

Extensive Characterization of Novel Classes of Inorganic Ion Specific Media Designed for Highly Selective Removal of Salient Liquid Waste Radionuclides: Co, Cs, Sr, Ni and Tc - 10251

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ABSTRACT

Proper management of certain radionuclides is necessary for clean, safe and secure radioactive waste management, both at commercial Nuclear Power Plants (NPPs) and at Department of Energy Environmental Management sites (DOE-EM).

Selective removal of specified isotopes through ion exchange is a proven treatment method for liquid waste, yet various aspects of existing technologies leave room for improvement with respect to both cost and effectiveness. In order to be good candidates, novel media must exhibit exceptional primary figures of merit, namely ion exchange capacities and distribution coefficients (Kd), but also superior secondary figures of merit, such as thermal, chemical and radiation stability. The secondary figures of merit are rarely exhibited by the state-of-art Ion Exchangers, based on Organic materials.

We herein report new data on the extended family of Inorganic Ion Specific Media (ISM): Surfactant Modified Media (SMM) and Surfactant Modified Zeolites (SMZ). The different media have been studied through seeding reactions of micrometric powders in a steered batch reactor. We report results of the characterization of the primary figures of merit, exchange capacities and Kd, for all the salient radionuclides (Ce, Co, Cs, Ni, Sr, and Tc) at relevant pHs for Nuclear Power Plants (pH 6-8) and DOE sites (pH>10). In near-neutral solution, the ISM had distribution coefficients (Kd) on the order of $\sim 10^4$ mL/g (i.e., $\log_{10}(Kd) \sim 4$) for most target metals analytes (cerium was not appreciably soluble in the filtered neutral solution with no sorbent added).

INTRODUCTION

Proper management of certain radionuclides is necessary for clean, safe and secure radioactive waste management, both at commercial Nuclear Power Plants (NPPs) and at Department of Energy Environmental Management sites.

In NPPs, radionuclides leak to the primary and/or secondary loop of light water nuclear reactors as a result of the decay of the radioactive fuel and subsequent cladding failure as well as through activation of reactor components and subsequent erosion-corrosion. Specifically, the most sought after radioactive isotopes are Cesium-137, Strontium-90 and Nickel-63. These radionuclides are very important in NPPs because their concentrations determine the majority of the Waste Class (A, B or C); hence constrain the options for the location and cost of disposal. Moreover, since the closure of the Barnwell commercial radioactive waste disposal facility at the end of June 2008, poor handling of the so call class-driving isotopes can lead to on-site storage of increasing volumes of secondary class B or C waste. Therefore there is a need for novel media used to achieve maximization of the amount of class A waste and minimization of the amount of Class B or C waste.

On the other side of the spectrum of Radioactive Waste Management, the Department of Energy Office of Environmental Management (DOE-EM) is responsible for the cleanup of the environmental legacy of the Nation's nuclear weapons program. At DOE sites, highly selective removal of Uranium (Cerium is often

used as a simulant), Cobalt (Co-58 or Co-60), Cesium-137, Strontium-90 and Technetium-99 is critical for waste treatment and environmental remediation. Media must be designed to efficiently segregate Low Level Waste from High Level Waste, minimizing the amount of the later and maximizing the amount of the former.

Selective removal of salient radionuclides through ion exchange is a proven treatment method for liquid waste, yet various aspects of existing technologies leave room for improvement with respect to both cost and effectiveness. In order to be good candidates, novel media must exhibit exceptional primary figures of merit, namely ion exchange capacities and distribution coefficients (Kd), but also superior secondary figures of merit, such as thermal, chemical and radiation stability. The later have long been identified as weaknesses for the most commonly used Ion Exchange Materials, namely Organic Ion Exchange Media. An alternative to these issues of organic ion-exchangers is emerging. Inorganic ion-exchangers, so-called Ion Specific Media (ISM) offer a superior chemical, thermal and radiation stability which is simply not achievable with organic compounds. They can be used to remove salient radionuclides with a high level of selectivity under a broad pH range. ISM can operate at acidic pH where protons inhibit ion exchange in alternative technologies. They can also be used at high pH which is typically found in conditions present in many nuclear waste types. For example, ISM have shown significant Strontium uptake from pH 1.9 to 14 [1]. In contrast to organic ion-exchangers, ISM are not synthesized via complex multi-step organic synthesis. Therefore, inorganic ion-exchangers are substantially more cost-effective when compared to organic ion-exchangers, and must be thoroughly evaluated as alternatives to Organic Ion Exchangers.

INTRODUCTION TO THE DIFFERENT MATERIALS

The variety of layered compounds known is astonishing. These include clays, layered double hydroxides (LDHs), transition metal oxides, metal oxo- or thio-phosphates, oxy-halides and oxy-sulfides [2-8]. A great deal of attention has been paid to the clays and LDHs because of their natural abundance and useful properties [2-5]. Specifically, the clays composed of aluminosilicate anionic slabs and alkali or alkaline earth counter cations are excellent cationic exchangers capable of incorporating a variety of guest ions ranging from simple inorganic ions to bulky organic species. Their ion exchange properties have found applications in diverse fields including environmental remediation, catalysis and nanocomposites. In this study, four different Inorganic materials have been identified and prepared so as to activate their surface to obtain enhanced Ion Exchange capabilities. Table 1 summarizes the main characteristics of the selected materials.

Table 1: The Four Inorganic Ion Specific Materials Selected for this Study.

Material	Particle size	Pre-Conditioning	Targeted Radionuclides
Surfactant Modified Media SMM-08-0662	Nominal 15 μm	Proprietary Organic treatment	Tc-99
Herschelite Fines SMZ-09-1771	Nominal 15 μm	Proprietary activation treatment	Co, Ni, Sr, Cs, Ce
Herschelite Granular SMZ-09-1772	297 μm -1.4 mm (14x50 U.S. mesh)	Proprietary activation treatment	Co, Ni, Sr, Cs, Ce
Herschelite Granular SMZ-09-1774	400 μm -1.4 mm (14x40 U.S. mesh)	Proprietary activation treatment	Co, Ni, Sr, Cs, Ce

Since all of these materials are based on naturally occurring mineral materials, the pre-conditioning treatment is key to activate the materials. The type of pre-conditioning employed is an equilibration in a high-molar ionic solution using mass action to convert metal binding sites to the exchangeable cationic form, and subsequently rinsing the media with de-ionized (DI) water, to remove excess cation [9]. This process is said to increase the subsequent binding capacity for radionuclides, by displacement of equivalent cations found in the mined material.

EXPERIMENTAL RESULTS

Aqueous Phases

The objective of the testing is to evaluate media performance against select natural (non-radioactive) analogs of priority radionuclides. The spiked metals of interest were small aliquots of the following metals in dilute nitric acid: cerium (Ce), a stand-in for soluble forms of actinide and lanthanide radionuclides (Stockdale et al., 1995); cobalt (Co), for soluble forms of Co-58 or Co-60; cesium (Cs), for Cs-137; nickel (Ni), for soluble forms of Ni-63; and strontium (Sr), for Sr-89 and Sr-90. Cerium was seldom soluble after spiking, being appreciably soluble only in the pH ~ 11.5 medium (containing chelating agents).

Series pH ~ 7 solutions were prepared by spiking sought-for metals into de-ionized water (DI-water) yielding a solution with initial pH ~ 2.7. The solution was then neutralized with a few drops of sodium bicarbonate (NaHCO₃) solution. The mixed, near-neutral solution was then filtered through Whatman 41 filter paper (Grade 4, with nominal retention of particles > 20 μm), to remove any flocculated insoluble metal complex that may have formed during neutralization.

Series pH ~ 11.5 solutions were prepared by spiking metals into a preparation designated 1073-49, followed by mixing and then filtration through Whatman 41 medium. The original solution 1073-49 was a simplified, synthetic surrogate for alkaline Hanford Tank waste AP-101 (1069-45; see Table 2 and 3 below), which had been previously pH-adjusted by addition of HNO₃ to pH ~ 11.6. The resulting supernate solution was decanted from insoluble Al(OH)₃ phase, and was then filtered through Whatman 41 medium before spiking the additional metals of interest for the present investigation. The solution had specific gravity ~ 1.22.

Series pH ~ 14 solutions were prepared by spiking metals into a preparation designated 1069-45, followed by mixing and then filtration through Whatman 41 medium. This preparation was a simplified synthetic surrogate for alkaline Hanford Tank waste AP-101 (which omitted toxic chromate ion and select trace constituents); see Table 2 and Table 3. The formulation was based upon the recommendations of Eibling for 50% Hanford Tank Waste Envelope A [10]. The resulting supernate solution was decanted from insoluble Al(OH)₃ phase, and was then filtered through Whatman 41 medium before spiking the additional metals of interest for the present investigation. The prepared solution had specific gravity ~ 1.26.

Table 2: Preparation of Simplified Surrogate AP-101

As-formulated (Preparation 1069-45)			
	Compound	Compound	As Compound
Compound Added	Formula	FW	As-prep. (mol/L)
Sodium Acetate	NaCH ₃ COO	82.03426	2.77E-02
Sodium Oxalate	Na ₂ C ₂ O ₄	133.9991	1.99E-02
Aluminum Nitrate nonahydrate	Al(NO ₃) ₃ *9H ₂ O	375.1331	1.25E-02
Calcium Nitrate Tetrahydrate	Ca(NO ₃) ₂ *4H ₂ O	236.1506	2.20E-04
Cesium Nitrate Tetrahydrate	CsNO ₃	194.9103	(6 ppm as Cs)
Boric Anhydride	B ₂ O ₃	69.6182	6.89E-04
Sodium Chloride	NaCl	58.44277	4.59E-02
Sodium Fluoride	NaF	41.98817	3.24E-03
Sodium Dihydrogen Phosphate	NaH ₂ PO ₄	119.9769	1.40E-02
Sodium Sulfate	Na ₂ SO ₄	142.0371	4.18E-02
Sodium Nitrate	NaNO ₃	84.99467	7.89E-01
Potassium Nitrate	KNO ₃	101.1032	2.22E-01
Sodium Hydroxide	NaOH	39.99707	3.33E+00
Sodium Meta-silicate	Na ₂ SiO ₃ *9H ₂ O	284.2	4.86E-03
Sodium Nitrite	NaNO ₂	68.99527	7.92E-01
Sodium Carbonate	Na ₂ CO ₃	105.9887	2.11E-01
Potassium Carbonate	K ₂ CO ₃	138.2058	2.88E-01

Table 3: Key Characteristics of the Simplified Surrogate AP-101

Characteristic	Value
SG (as prepared)	1.25
pH (as prepared)	≥ 14
Total Na, as prepared (mol/L)	5.56
Total NO ₃ , as prepared (mol/L)	1.05
Cs (ppm)	6

The final part of this study was to evaluate the potential utility of a Surfactant Modified Media for the removal of the radionuclide Tc-99 (as the pertechnetate anion, 99TcO_4^-) from aqueous solution. The aqueous phase used was Tc-99 (from NH_4TcO_4 stock solution) diluted in DI water.

Phase Contact, Separation and Analysis

Forty milliliters of each aqueous phase was contacted with 100 mg of each of the media. For all salient radionuclide except Tc-99, phases in sealed 50-cc plastic centrifuge cones were initially contacted by shaking for 6 hours on a Burrell shaker, and then they were transferred to a TCLP tumbler, rotated at 30 rotations per minutes (RPM) for a gentler overnight phase contact. After phase contact, the sample cones were placed on a peg board to observe gravimetric sedimentation over a period of 2-h.

In the case of the pertechnetate solution, the phase sealed in a 50-cc plastic centrifuge cone was contact for 4 hours tumbling the phases at 30 RPM in the TCLP apparatus.

Following contact, phases were separated by filtration of Whatman 41 filter paper except for the pertechnetate experiments where phases were separated by centrifugation at 1000 RPM for 5-min.

For all radionuclides except Tc-99, 20 mL of aliquots of filtrate were reserved for digestion preparatory for select metals analysis by inductively coupled plasma (ICP) with mass spectrometric (ICP-MS) detection.

In the case of Tc-99, small aliquots of the supernate solution were taken for subsequent counting. Technetium activity in the solution phase was estimated by liquid scintillation counting (LCS), with alpha and beta discrimination.

Distribution Coefficients

The distribution coefficient (Kd) of salient radionuclide to the different media was measured as a key indicator of affinity. The distribution coefficient describes the sorption/desorption propensity of a compound for given radionuclide. Except in the case of Tc, all Kd are relative Kd since they not only measure the affinity of a given media for a given radionuclide, they are also an indication of selectivity, i.e. the ability of the ISM to select for the salient radionuclides in the presence of other cations.

The value of the distribution coefficient is computed using the formalism:

$$Kd \text{ (mL/g)} = (V/M) * (C_o - C_e) / C_e \quad (\text{Eq. 1})$$

Where:

V = volume (mL) of aqueous phase taken

M = mass (g) of solid phase taken

C_o = original concentration of analyte in filtered test solution (i.e., with no solid medium added)

C_e = final (“equilibrium”) concentration of analyte in filtered solution after phase contact with test sorbent

Results for the salient radionuclides other than Tc-99 are presented figure 1 (a, b and c). For the Tc-99 experiment, Kd was determined to be 2.3×10^5 mL/g.

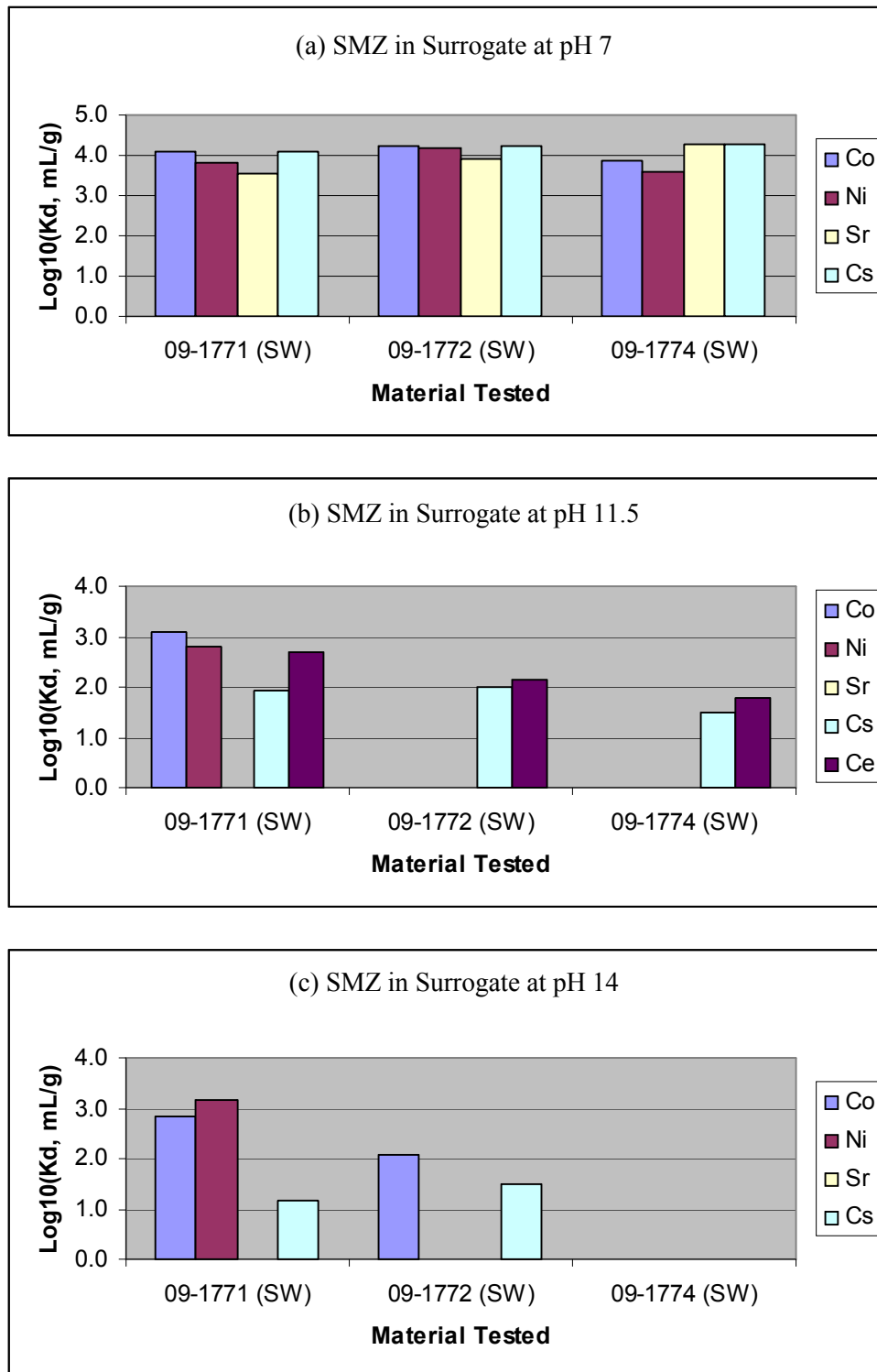


Figure 1: Logarithm of the Relative Distribution Coefficients (Kd) of the tested Surfactant Modified Zeolites (SMZ) for salient radionuclides in surrogates at pH 7 (a), 11.5 (b) and 14(c). (Note that at pH 7 and 14 Ce precipitated out of solution, hence Kd could not be determined)

As can be seen from Figure 1, in near-neutral solution the K_d exhibited by all materials are in the 10^4 mL/g range, which is very high and signals that these low cost, mineral materials are suitable for the removal of salient radionuclides from liquid radioactive wastes at commercial Nuclear Power Plants.

At higher pH in surrogates, with many ions present in the solution, the situation is more complicated. However, even in such harsh conditions, high selectivity as well as high distribution coefficients are exhibited, particularly for the 09-1771 SMZ Media for Co, Ni, Ce and Cs at pH 11.5 and Co, Ni at pH 14.

SUMMARY

Surfactant Modified Zeolites (SMZ) and Surfactant Modified Media (SMM) are extremely low cost modified mineral materials with high distribution coefficient that make them suitable for the removal of salient radionuclides from liquid radioactive waste. These Inorganic Ion Specific Media (ISM), because they are naturally occurring minerals, exhibit high chemical and thermal stability. These new materials are poised to play a significant role in the treatment of liquid wastes present at both commercial and DOE EM sites, allowing for improved waste classification and management in commercial nuclear power plants (for the separation of Class A from B/C wastes) and DOE tank farms (for the separation of LLW from HLW). Future testing and verification studies will involve the development of further modified media for other isotopes and even greater suitability at the relevant pH and waste composition for DOE.

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