Novel Inorganic Sorbent for Iodine Removal in Pump and Treat System – 15020

Tatiana Levitskaia *, Syandev Chatterjee *, James Peterson *, Natasha Pence *, Jesus Romero *

* Pacific Northwest National Laboratory

ABSTRACT

The radioisotope [129]I is one of the key risk components in the migrating subsurface plumes present in the Hanford Site vadose zone due to its long half-life, large inventory, high toxicity, and high mobility in the aquifer. Removal of iodine from groundwater in the 200 Area is an essential component for managing the Hanford Site cleanup and protecting the Columbia River.   In the subsurface aquatic environment it mainly exist as iodide, iodate, and organic derivatives of iodine. Because of different chemical properties of these species and significantly lower concentration than other constituents in the subsurface plumes their removal using commercial ion exchange resins is problematic. In addition, availability of a stable matrix for a long-term waste form for iodine is needed. Novel engineered inorganic composites that possess superior characteristics including large surface area, high sorption capacity, and good chemical-mechanical-thermal stability may potentially offer a solution. These two-in-one novel materials can be designed to serve as an efficient sorbent for the simultaneous removal of the dissimilar iodine species and a durable waste form under environmentally relevant conditions. This paper describes our current results on identification, characterization, and testing of the iodine-selective inorganic sorbents.

INTRODUCTION

There are large amounts iodine-129 ([129]I) in the groundwater under the Hanford Site—threatening the nearby Columbia River and making it a key risk component in the subsurface plumes because of its toxicity and mobility—but there are no established methods or materials that can be used to remove it. In the subsurface aquatic environment, iodine exhibits complex biogeochemical behavior and occurs in multiple chemical forms including iodate (IO_3^-), iodide (I^-), elemental iodine (I_2), and organic derivatives of iodine.   It has been previously established that the Hanford groundwater contains predominantly IO_3^-, accounting up to 84% of total iodine (Zhang et al. 2013), and its removal using commercial ion exchange resins is problematic.   To address the need for selective removal of iodine in the form of iodate (IO_3^-) from the Hanford Site subsurface water, readily available (economic and easy-to-synthesize) inorganic solid-state composite materials have been investigated.

The structures of the inorganic composite materials investigated in this study are similar to layered double hydroxides (LDHs), a class of materials that can be thought of as anionic clays consisting of ordered, positively charged sheets intercalated with interchangeable hydrated anions.   Originally, LDH structures were derived from the mineral brucite, $Mg(OH)_2$, in which a fraction of the Mg^{2+} ions are substituted for trivalent metal ions (Rojas et al. 2011).   LDH sorbents have been previously demonstrated as promising materials for the removal of harmful oxyanions such as arsenate, chromate, perchlorate, pertechnetate, iodate, and others from contaminated and waste waters (Goh et al. 2008 and references therein).   These materials typically consist of two-dimensional nano-structured divalent cations, octahedrally coordinated by hydroxide ions, where some of the divalent cations are isomorphously replaced by tri- or tetravalent cations.   Such a replacement results in the charged sheets, where the net positive charge is compensated by anions in the interlayer region.   LDH materials can be represented by the general formulae

$[M_{1-x}^{2+}M_x^{m+}(OH)_2]^{x+}(A^{n-})_{x/n}yH_2O$, where M^{2+} is a divalent cation and M^{m+} is a trivalent or tetravalent cation; the value of x is equal to the molar ratio of $M^{m+}/(M^{2+} + M^{m+})$, whereas A^{n-} is the interlayer anion. The identities of M^{2+}, M^{m+}, x, and A^{n-} can be varied over a wide range, giving rise to a large class of isostructural materials with physicochemical properties that can be tailored to achieve high selectivity and capacity for the uptake of an anion of interest (Wang and Gao 2006).   Several studies have demonstrated potential of Mg^{2+}/Al^{3+}-based LDH materials with different parent anion for the removal of I^- and IO_3^- anions from contaminated water samples (Curtius and Kattilparampil 2005; Chen et al. 2012; Toraishi et al. 2002).

Our previous proof-of-concept experiments demonstrated that the selective IO_3^- uptake from the Hanford groundwater is feasible using synthesized candidate composite materials in our laboratory (Levitskaia et al. 2014).   A large library of the composite materials was obtained and tested for the IO_3^- affinity.   It was discovered that M(II)-Cr(III) composites exhibited preferential IO_3^- uptake from the Hanford groundwater at high sorption capacity.   Our experimentation suggested that the selectivity of this uptake can be in part attributed to the reduction of IO_3^- to I^-.

The objective of this work was to expand the range of materials promising for iodine removal from the Hanford groundwater with the focus on non-Cr(III) based composites.   For this purpose, we selected two Ag- and Bi-based materials and compared their performance with the Cr(III) composite in the systematic batch contact testing.

EXPERIMENTAL

Synthesis of the Composite Materials
The general synthetic procedure included weighing the appropriate starting transition metal salts for the specific LDH synthesis.   The compounds then were combined in ~50 mL deionized (DI) water.   The solution was stirred for about an hour and the initial pH measured, then Na(K)OH was added to solution under stirring until the desired pH was achieved.   Some of the composite materials were aged at alkaline pH under vigorous stirring.   The mixture was then transferred to a Teflon-lined autoclave for hydrothermal synthesis at 110 °C for 72 hours in a oven to yield the LDH aggregate.   The set temperature variation was within ± 5 °C.   The resulting composite was filtered from the solution under gravity and allowed to air dry.   The dried compound was then ground into a fine powder with mortar and pestle, rinsed with water until the filtrate ran clear, and air-dried before being ground into a fine powder.

Hanford Groundwater Used in the Testing
To test the performance of the composite materials for IO_3^- and I^- removal from the solutions containing potentially interfering constituents, Hanford groundwater from well 299-W19-36 was used.   The major inorganic constituents present in the groundwater are listed in Table 1 (Mattigod et al. 2010).   In this work, the total iodine concentration in the groundwater measured by inductively coupled plasma-mass spectrometry (ICP-MS) was determined to be 8.6 ± 0.9 µg/L.

TABLE 1. Concentrations of the selected specified constituents in 299-W19-36 source water taken from Mattigod et al. 2010.

Constituent	Concentration (µg/L)	Molar Mass	Molarity
Barium	113	137.3270	8.23E-07
Calcium	122,000	40.0780	3.04E-03
Chloride	181,000	35.4515	5.11E-03

Total Cr	17.3	51.9961	3.33E-07
Cr(VI)	0.05	51.9961	9.62E-10
Magnesium	36,400	24.3050	1.50E-03
Molybdenum	65.9	95.9400	6.87E-07
Nitrate	317,000	62.0049	5.11E-03
Potassium	7,010	39.0983	1.79E-04
Sodium	118,000	22.9898	5.13E-03
Sulfate	50,000	96.0600	5.21E-04
Strontium	618	87.6200	7.05E-06
Tin	216	118.7100	1.82E-06
Alkalinity ($CaCO_3$)	116,000	100.0869	1.16E-03
Uranium	174	238.0289	7.31E-07
Total iodine	8.6 ± 0.9[a]	127	6.8E-08
(a) Measured in this work.			

Raman Screening of IO_3^- Uptake by Composite Materials

The affinity of the synthesized sorbents for IO_3^- was initially assessed by monitoring IO_3^- uptake from the Hanford groundwater using Raman spectroscopy.   An InPhotonics Raman system operating with MoleCue software and equipped with a 670 nm laser and fiber optic and an InPhotonics probe was used for the continuous monitoring of IO_3^- sorption.   Typical sample preparation involved mixing 100 mg of LDH with 1 mL of 0.025M KIO_3 solution in DI water in a glass vial.   The vial was then centrifuged at 4,000 rpm for 10 to 30 minutes until the sorbent settled at the bottom, leaving a clear solution at the top, which was monitored by Raman spectroscopy.   An initial spectrum of the 0.025M KIO_3 and a spectrum of the groundwater using identical glass vials served as the reference.   In a typical experiment, continuous monitoring of the solution was done for 180 acquisitions, each with 10-second integration time, with a 50-second delay between measurements.   After 3 hours of monitoring, the solid composite material was re-suspended in the solution and the sample was stirred overnight (unless otherwise indicated), and Raman measurements were continued the next day after re-centrifuging the samples. The spectra were baseline-corrected and normalized to the water band.   A water spectrum was subtracted from each sample spectrum.   The Raman intensity of the IO_3^- band at 801 cm^{-1} was used to quantify the IO_3^- uptake by the composite material.

Batch Contact Testing

Five composite materials, including Ni(II)-Cr(III), Co(II)-Cr(III), Ag(I)-Al(III)-Zr(IV), Ni(II)-Bi(III)-Al(III), and Co(II)-Bi(III)-Al(III), were selected for the systematic batch contact experiments with the groundwater containing 15 to 130,000 µg/L concentration of either IO_3^- or I^- adjusted by either KIO_3 or NaI.   For each batch contact sample, ~70 mg of composite material was weighed and contacted with 15 mL of the test solution.   The samples were placed in the 20 mL glass scintillation vials, agitated for 24 hours at room temperature, and centrifuged.   The initial pre-contact feed and separated post-contact solutions were subjected to the ICP-MS analysis to determine IO_3^- or I^- concentrations.   Post-contact solutions were also analyzed by ICP-OES or ICP-MS for the concentration of metal comprising tested composite materials.

To quantify the efficiency of iodine removal, the distribution coefficient, K_d (mL/g), was calculated by using the following equation:

$$K_d = \frac{C_i - C_e}{C_e} \times \frac{V_{GW}}{W_C}$$

where C_i is the initial concentration of iodine in the groundwater, C_e is the equilibrium concentration of iodine in the post-contact groundwater, V_{GW} is the volume of iodine solution in groundwater in milliliters, and W_C is the weight of the dry composite material in grams.   Iodine analysis was done using ICP-MS. The instrument was calibrated using high-purity National Institute of Standards and Technology (NIST)-traceable calibration standards to generate calibration curves and verify continuing calibration during the analytical run.   All standard preparations and sample dilutions were done using a 0.5% Spectrasol solution CFA-C to prevent buildup/memory of iodine in the ICP-MS introduction system.

RESULTS AND DISCUSSION

To rapidly evaluate the synthesized composites for their affinity for IO_3^-, the Raman scoping experiments were conducted using Hanford groundwater from well 299-W19-36.   No stirring was applied during the first 3 hours of contact, and therefore the IO_3^- uptake was diffusion-limited.   Table 2 compares the 24-hour IO_3^- sorption performance of the representative composite materials.

TABLE 2. Selected results of the scoping evaluation of the IO_3^- uptake by the synthesized composite materials using Raman spectroscopy.   In the IO_3^- tests, ~100 mg of the composite material was contacted with 1 mL of 0.025 M IO_3^- solution in groundwater for 24 hours.

Sample ID	Composite Material	IO_3^- Percent Sorption from Groundwater
1	Ag(I)-Al(III)-Zr(IV) pH=8 Aged/non-aged	>99.5
2	Ni(II)-Cr(III) pH=8 Non-aged	>99.5
3	Mn(II)-Cr(III) pH=8 Aged/non-aged	>99.5
4	Cu(II)-Bi(III)-Al(III) pH=9 Aged	>99.5
5	Co(II)-Bi(III)-Al(III) pH=8.5 Aged	>99.5
6	Cu(II)-Cr(III) pH=12 Non-aged	>99.5
7	Ag(I)-Ni(II)-Al(III)-Zr(IV) pH=8 Non-aged	>99.5
8	Ag(I)-$C_{16}H_{36}$NCl pH=8 Non-aged	>99.5
9	Zn(II)-Cr(III) pH=12 Non-aged	>99.5
10	Ni(II)-Cr(III) pH=12 Non-aged	98
11	Ni(II)-Bi(III)-Al(III) pH=8 Aged	96
12	Cu(II)-Ni(II)-Al(III) pH=8 Aged	94
13	Ni(II)-Fe(III) pH=8 Aged	93
14	Co(II)-Cr(III) pH=8 Non-aged	92
15	Co(III)-Fe(III) pH=8 Aged	87
16	Ni(II)-Al(III)-Fe(III) pH=8 Aged	66
17	Ni(II)-Fe(III) pH=8, 12 Aged	62-64
18	Ni(II)-Al(III) pH=8 Aged	32
19	Mg(II)-Al(III) pH=12 Non-aged	27
20	Zn(II)-Al(III)-Zr(IV) pH=12 Non-aged	20 – 25
21	Zn(II)-Al(III) pH=9 Non-aged	24
22	Zn(II)-Fe(III) pH=9 Non-aged	20
23	Ni(II)-Al(III)-Zr(IV) in 0.5M PO_4 Aged	19
24	Cu(II)-Al(III) pH=12 Non-aged	15
25	Co(II)-Fe(III) pH=12 Aged	15
26	Cu(II)-Fe(III) pH=12 Aged	13

Table 2 reveals a few systematic trends.   Most notably, it was observed that three types of composites based on the Cr(III), Ag(I), and Bi(III) metals exhibited nearly quantitative uptake of IO_3^-.   The finding that M(II)-Cr(III) composites efficiently sorb IO_3^- is consistent with our previous results (Levitskaia et al. 2014).   Ag(I)-based composites represent the class of materials with a high affinity to both IO_3^- (Table 2) and I^- (Mattigod et al. 2003 and references therein).   The high affinity of the Ag-impregnated materials for iodine is well-established and is usually attributed to the consideration that soft cations (Ag^+) tend to bind strongly with soft anions (low electronegativity, high polarizability, prone to oxidation) such as iodide (Faghihian et al. 2002; Hoskins and Karanfil 2002).   The efficient IO_3^- uptake by the Ag(I)-based composites can in part be attributed to the reduction of IO_3^- to I^- and formation of the strongly retained AgI.   Bi(III) composites represent another class of materials with the high affinity to IO_3^-.   The Bi(III)-containing layered composites were first obtained by Tsuji et al. (2000) as selenium sequestration agents.   Although these composites possess layered arrangement, they lack octahedral structure and do not belong to the hydrotalcite mineral family as native LDH material.   Bi(III) materials were later synthesized and tested to identify "getters" to mitigate possible leaks beneath high-level waste packages in the repository planned by the Yucca Mountain Project (Krumhansl et al. 2006).   Some composites were demonstrated to exhibit high affinity to both IO_3^- and I^- when contacted with the low sodium (0.0025M) and low nitrate (0.00014M) Yucca Mountain groundwater J-13 simulant solution.   Our results are consistent with these findings.   The hydrotalcite-like layered Bi(III) material has been previously suggested as a durable iodine waste form that incorporates IO_3^- and I^- between Bi oxide layers in the lattice (Krumhansl and Nenoff 2011).

Based on these preliminary scoping results, materials exhibiting efficient IO_3^- sorption and fast kinetics including Co(II)-Cr(III), Co(II)-Bi(III)-Al(III), and Ag(I)-Al(III)-Zr(IV) were down selected for the systematic batch contact experiments to test iodine removal from the Hanford groundwater. Figure 1 shows the Raman measurements monitoring the IO_3^- uptake by the composite materials selected for the batch contact testing, including Co(II)-Cr(III), Co(II)-Bi(III)-Al(III), and Ag(I)-Al(III)-Zr(IV).
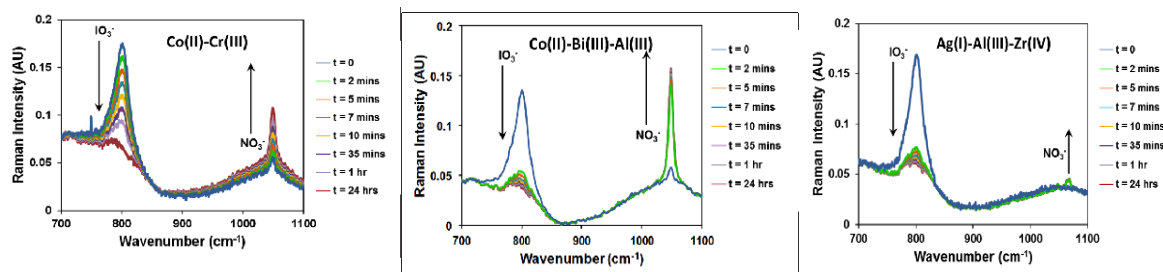

FIGURE 1. Time-dependent IO_3^- uptake by the Co(II)-Cr(III), Co(II)-Bi(III)-Al(III), and Ag(I)-Al(III)-Zr(IV) composite materials selected for the systematic batch contact testing.   The IO_3^- uptake is monitored by the time reduction of the Raman intensity of 801 cm^{-1} iodate band upon addition of 100 mg composite to 1 mL of 0.025 M IO_3^- solution.   Spectrum taken at t = 0 corresponds to 25 mM IO_3^- solution before the addition of the composite material.   The broad spectral feature observed in the 770 to 830 cm^{-1} range is due to the glass absorption.   The small band at 1049 cm^{-1} corresponds to the NO_3^- anion present in the Hanford groundwater.

In the batch contact samples, the same weight of the composite (approximately 70 mg) and the groundwater volume (15 mL) were used so that solution-to-solid ratio was 214.3 in all samples.   The

concentration of IO_3^- or I^- in the Hanford groundwater collected from well 299-W19-36 was adjusted in the 15 to 130,000 µg/L range.   In addition, non-modified groundwater was subjected to batch contact testing; the total iodine concentration in groundwater was determined to be 8.6 ± 0.9 µg/L by ICP-MS analysis.   The batch contact samples were placed in the glass scintillation vials, agitated for 24 hours at room temperature, and centrifuged.   The contact solutions were separated from the composite material and subjected to the ICP-MS analysis to determine iodine concentration.   The iodine batch sorption results are summarized in Tables 3 – 5.

TABLE 3. Iodine uptake from the Hanford groundwater (well 299-W19-36) by the Co(II)-Cr(III) composite material.

Sorbent weight (g)	Solution volume (mL)	Iodine concentration (µg/L)		$K_d(I)$ (mL/g)	Iodine sorbed (µg/g)
		Initial	Final		
Iodate IO_3^-					
0.0704	15	130,000	48,100	363	17,500
0.0710	15	96,500	32,100	424	13,600
0.0707	15	62,000	18,300	507	9,270
0.0698	15	32,600	7,340	740	5,430
0.0706	15	12,500	2,420	885	2,140
0.0697	15	10,100	1,970	888	1,750
0.0701	15	6,400	1,190	937	1,120
0.0701	15	2,330	375	1,120	217
0.0711	15	1,240	212	1,020	185
0.0706	15	1,010	137	1,350	108
0.0715	15	613	99	1,090	418
0.0697	15	130	18.2	1,320	24
0.0718	15	74	8.9	1,540	14
Iodide I^-					
0.0707	15	120,000	83,200	94	7,810
0.0698	15	79,400	58,400	77	4,510
0.0693	15	54,900	28,600	199	5,693
0.0709	15	27,800	2,780	1,900	5,300
0.0710	15	13,000	17.6	156,000	2,740
0.0709	15	10,800	5.7	401,000	2,280
0.0712	15	8,710	12.5	147,000	1,830
0.0703	15	5,480	5.5	212,000	1,170
0.0713	15	2,910	5.4	113,000	611
0.0707	15	1,050	4.3	51,000	222
0.0700	15	837	2.3	79,000	179
0.0719	15	584	2.1	57,000	121
0.0709	15	292	2.2	28,000	61
0.0700	15	116	1.8	13,400	24
0.0703	15	59	1.6	7,800	12
Total iodine in unmodified groundwater					
0.0691	15	8.6 ± 0.9	1.5	1,058	1.6
0.0712	15		1.5	1,010	1.5

TABLE 4. Iodine uptake from the Hanford groundwater (well 299-W19-36) by the Co(II)-Bi(III)-Al(III) composite material.

Sorbent weight (g)	Solution volume (mL)	Iodine concentration (μg/L)		$K_d(I)$ (mL/g)	Iodine sorbed (μg/g)
		Initial	Final		
Iodate IO$_3^-$					
0.0684	15	98,200	43,300	278	12,040
0.0680	15	65,200	44,400	103	4,590
0.0608	15	32,800	17,900	184	3,290
0.0686	15	16,200	6,540	323	2,110
0.0700	15	12,400	4,980	319	1,590
0.0692	15	9,870	3,190	454	1,450
0.0693	15	6,180	1,670	585	976
0.0693	15	3,100	634	842	534
0.0678	15	1,340	234	1,050	245
0.0678	15	960	132	1,390	183
0.0678	15	645	81	1,530	125
0.0679	15	132	23	1,050	94
0.0680	15	70	8.1	1,700	24
0.0677	15	38.4	3.6	2,120	14
0.0685	15	17.5	2.2	1,520	7.7
Iodide I$^-$					
0.0682	15	86,400	59,100	102	6,000
0.0677	15	57,000	34,800	141	4,920
0.0704	15	28,300	14,400	206	2,960
0.0688	15	11,400	3,990	405	1,620
0.0690	15	8,680	2,860	442	1,270
0.0678	15	5,640	2,110	370	781
0.0682	15	2,960	705	704	496
0.0677	15	1,100	200	997	199
0.0693	15	561	86.9	1,180	182
0.0679	15	279	11.9	4,960	103
0.0676	15	113	2.8	8,900	59
0.0703	15	59	1.80	6,770	24
0.0691	15	31.6	2.46	2,570	12
0.0678	15	16.1	2.30	1,330	6.3
Total iodine in unmodified groundwater					
0.0679	15	8.6 ± 0.9	1.80	857	1.5
0.0702	15		1.75	829	1.5

TABLE 5. Iodine uptake from the Hanford groundwater (well 299-W19-36) by the Ag(I)-Al(III)-Zr(IV) composite material.

Sorbent weight (g)	Solution volume (mL)	Iodine concentration (µg/L)		$K_d(I)$ (mL/g)	Iodine sorbed (µg/g)
		Initial	Final		
Iodate IO_3^-					
0.0707	15	130,000	6,330	4,150	26,200
0.0697	15	96,500	6,060	3,210	19,500
0.0702	15	62,000	6,900	1,710	11,800
0.0710	15	32,600	6,490	850	5,520
0.0714	15	14,900	11,500	62	714
0.0703	15	12,500	10,300	46	469
0.0712	15	10,100	7,710	65	504
0.0701	15	6,400	4,880	67	325
0.0698	15	3,100	2,280	77	176
0.0710	15	1,240	801	116	93
0.0707	15	1,010	590	151	89
0.0700	15	613	444	82	36
0.0694	15	2,160	1,870	34	63
0.0720	15	130	76	146	11
0.0704	15	74	39	190	7.5
0.0707	15	38	17	282	4.6
0.0701	15	18	6.7	343	2.3
Iodide I^-					
0.0710	15	120,000	<50[a]	>507,000[a]	>26,000[a]
0.0697	15	79,400	<50[a]	>342,000[a]	>17,000[a]
0.0698	15	54,900	<50[a]	>236,000[a]	>12,000[a]
0.0700	15	27,800	<50[a]	>119,000[a]	>6,000[a]
0.0706	15	13,000	<50[a]	>55,000[a]	>2,800[a]
0.0694	15	10,800	<50[a]	>46,000[a]	>2,300[a]
0.0714	15	8,710	2.12	863,000	1,830
0.0707	15	5,480	2.01	578,000	1,160
0.0712	15	2,910	<2.5[b]	>250,000[b]	>610[b]
0.0717	15	837	1.49	117,000[a]	226
0.0717	15	584	1.53	79,600	175
0.0702	15	292	1.53	40,600	122
0.0708	15	116	1.36	17,900	62
0.0706	15	59	1.30	9,400	24
0.0700	15	32	0.83	7,930	12
0.0694	15	16	0.88	3,750	6.6
Total iodine in unmodified groundwater					
0.0711	15	8.6 ± 0.9	1.0	1,830	1.6
0.0699	15		0.83	1,840	1.7

(a) Calculated based on an estimated quantitation limit (EQL) of 50 µg/L.
(b) Calculated based on EQL of 2.5 µg/L.

Co(II)-Cr(III) and Co(II)-Bi(III)-Al(III) composites exhibited efficient sorption of both IO_3^- and I^- in the batch contact tests.   To compare performance of these materials, corresponding $K_d(IO_3^-)$ and $K_d(I^-)$ values were plotted against post-contact iodine concentration in the groundwater (Figure 2).
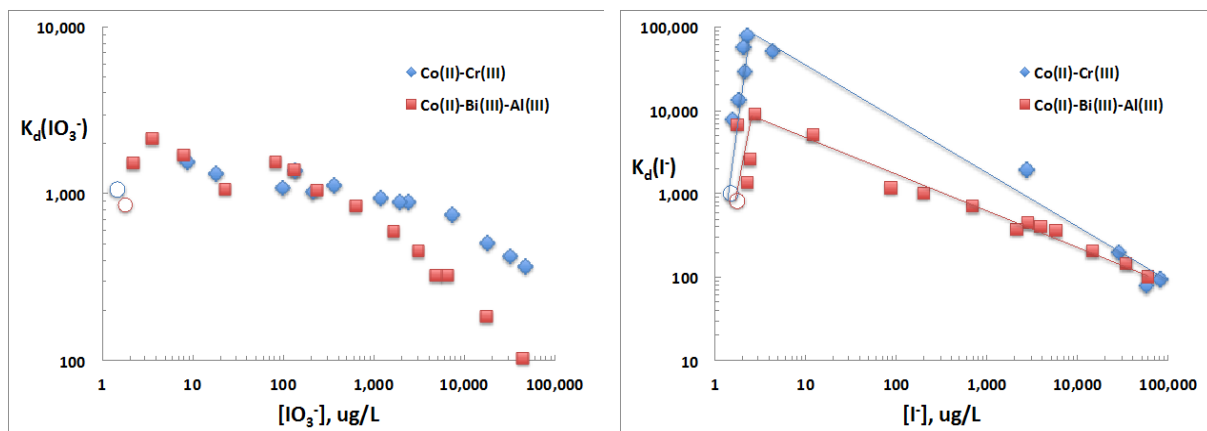

FIGURE 2.   Comparison of the sorption performance of the Co(II)-Cr(III) and Co(II)-Bi(III)-Al(III) composite materials for IO_3^- (left pane) and I^- (right pane) from the Hanford groundwater.   Diamond symbols represent groundwater with adjusted IO_3^- or I^- concentration.   Empty round symbols represent unmodified groundwater.

The IO_3^- sorption isotherm profiles for the Co(II)-Cr(III) and Co(II)-Bi(III)-Al(III) composites are remarkably similar under low loading conditions and exhibit maximum $K_d(IO_3^-)$ values of ~2,000 mL/g (Figure 2, left pane).   The IO_3^- loading profile is more pronounced for the Bi(III)-based composite than for the Cr(III) one, so that the corresponding $K_d(IO_3^-)$ values of are reduced to ~100 mL/g and ~500 mL/g at high loading.

Different I^- sorption profiles were observed for the Co(II)-Cr(III) and Co(II)-Bi(III)-Al(III) composite materials (Figure 2, right pane).   The Co(II)-Cr(III) material demonstrated high affinity for I^-, with the highest $K_d(I^-)$ values measured at ~400,000 mL/g. The Co(II)-Bi(III)-Al(III) composite exhibited efficient sorption of I^-, with maximum $K_d(I^-)$ values of ~9,000 mL/g.   The I^- loading isotherms for the Co(II)-Cr(III) and Co(II)-Bi(III)-Al(III) composites demonstrated that the $K_d(I^-)$ values initially increased nearly linearly as post-contact iodine concentration in the groundwater increased, reached the maximum, and then sharply decreased again following the nearly linear trend.   This behavior can be explained by the effect of the total iodine concentration in the Hanford groundwater.   Previous literature indicates that the Hanford groundwater contains predominantly IO_3^-, accounting for up to 84% of total iodine (Zhang et al. 2013).   The ICP-MS analytical method used in this work to quantify iodine uptake does not discriminate among different chemical species of iodine.   Thus, it is expected that at the low concentrations of I^- added to the groundwater, the iodine overall sorption behavior will be dominated by IO_3^- naturally occurring in the groundwater and not introduced I^-.   This is supported by the observation that the K_d values for the total iodine observed for the unmodified groundwater generally follow the IO_3^- sorption profiles.

The Ag(I)-Al(III)-Zr(IV) composite exhibited efficient IO_3^- uptake when its initial concentration in the groundwater was high Table 5.   As the IO_3^- concentration in the groundwater decreased, the $K_d(IO_3^-)$ values sharply decreased, from ~4,000 mL/g to less than 100 mL/g, and then increased again.   The

reason for this behavior is currently unclear.   The I^- loading profile for the Ag(I)-Al(III)-Zr(IV) composite exhibited a similar general trend, with the $K_d(I^-)$ values being significantly higher.   In fact, for many test samples, at the highest I^- concentration, the $K_d(I^-)$ values could not be determined because the post-contact iodine concentration was below the ICP-MS method EQL.   The measured $K_d(I^-)$ values ranged from ~3,700 to ~860,000 mL/g.   This efficient removal of I^- from the groundwater can be explained by its precipitation as AgI on the surface of the composite material.

The performance of the inorganic composite materials tested for the uptake of iodine from the unmodified Hanford groundwater is of particular interest and can help predict the removal of I-129 from the vadose zone.   To the end, the Ag(I)-Al(III)-Zr(IV) composite exhibited superior performance with the K_d(iodine) values above 1,800 mL/g (Table 5).   The corresponding values for the Co(II)-Cr(III) and Co(II)-Bi(III)-Al(III) composites were found to be ~1,000 and 840mL/g, respectively.   These results suggest that the evaluated sorbents are highly selective for iodine as the total iodine concentration is several orders of magnitude less than that of other anionic constituents found in the groundwater, including nitrate, chloride, sulfate, carbonate, and others (Table 1).

CONCLUSIONS

Several inorganic composite materials were synthesized and screened by Raman spectroscopy for IO_3^- uptake from the Hanford 200 Area groundwater collected from well 299-W19-36.   It was determined that the materials containing Cr(III)-, Ag(I)-, or Bi(III) exhibited nearly quantitative IO_3^- sorption.

The IO_3^- and I^- sorption performance of the three composite materials—Co(II)-Cr(III), Co(II)-Bi(III)-Al(III), and Ag(I)-Al(III)-Zr(IV)—was further evaluated using Hanford groundwater from well 299-W19-36 in the systematic batch contact testing.   In these tests, the IO_3^- or I^- concentration in the groundwater was adjusted to 15 to 130,000 μg/L.   The unmodified groundwater containing 8.6 μg/L total iodine was tested as well.   The ICP-MS method was used to quantify iodine uptake. The $K_d(IO_3^-)$ values observed for the Co(II)-Cr(III), Ni(II)-Cr(III), and Co(II)-Bi(III)-Al(III) composites were in the 1,000 to 2,000 mL/g range at low sorbent loading.   Both materials exhibited very effective iodide uptake.

The Ag(I)-Al(III)-Zr(IV) composite was very effective for the I^- uptake, with the $K_d(I^-)$ values approaching 900,000 mL/g.   This composite was also superior at removing iodine from the unmodified Hanford groundwater, with K_d(iodine) values of ~1,800 mL/g.   This corresponds to the removal of 90% total iodine from the groundwater.   Other evaluated composites exhibited moderately efficient removal of total iodine from the unmodified groundwater with the K_d(iodine) values ranging from 690 to 1,040 mL/g, removing 75% to 83% iodine.

REFERENCES

1. Chen J, L Lv, J He, and L Xv.   2012.   Kinetic and equilibrium study on uptake of iodide ion by calcined layered double hydroxides.   *Desalination and Water Treatment* 42:279–288.

2. Curtius H and Z Kattilparampil.   2005.   Sorption of iodine on Mg-Al-layered double hydroxide.   *Clay Minerals* 40:455–461.

3. Faghihian H, MG Maragheh, A Malekpour.   2002.   Adsorption of radioactive iodide by natural zeolites.   *Journal of Radioanalytical and Nuclear Chemistry* 254(3):545-550.

4. Goh K-H, TT Lim, and Z Dong.   2008.   Application of layered double hydroxides for removal of oxyanions: A review.   *Water Research* 42:1343-1368.

5. Hoskins JS and T Karanfil.   2002.   Removal and Sequestration of Iodide Using Silver-Impregnated Activated Carbon.   *Environmental Science & Technology* 36:784-789.

6. Krumhansl JL, JD Pless, JB Chwirka, and KC Holt.   2006.   *Yucca Mountain Project Getter Program Results (Year 1): I-129 and Other Anions of Concern*.   SAND2006-3869, Sandia National Laboratories, Albuquerque, NM.

7. Krumhansl JL and TM Nenoff.   2011.   Hydrotalcite-like layered bismuth–iodine–oxides as waste forms.   *Applied Geochemistry* 26:57–64.

8. Kulyukhin SA.   2012.   Fundamental and applied aspects of the chemistry of radioactive iodine in gas and aqueous media.   *Russian Chemical Reviews* 81(10):960–982.

9. Levitskaia TG, S Chatterjee, JM Peterson, and EL Valerio.   2013.   *Inorganic Sorbents for Iodine Removal from Subsurface Plumes*.   PNNL-22865, Pacific Northwest National Laboratory, Richland, WA.

10. Mattigod SV, RJ Serne, and GE Fryxell.   2003.   *Selection and Testing of "Getters" for Adsorption of Iodine-129 and Technetium-99: A Review*.   PNNL-14208, Pacific Northwest National Laboratory, Richland, WA.

11. Mattigod SV, DM Wellman, EC Golovich, E Cordova, and RM Smith.   2010.   *Tc-99 Adsorption on Selected Activated Carbons*.   PNNL-20136, Pacific Northwest National Laboratory, Richland, WA.

12. McIntyre NS and MG Cook.   1975.   X-ray photoelectron studies on some oxides and hydroxides of cobalt, nickel, and copper.   *Analytical Chemistry* 47(13):2208-2213.

13. Rojas R, F Bruna, CP de Pauli, M Ángeles Ulibarri, and CE Giacomelli.   2011.   The effect of interlayer anion on the reactivity of Mg–Al layered double hydroxides: Improving and extending the customization capacity of anionic clays.   *Journal of Colloid and Interface Science* 359:136-141.

14. Toraishi T, S Nagasaki, and S Tanaka.   2002.   Adsorption behavior of IO_3^- by CO_3^{2-} and NO_3^- hydrotalcite.   *Applied Clay Science* 22:17-23.

15. Tsuji M, Y Ikeda, M Sazarashi, M Yamaguchi, J Matsunami, and Y Tamaura.   2000.   A new family of anion exchangers: mixed hydroxide carbonates of Bi+3 and divalent, metals showing high selectivity for SeO3-2.   *Material Research Bulletin* 35:2109-2122.

16. Wang Y and H Gao.   2006.   Compositional and structural control on anion sorption capability of layered double hydroxides (LDHs).   *Journal of Colloid and Interface Science* 301:19-26.

17. Zhang S, C Xu, D Creeley, Y-F Ho, H-P Li, R Grandbois, KA Schwehr, DI Kaplan, CM Yeager, D Wellman, and PH Santschi.   2013.   Iodine-129 and Iodine-127 Speciation in Groundwater at

the Hanford Site, U.S.: Iodate Incorporation into Calcite.   *Environmental Science & Technology* 47:9635−9642.