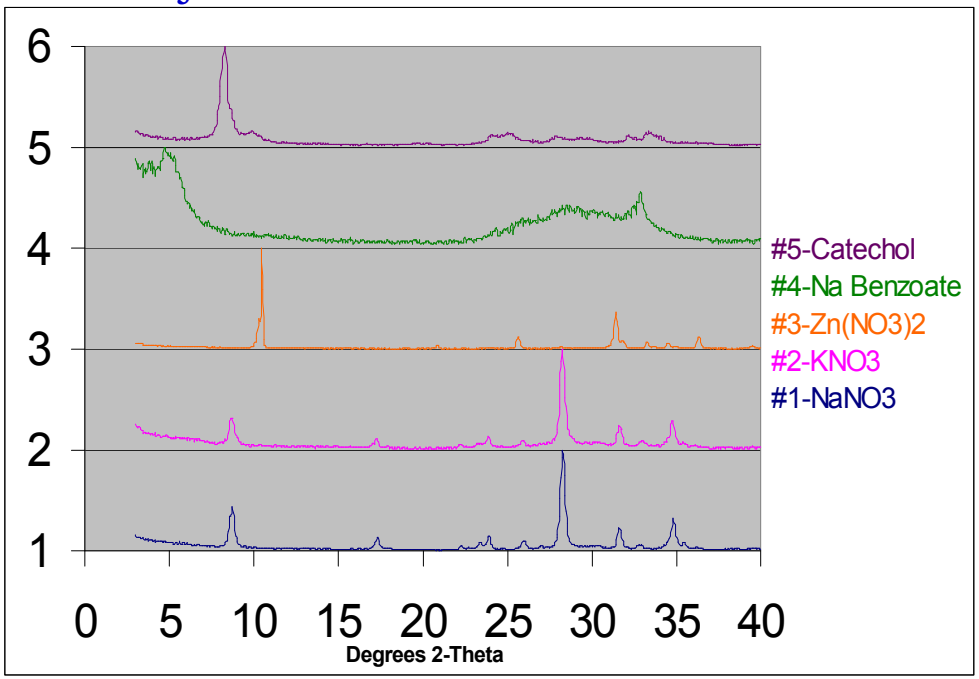
Bi-O-I getters selected for initial study

I^- Kd values - 5 getters in 3 solutions.

Synthesis Salt ↓	0.05 M NaCl	0.05 M Na_2SO_4	0.05 M $Na\ HCO_3$
#5 Catechol	35	42	46
#4 Na-Benzoate	28	2780	356
#3 $Zn(NO_3)_2$	27.1	18	74
#2 KNO_3	220	982	202
#1 $NaNO_3$	158	185	124



1. Adding various salts during synthesis gives differing affinities for I^-; KNO_3 has the best overall response.

2. $SO_4^=$ interferes less than Cl^- or HCO_3^- with I^- uptake.

3. XRD Peaks between 5° and 10° indicate that all materials have a layered crystal structure.

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Temperature Increases with Depth
25°C Kd (60° C Kd)

Synthesis Salt↓	0.05 M NaCl	0.05 M Na_2SO_4	0.05 M Na HCO_3
#5 Catechol	35 (38)	42 (42)	46 (704)
#4 Na-Benzoate	28 (34)	2780 (691)	356 (203)
#3 $Zn(NO_3)_2$	27.1 (33)	18 (42)	74 (319)
#2 KNO_3	220 (146)	982 (601)	202 (374)
#1 $NaNO_3$	158 (141)	185 (216)	124 (272)

For the best performing materials increasing the temperature to 60° C decreases Kd values somewhat where sulfate and chloride are concerned, but results in an increased Kd values in bicarbonate solutions.

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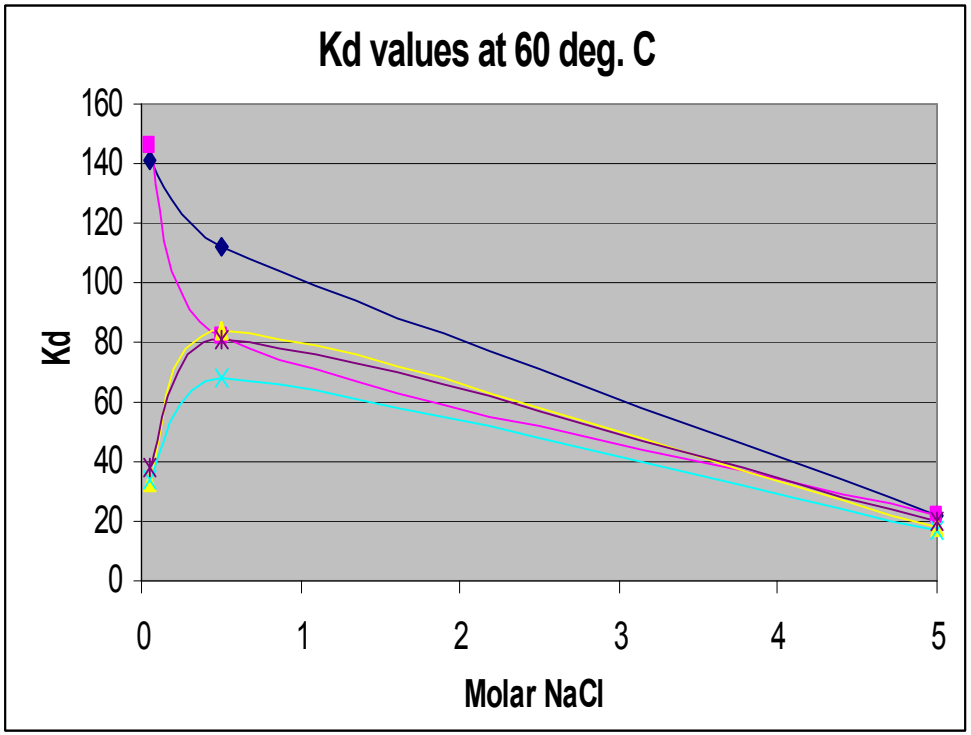
Realistically temperature increases are correlated with salinity increases:

Kd values at 60° C in various NaCl solutions

NaCl	Na-Nitrate	K-Nitrate	Zn-Nitrate	Na Benzoate	Catechol
0.05 M	141	146	33	34	38
0.5 M	112	82	84	68	81
5.0 M	22	22	18	17	20



Small Cl^- concentrations may improve poor performers but are detrimental to better ones.

Above 0.5 M NaCl materials all perform similarly, and performance decreases as Cl^- increases.

Some I-retention still occurs in 5M NaCl solutions

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Effect of Further Temperature Increases

Kd @ 90° C / Kd @ 60° C

Synthesis Salt ↓	5.0 M NaCl	0. 5 M NaCl	0. 5 M Na_2SO_4	0. 5 M Na HCO_3
#5 Catechol	0.9	1.7	7.4	0.1
#4 Na-Benzoate	1.3	1.7	1.4	0.3
#3 $Zn(NO_3)_2$	1.5	1.8	8.3	0.4
#2 KNO_3	0.6	1.8	3.4	0.2
#1 $NaNO_3$	1.4	1.7	7.4	0.4

At higher concentrations the impacts of reaching 90° C are opposite what was observed in dilute (0.05 M) brines going from 25° to 60°. HCO_3^- interferences could become particularly problematic.

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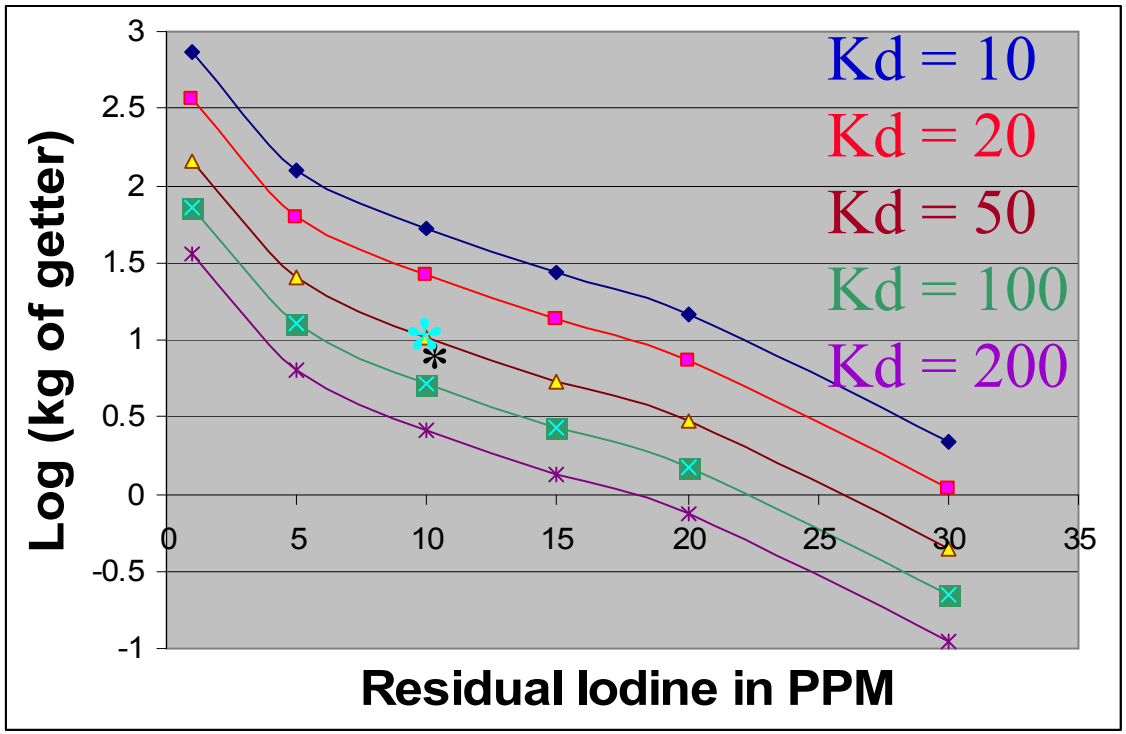
Kd's can also be used to estimate getter loadings as a function of residual I^- levels

Kd = (Solid Concentration)/(Liquid Concentration), or

Solid Concentration = Kd x (Liquid Concentration).

Kg of getter per PWR Fuel Assembly

(107.1x 0.07 g iodine in 228 liters of fluid)



Significant masses of getter are needed if the Kd is less than 50 or residual iodine is less than 10 ppm (*) is needed.

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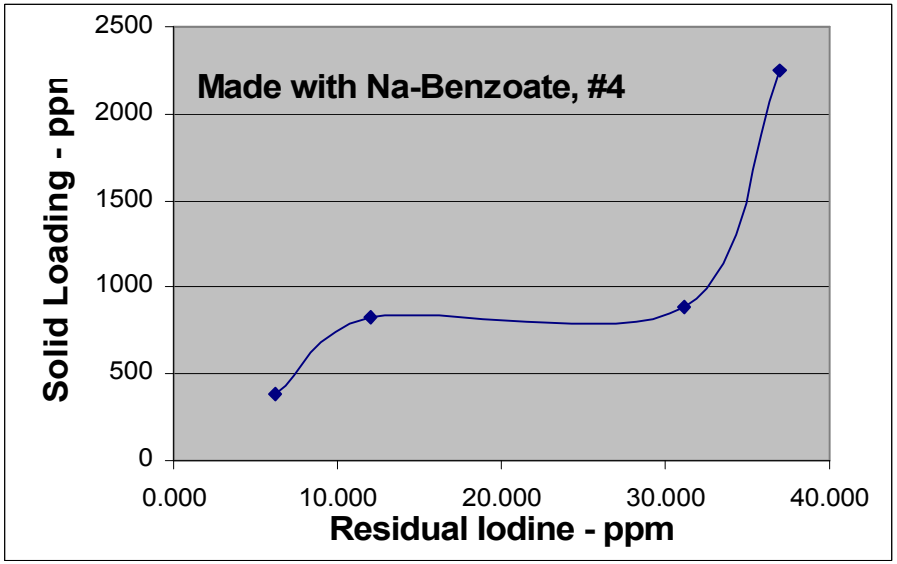
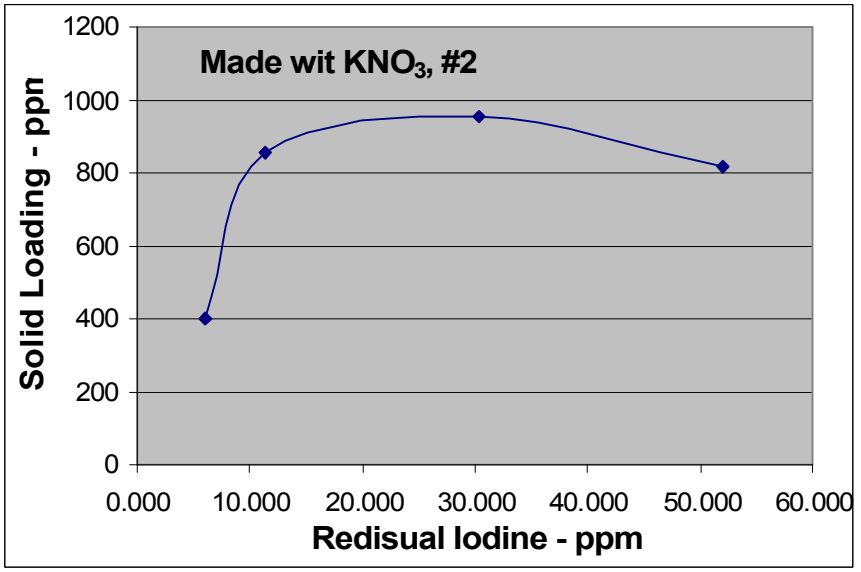
Actual Getter Loading Curves in 0.5 M NaCl at 60° C





At around 12 ppm residual I^- both getters "saturate" after picking up about 800 ppm I on the solid. This corresponds to a Kd of ≈ 66, and would require about 6 kg of getter per PWR assembly to achieve.

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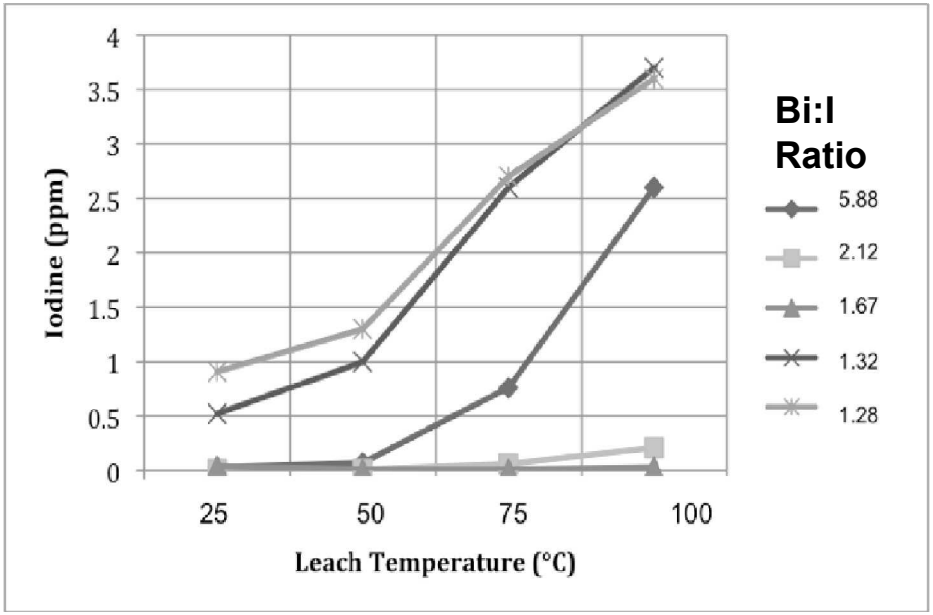
The odd behavior of the Na-benzoate-getter at high I suggests additional possibilities for iodine sequestration

- Na-Benzoate getter (#4) was very poorly crystallized initially.
- It is likely that the large step in sequestered iodine reflects crystallization of discrete iodine-containing compounds.
- Depending on Bi:I ratios discrete Bi-O-I phases have low solubilities over large temperature ranges, and may incorporate much more iodine that is sorbed on getters.



Such materials may also reflect the long-term fate of iodine initially scavenged by the getters.

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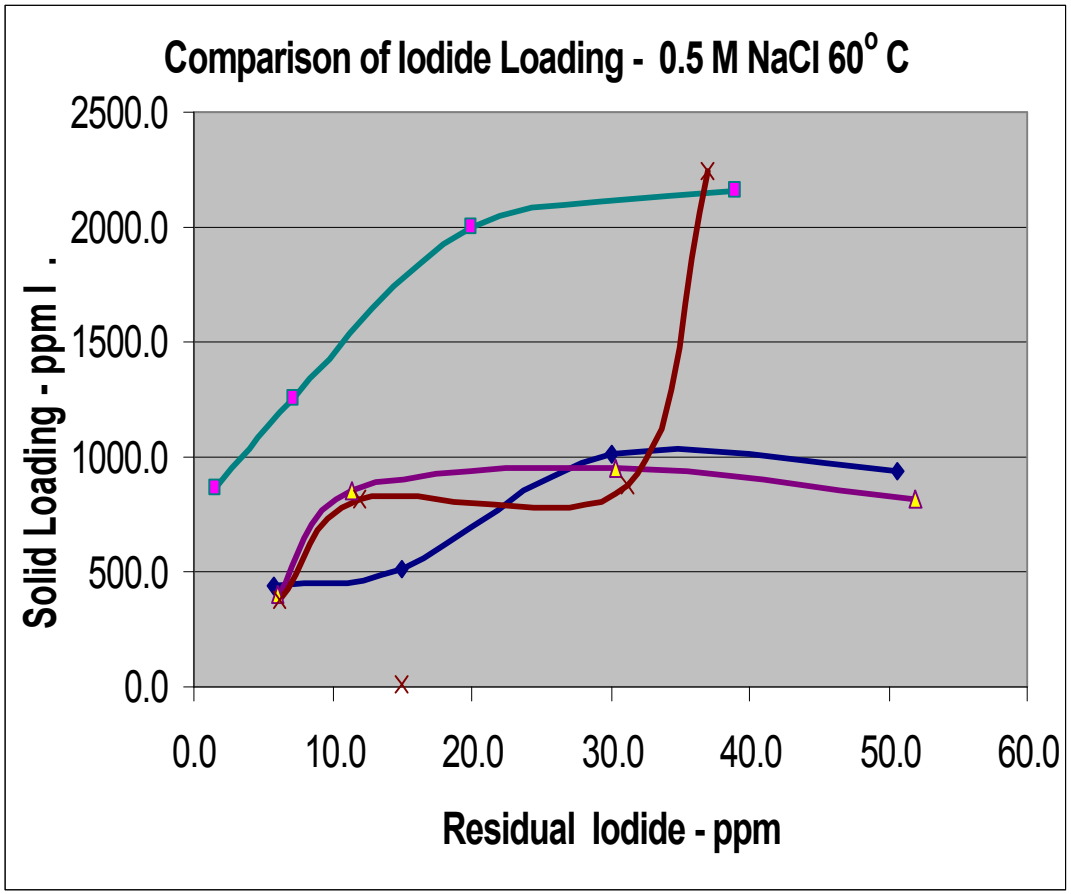
The Overall Deep Borehole Disposal Concept Also Employs Bentonite Seals

An alternate to synthesizing pure getters is to precipitate the Bi-O getter phases in the presence of bentonite.



Blue lines are clay-getter mixes, rust and purple are the previously shown loading curves for pure getters.

Again, synthesis makes a large difference in the result, and may markedly Improve performance!

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Kd Values in Acid Solutions for Various Radionuclides (0.05 g of getter in 20 ml of 20 ppm solutions of 0.5 M NaCl)

Type of Clay	g Bi-Nitrate per g Clay	pH	Log(Kd) **I**	Log(Kd) **Re**	Log(Kd) **Cs**	Log(Kd) **Nd**
Bentonite	0.13*&	3.1	1.5	1.2	1.4	1.8
Bentonite	0.13*	2.7	2.9	0.6	1.5	1.8
Bentonite	0.14	2.6	2.5	0.5	1.5	1.8
Bentonite	0.42	2.6	2.2	0.3	1.4	1.7
Kaolinite	0.13	2.6	-0.2	NS	NS	NS
Kaolinite	0.41	2.4	0.8	NS	NS	NS

NS No Soprption

* Bi-nitrate completely dissolved in dilute acetic acid prior to mixing with the clay

& Excess MgO added prior to adding Bi-nitrate solution

\# ReO4- is used as a non-radioactive surrogate for TcO4-.

Fabrication on a bentonite is much better than using kaolinite, thus the interlayer spaces of the clay participate in removal processed.

A bismuth oxide getter with clay will also retard Cs and Nd effectively, but does not work well for TcO_4^- (e.g. ReO_4^-) .

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Kd Values in Basic Solutions for Various Radionuclides (0.05 g of getter in 20 ml of 20 ppm solutions of 0.5 M NaCl)

Type of Clay	g Bi-Nitrate per g Clay	pH	Log(Kd) I	Log(Kd) Re	Log(Kd) Cs	Log(Kd) Nd
Bentonite	0.13*&	**6.8**	0.1	1.1	1.8	3.9
Bentonite	0.13*	**8.4**	2.3	0.8	1.6	4.6
Bentonite	0.14	**7.1**	2.5	1.0	1.6	4.6
Bentonite	0.42	**7.0**	2.0	0.6	1.6	3.8
Kaolinite	0.13	**7.2**	-0.2	0.5	0.0	3.8
Kaolinite	0.41	**7.2**	-0.1	0.6	0.4	3.6

NS No Soprption

* Bi-nitrate completely dissolved in dilute acetic acid prior to mixing with the clay

& Excess MgO added prior to adding Bi-nitrate solution

ReO4- is used as a non-radioactive surrogate for TcO4-.

Fabrication on bentonite substrate is still better than using kaolinite.

As expected, when sorption is involved in removing radionuclides Kd values for anions (I^-, ReO_4^-) decrease with increasing pH while Kd values for cations (Cs^+ and Nd^{+3}) increase.

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Summary and Conclusions

- **Bismuth Oxide-based getters will retard iodine mobility over the range of temperatures and groundwater chemistries expected at Deep Borehole Disposal Sites – chloride levels below 0.5 molar, and low bicarbonate waters, are preferable.**

- **The mass of material required seems prohibitive in some cases but many opportunities still remain to be explored for materials optimization.**

- **Placement of the getter in bentonite seals, rather next to waste packages, appears to be viable.**

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