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SELECTIVE CAPTURE AND ENCAPSULATION OF METALLIC CATIONS BY HYDROGELS CONSISTING OF COPOLY(N-ISOPROPYLACRYLAMIDE/FUNCTIONAL MONOMER) NETWORKS

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ABSTRACT

Under the U.S. Department of Energy Waste Treatment Baseline and Integrated Waste Management Strategy the recycling of spent nuclear fuel to minimize waste, to assure maximum energy recovery and to pursue science-based R&D to possibly eliminate the need for geologic waste repositories, are programmatic goals. We have developed both polymer gel and porous materials for separation and adsorption of targeted contaminants. Here, we have investigated capture and encapsulation capabilities of hydrogels consisting of thermally-sensitive copoly[*N*-isopropylacrylamide(1-*x*)/*functional* monomer(x)] networks, where *functional* denotes carboxylic, hydroxyl, or cyanide group (mol fraction *x*); the captured and encapsulated species were: Cr^{3+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Eu^{3+},Ho^{3+} and Tb^{3+} present in aqueous medium. Natural diffusions of cations into gel phase and the physico-chemical affinity of functional groups for cations played a major role in capturing cations. Encapsulation of cations trapped in hydrogels was achieved by loss of water and conformational transformation of networks through a volumetric phase transition. Experimental determinations of cation amounts (mass) and copolymer composition were carried out by atomic absorption and elemental analyses of carbon, nitrogen and hydrogen, respectively. We developed two approaches for determination of efficiency and selectivity metrics describing capture and encapsulation of cations by functional groups using two theories: 1) mean field theory and 2) first-order thermodynamic perturbation theory. The integrated results thus obtained show that: Cu^{2+} and Co^{2+} were selectively encapsulated by carboxylic and cyanide groups, respectively. Carboxylic and hydroxyl groups were superior extractants for Cr^{3+}, Eu^{3+} and Ho^{3+}. Further the cyanide group was also effective for Eu^{3}+ and Ho^{3+}. However, all functional groups examined here were ineffective in capture and encapsulation of Ni^{2+}. (259)

KEYWORDS: hydrogels, networks, capture, metallic cations, N-isopropylacrylamide, functional monomer, waste remediation, lanthanides, rare earths

RESUMO

Foram investigadas as capabilidades de redes de hidrogeis termicamente sensitivos de copoli[N-isopropilacrilamida(1-x)/monómero funcional(x)] para capturar seletivamente e encapsular cátions metálicos provenientes de combústivel nuclear. Os grupos funcionais foram o carboxílico, hidroxila e cianeto. As espécies capturadas e encapsuladas foram cátions trivalentes de Cr,Eu, Ho, Tb e bivalentes de Co, Cu e Ni.. Os resultados experimentais foram avaliados usando a Teoria do Campo Médio (MFT) e a Teoria de Perturbação Termodinâmica de Primeira Ordem (FOTHPER)

PALAVRAS CHAVE: hidrogeis. redes, captura, cátions metálicos,monómero funcional, N-isopropilacrilamida, remediação de resíduos, lantanídeos, terras raras

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I. INTRODUCTION

Under the U.S. Department of Energy (DOE)Waste Treatment Baseline and Integrated Waste Management Strategy (WTB-IWMS) reported by Gombert,[1,2] an important aspect toward minimizing or even eliminating the need for long-term geologic waste storage is the shedding the country's dependence on fossil fuels, while concurrently minimizing/reducing the recycling of spent nuclear fuel such as to minimize waste and to assure maximum energy recovery (high burn-up) of fuel. It is self-evident that science-based R&D is needed to achieve this objective. Tokuhiro, Bertino, Leventis and co-workers, over past 5-7 years, developed various polymer gel and porous materials for separation and adsorption; many have relevant application in processing of waste-based contaminants. For example, Bertino, Tokuhiro and Leventis have developed sol-gel materials with high mechanical strength, tunable porosity and tunable surface chemistry[3,4].

Radioactive waste, whether as high or low-level, contains a variety of elements as cations in water or similar solutions. Within the management of radioactive waste, we sought to consider new approaches for radioactive hazardous waste processing in aqueous or similar forms and in fact, 'contaminants of concern(CoC)' often stored as diluted aqueous solutions of radioactive (or non-radioactive) elements and contained in storage containers. The CoC, for example are generated from 'washing', as noted in Figure 1.

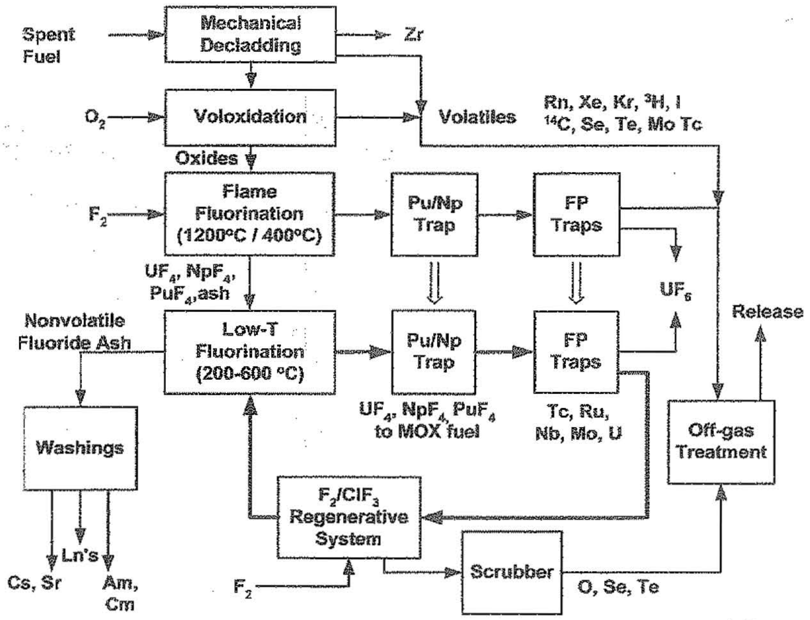

Figure 1. Spent nuclear fuel treatment process overview[1,2]

One of the general problems associated with mixed liquid waste is the lack of an efficient, effective, and inexpensive means of processing (separating) its constituents. Two of the objectives in processing solid-containing radioactive low-level liquid waste, LLW, are as follows: 1) to separate or extract radioisotopes from the rest of the mixed constituents, and 2) to produce stable solidified forms encapsulating radioactive elements. Recent R&D in the physical chemistry of gel materials, have identified promising approach to simultaneously achieve the above objectives.By utilizing and manipulating the physico-chemical properties of various silica- and polymer-based gels at the nanoscale, we have demonstrated a process by which specific chemical species are encapsulated[5,6a,6b)]. Here, we limit our discussion to hydrogels of thermally-responsive poly[*N*-isopropylacrylamide (NIPA)] networks that reversibly exhibit contraction-expansion of gel volume with increasing-decreasing temperature. This change is highlighted by a transition from the swollen (sw) to shrunken(sh) state at just above ambient temperature; here for NIPA at the transition temperature, T_{tr} = 33.4°C. The total volume of gels per single polymeric residue and associated water in this transition changes in order from several to several tenths cubic nanometers [nm^3]. This volume change is caused by loss/gain of water molecules accompanied by a change in conformation of polymer networks, i.e., from an expanded to a contracted form[3, 4)]. We note that replacement of NIPA, in part by polymeric residues containing other polar or ionizable groups, shifts T_{tr} to higher temperature[7-9,10-21)] and simultaneously contributes chemically different characteristics to the overall polymer networks (functionalization). Moreover, we emphasize that all hydrogels form a phase independent of the liquid phase and thus, are amenable to simple physical filtration.

If a polymer component containing functional group is capable of capturing metallic cations in aqueous medium, hydrogels of copoly[NIPA(1-*x*)/functional-monomer] (where x stands for mol fraction) may retain cations in gels. Such gels can potentially serve as (candidate) extractant material for separation of radioactive metallic cations from waste streams in a simple manner.

Here, we investigated such possibility by studying the metal binding capability/retainability of hydrogels consisting of copoly[NIPA(1-*x*)/functional-monomer]. Functional groups were amide group in NIPA, carboxylic, hydroxyl and cyanide groups. We examined cations of transition metals (Cr^{3+}, Co^{2+}, Cu^{2+}, and Ni^{2+}) and of rare-earth elements (Eu^{3+}, Tb^{3+} and Ho^{3+}) dissolved in water. We particularly focused on analysis of data to find quantitative relationship between numbers of cations caught in gels and those of functional groups at the molecular level. We developed two analytical approaches.: 1) mean field theory and 2) first order thermodynamic perturbation theory. By applying two approaches, we will express the results as efficiency and selectivity of functional groups *versus* cations.

II. EXPERIMENTAL

1. Synthesis of copoly[NIPA(1-*x*)/functional-monomer] networks

Syntheses of copoly[NIPA(1-*x*)/functional-monomer] networks and gelation were carried out at 5°C as described in the literature.[3-6, 7-18)]. In aqueous pre-gel solutions, the concentrations of total monomers, a functional-monomer and, cross-linker [methylene-bis-*N*-acrylamide (BIS)] were kept constant at 700 mM, 175 mM (x = 0.25) and 8.6 mM, respectively. Hydrogels thus synthesized were washed with a large amount of water by replacing the aqueous medium with fresh O_2/CO_2 free de-ionized water, at least once per day over a week at room temperature.

Copolymer networks were obtained by lyophilizing hydrogel pieces using a freeze-drying method [7-10] over 36 hours.

2. Determination of chemical composition of copolymer networks

Chemical composition of lyophilized gel pieces was determined experimentally by performing elemental analysis for hydrogen, carbon and nitrogen[5,6]. Accuracy of the Perkin Elmer Model 2400 Elemental Analyzer was checked by using re-crystallized NIPA. The results showed that experimental values for all atomic species expressed in atomic weight percent agree with theoretical values with less than 1.0% error. On this basis, we[5,6] determined the stoichiometric ratio of functional-monomer (x) namely, sodium carboxylate, allyl alcohol or allyl cyanide versus the major component, NIPA. The calculation of atomic weight percent for hydrogen, carbon and nitrogen was repeated by varying the stoichiometric ratio (x) in an iterative procedure until all atomic percentages reached less than 2% error.

3. Determination of amounts of cations caught in hydogels by atomic absorption flame photometry (AA)

(a) Calibration with standard solutions

Digitized values of absorption intensity obtained by the spectrometer (Perkin Elmer Model 2380) were calibrated with standard solutions. Original standard solutions were obtained from commercial sources[20]. Since bottles were individually labeled with the absolute concentration, all diluted solutions used for calibration were prepared accordingly. We found all absorption intensities I_{abs} basically followed Lambert-Beer's law over low concentration of ions [C]. However, we showed experimentally that I_{abs} covering wider [C] range is well represented by a continuous but somewhat non-linear curve without any peaks. Therefore, we expressed I_{abs} by a power series expansion of [C] (in units of mg of metal/L of solutions). Here, Greek letters stand for coefficients and are experimentally determined for all cations examined in this study. We found that Eq. [1] exhibits a good convergence character.

$$I_{\mathrm{abs}} = \alpha + \beta[\mathrm{C}] + \gamma[\mathrm{C}]^2 + \delta[\mathrm{C}]^3 + \varepsilon[\mathrm{C}]^4, \quad [1]$$

Table 1 summarizes wavelength, flame environment, and coefficients for all cations examined. In practice, we thus used Eq. [1] for determination of [C] in unknown samples by solving Eq. [1] as the general solutions for quadratic, cubic and quartic equations are available.

Table 1. Wavelength, flame environment in AA method, and coefficients in Eq. (1) for all cations examined

Cation	λ (nm)	Environment	α	β	γ	δ
Cr3+	357.90	Air-Acetylene	-6.00E+06	6.65E+03	-1.20E-03	0.00E+00
Co2+	240.70	ditto	1.00E+13	-5.00E+08	1.82E+04	3.20E-03
Ni2+	232.00	ditto	9.00E+12	-5.00E+08	1.95E+04	1.02E-02
Cu2+	324.80	ditto	-3.00E+08	2.58E+04	4.80E-03	0.00E+00
Eu3+	459.40	NO-acetylene	9.02E-03	6.53E-04	2.27E-05	-7.74E-08
Tb3+	432.60	ditto	1.99E-05	2.25E-04	1.56E-07	0.00E+00
Ho3+	410.40	ditto	-5.66E-03	1.20E-03	0.00E+00	0.00E+00
Na+	589.00	Air-acetylene	4.71E-02	4.09E+03	0.00E+00	0.00E+00

(b) Preparation of samples for AA Measurement

All gel pieces were digested by gently boiling concentrated nitric acid in a Kjeldahl flask for 24 – 36 hours. Digested solutions (about 2 mL) were transferred to a 50 or 25 mL volumetric flask, washed flask with deionized water a few times and filled up to a fiducial mark. These solutions were used for AA determination. The amount of cations, as determined by AA method, is expressed in units of g/mL (solution), by the AA photometer. Then, the total amount of cations present in a sample was calculated in units of gram. For determination of the ratio of the number of cations per a single functional group, this was eventually expressed as the number of mols by knowing the atomic mass for the respective cations.

4. Capture and encapsulation of cations

In order to assess the anticipated dynamic phenomena that could be encountered in *in-situ* waste processing, a static condition must be established and taken as the reference case. This permits us to evaluate the effects introduced by dynamic processing measures, such as mechanical stirring. The term static implies the absence of any macroscopic motions such as convective currents in contrast to inherent molecular motions. To determine the quantitative relationship between the number of functional groups and the number of cations captured and encapsulated in polymer gel pieces, the following capturing and encapsulating processes were performed. Step 1) was to determine the metal binding capability of functional groups. Swollen gel pieces (in the sw state) were left in aqueous solutions of various cations for 7 days at 30°±1°C. The amount of cations caught in the gels was determined by AA-method. Step 2) was to evaluate the retainability of functional groups. We determined the quantity of cations remaining in gel pieces (by AA method), after transforming the polymer networks from the sw(swollen) to sh(shrunken) state. This is the encapsulation process in brief.

In practice, the actual experiments were conducted as follows: Step 1) Pieces of lyophilized polymer gels were weighed and left in deionized water for more than a week at room temperature. After discarding the water, aqueous solutions (100 mL) of 100 mM nitrates of Cr (III), Co (II), Cu (II), or Nil (II) and also acetates of Eu (III), Tb (III) or Ho(III) were added to now swollen gel pieces. Amounts of cations caught in gel pieces were indirectly determined (AA method) by monitoring decreasing concentration of cations in solution by taking 1.0 mL solution samples every day. As drop in concentration for all cations in solutions reached plateaus within one full week (see Fig. 2), solutions were removed from all (28) samples on the 7th day and 14 samples were subjected for determination of cations caught in gel pieces The other 14 samples were used in Step 2).

In Step 1), the samples, which were now colored gel pieces were transferred carefully without touching them to another small vial. The vials were then immersed in a small, thermo-regulated water bath whose temperature was adjusted to slightly above the respective T_{tr}. As the vial temperature rose rapidly above the respective T_{tr}, the small gel pieces shrank in volume within a matter of a few minutes. Water released from the gel pieces was quickly removed and vials were transferred in a large thermo-regulated water bath (65°C ± 0.1°C). All vials were left closed for 3 full days. Further shrinkage of gel pieces produced additional water. After carefully removing the residual solution while maintaining the same bath temperature, the closed vials were quickly removed tightly capped and left to acclimate to room temperature. This process completed the encapsulation of cations in gel pieces. The shrunken small gel pieces so produced were deeply colored as compared to gel pieces produced by step 1) . Colors of Co^2+, Cr^{3+}, Cu^{2+}, and Ni^{2+} were pink, purple, blue, and green, respectively, as shown in Fig. 3. Then, each vial was weighed and the mass of a gel piece was recorded.

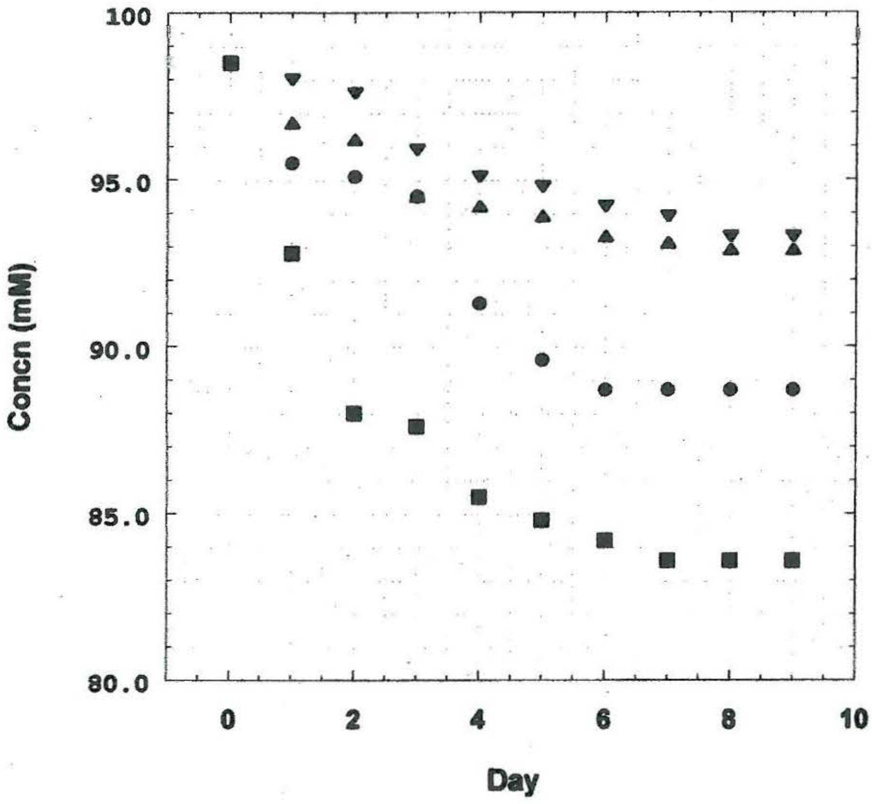

Figure 2. Capture of Ni^{2+} by hydrogels consisting of copoy[NIPA(1-x)/ functional monomer(x)] networks at 303.0 *K* Legend: circle: NIPA; square: NaAc; triangle: Allyl alcohol; inverted triangle: allyl cyanide

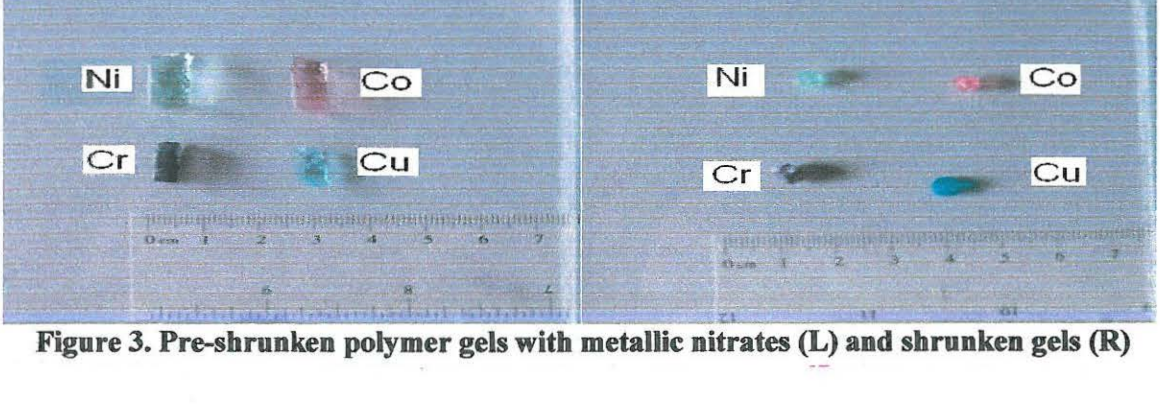

Figure 3. Pre-shrunken polymer gels with metallic nitrates (L) and shrunken gels (R)

III. RESULTS AND DISCUSSION

1. Chemical composition of copolymer networks

The final stoichiomeric ratios for copolymers are shown in **Table 2** The results indicated that mol fractions for functional-monomer x were smaller than the original value (0.25) used in pre-gel solutions for all functional groups. If the original value for x was materialized in real synthesis and, if all functional groups are assumed to be randomly distributed in networks, this would mean that all functional groups were directly bonded to one NIPA molecule on one side and two NIPA residues on the other side. However, the actual values implied that all functional groups are well separated by the major NIPA residues.

Table 2. Chemical composition of copoly[NIPA(1-x)/functional-monomer(x)] networks. x denotes mol fraction of functional component

Copolymer Composition		
NIPA(1-x)/minor(x)	x	mean F. M.
minor group		
Sodium Acrylate (NaAc)	0.154	110.216
Allyl Alcohol (A Al)	0.097	107.817
Allyl Cyanide (A Cn)	0.060	110.395

It is a good approximation to assume that the mass of dried polymer networks m_p (g) consists of many multiples of the polymeric residues[3-6]. Thus, m_p (g) = n_p x [formula mass (F.M.) of polymeric residue] where n_p stands for the number of mols. This concept for polymer networks consisting of mono-polymer component, poly(NIPA), has experimentally been verified within the experimental error range in the elemental analysis . On this basis, the mean mass of networks consisting of copoly[NIPA(1-x)/functional-monomer(x)] was defined as,

$$\text{mean F. M.} = \text{F.M.(NIPA)}\cdot(1-x) + \text{F.M.(functional-monomer)}\cdot(x) \quad [2]$$

Table2 lists the experimental results for three functional monomers obtained by the procedure presented in Section II-2 and Eq. [2].

2. Physical property of hydrogels consisting of copoly[NIPA(1-x)/functional-monomer(x)] networks

A summary of stoichiometry of all gels for transition metal cations is tabulated in **Table 3**.. Amounts of the respective polymer networks were calculated by using Eq. (2) and x values listed in **Table 2**. The results are expressed in units of number of μmol (column 7). Differences in the state of hydration between the sw and sh states are well represented by the number of water molecules per a single mean polymeric residue N_s(gel)[3)] (column 9),the ratio of water vs. networks. These varied rather extensively with kinds of cations and of functional groups. N_s(gel) in the sw state were merely several to more than one hundred times the value in the corresponding sh state.

Table 3. Physical property of hydrogels consisting of copoy[NIPA(1-x)/ functional-monomer (x)] networks in the swollen and shrunken states

(Swollen State)								
			Experimental				calculated	
	Polymer	mass of	mass of	mass of	mass of	amount of	amount of	ratio
Cation	networks	networks	gels	cations	water	networks	water	water vs.
		mg	mg	µg	mg	µmol	mmol	networks
	NIPA	15.1	423.2	1954.0	406.1	133.0	22.6	169.0
Cr3+	NIPA/NaAc	12.0	212.3	1785.0	198.5	105.0	11.0	105.0
	NIPA/AAL	6.7	245.3	1816.0	236.8	63.0	13.2	210.0
	NIPA/ACN	11.2	297.1	2091.0	283.8	101.0	15.8	155.0
	NIPA	15.3	476.6	1365.0	459.9	135.0	25.6	189.0
Co2+	NIPA/NaAc	10.9	552.7	1530.0	540.3	96.0	30.0	314.0
	NIPA/AAL	6.6	384.9	1256.0	377.0	62.0	21.0	339.0
	NIPA/ACN	6.4	342.0	1191.0	334.4	58.0	18.6	321.0
	NIPA	13.5	396.3	1116.0	381.7	119.0	21.2	178.0
Cu2+	NIPA/NaAc	10.9	370.2	1061.0	358.2	96.0	19.9	208.0
	NIPA/AAL	5.4	217.3	187.0	211.7	50.0	11.8	233.0
	NIPA/ACN	8.0	201.1	223.0	192.9	72.0	10.7	148.0
	NIPA	12.2	410.8	18.0	398.6	108.0	22.1	205.0
Ni2+	NIPA/NaAc	16.6	498.9	25.0	482.3	146.0	26.8	184.0
	NIPA/AAL	7.0	205.9	18.0	198.9	65.0	11.1	169.0
	NIPA/ACN	7.1	228.1	18.0	221.0	64.0	12.3	191.0

(Shrunken State)								
			Experimental				calculated	
	Polymer	mass of	mass of	mass of	mass of	amount of	amount of	ratio
Cation	networks	networks	gels	cations	water	networks	water	water vs.
		mg	mg	µg	mg	µmol	mmol	networks
	NIPA	15.1	25.7	1675.0	8.9	133.0	500.0	3.7
Cr3+	NIPA/NaAc	6.1	24.7	649.0	18.0	53.0	1000.0	18.6
	NIPA/AAL	2.5	33.6	477.0	30.6	23.0	1700.0	72.9
	NIPA/ACN	8.6	91.6	905.0	82.1	78.0	4560.0	58.5
	NIPA	14.1	38.5	779.0	23.6	125.0	1310.0	10.5
Co2+	NIPA/NaAc	4.5	45.6	209.0	40.9	39.0	2270.0	57.6
	NIPA/AAL	6.6	8.1	192.0	1.0	62.0	70.0	1.2
	NIPA/ACN	12.5	28.2	1375.0	14.3	113.0	800.0	7.0
	NIPA	13.5	55.3	632.0	41.2	119.0	2290.0	19.2
Cu2+	NIPA/NaAc	2.7	11.2	270.0	8.2	24.0	460.0	19.3
	NIPA/AAL	6.9	57.3	83.0	50.3	64.0	2800.0	43.4
	NIPA/ACN	11.5	75.5	268.0	63.7	104.0	3540.0	34.0
	NIPA	13.0	25.3	2.0	12.3	115.0	680.0	5.9
Ni2+	NIPA/NaAc	6.4	13.9	10.0	7.5	56.0	420.0	7.4
	NIPA/AAL	3.6	11.5	15.0	7.9	34.0	440.0	13.0
	NIPA/ACN	13.3	34.4	18	21.1	120.0	1170.0	9.7

3. Data analysis of cations captured in swollen gels and encapsulated in shrunken states

Further understanding of the qualitative nature of the process in Step 1) was achieved by reversing the process itself. Namely, all colored (shrunken) gels obtained were re-immersed in pure deionized water and left intact at 31°C for one full week. The result was that the colored gel pieces returned to their transparent, uncolored state (judged by visual inspection) and the water became colored. This reversible infusion of cations into hydrogel pieces is thus a simple diffusion of cations in and out of the gel phase, and is likely driven by the concentration gradient of cations. However, differences in time dependences of process (see Fig. 1) and in amounts of cations caught in gels indicated that physical-chemical interactions between cations and functional groups also played an important role. The gels thus serve as a filter that extracts targeted species[20].

The capturing processes for Ni^{2+} by hydrogels consisting of copoly[NIPA(1-x)/functional-monomer(x)] is plotted using concentration and time in Fig. 2.
Experiments showed that: 1) all hydrogel pieces in the sw-state reached equilibrium within 6-7 days, and 2) the time dependence of uptake of the different respective cations varied significantly among different copolymer networks before reaching eventual equilibrium. These semi-quantitative results will serve as the reference with respect to evaluation of effects from possible dynamic method(s) introduced in actual processing of waste streams.

Previous studies[24-31)] for adsorption of metallic cations present in aqueous media have mostly focused on identifying suitable functional groups, determining the adsorption process in the time domain, and determining the nature of chemical adsorption for the functional groups in a semi-quantitative manner. Experimental methods for determination of the amount of cations bound to functional groups were indirectly carried out by spectrometric measurements (in UV and visible region) of cations remaining under aqueous solutions. Direct determinations of bound cations were not implemented. These past studies were at the macroscopic level. On the other hand, we have carried out direct determination as described in the preceding section and developed two different analytical approaches for determination of effectiveness of capture and encapsulation of cations at the molecular level. That is, we utilized both mean field theory, MFT, and first-order thermodynamic perturbation theory, FOTPER. The primary focus of our analysis was to express the efficiency and selectivity of capture and encapsulation of cations by functional groups in a quantitative manner.

(a) Mean field (MFT) theory

Mean Field Theory, MFT, was applied to determine the following: 1) metal binding capability of functional groups exhibited in the sw state (**Table 4**) ; and 2) retainability of metallic cations manifested in the sh state (**Table 5**) . We could easily calculate the number of polymeric residues needed for capturing a single cation (5th column) from the number of mol of metallic cations determined by AA (3rd column) and a number of mols of polymeric residues in gel piece (4th column) on the basis of Eq. (2). Taking values thus obtained or poly(NIPA) networks (5th column) as a reference, values listed in 5th column for other copoly[(NIPA(1-

Table 4. Captured cations in hydrogels consisting of copoy[NIPA(1-x)/ functional-monomer (x)] networks (swollen state)

				Mean Field	Field	Perturbation	
ion	polymer	cation	Amount	Number	Efficiency	Number	Ratio
	netorks	in gels	of polymer		versus	of minor	minor vs
		µmol	µmol	per cation	NIPA	per cation	NIPA
	NIPA	37.40	133.00	3.57	1.00	0.00	1.00
Cr3+	NIPA/NaAc	33.80	109.00	3.22	1.11	0.50	0.32
	NIPA/Aal	0.00	62.10	18000	0.00	3.17	1.20
	NIPA/Acn	39.90	102.00	2.54	1.41	2.19	0.50
	NIPA	23.80	135.00	5.68	1.00	0.00	1.00
Co2+	NIPA/NaAc	26.90	98.90	3.68	1.54	0.76	0.81
	NIPA/Aal	21.80	61.20	2.81	2.02	1.99	1.30
	NIPA/Acn	20.60	58.10	2.81	2.02	3.10	1.20
	NIPA	17.40	119.00	6.86	1.00	0.00	1.00
Cu2+	NIPA/NaAc	16.50	98.90	5.98	1.14	0.29	0.36
	NIPA/Aal	2.94	50.10	17.00	0.40	~ 0	~ 0
	NIPA/Acn	4.83	72.50	20.80	0.33	~ 0	~ 0
	NIPA	0.30	108.00	360.00	1.00	0.00	1.00
Ni2+	NIPA/NaAc	0.47	151.00	321.00	1.12	0.00	0.22
	NIPA/Aal	0.30	64.90	217.00	1.66	0.02	0.84
	NIPA/Acn	0.30	64.30	215.00	1.67	0.03	0.78
	NIPA	15.90	124.00	7.80	1.00	0.00	1.00
Eu3+	NIPA/NaAc	11.20	65.30	5.84	1.30	0.41	0.58
	NIPA/Aal	6.73	39.90	5.92	1.30	0.55	0.46
	NIPA/Acn	13.40	114.00	8.52	0.92	~ 0	1.00
	NIPA	12.50	190.00	15.20	1.00	0.00	1.00
Tb3+	NIPA/NaAc	6.77	72.60	10.70	1.40	0.24	0.68
	NIPA/Aal	15.00	39.00	25.90	0.59	~ 0	1.00
	NIPA/Acn	10.60	125.00	11.80	1.30	0.38	0.37
	NIPA	12.70	213.00	16.80	1.00	0.00	1.00
Ho3+	NIPA/NaAc	9.81	113.00	11.60	1.50	0.23	0.71
	NIPA/Aal	3.12	29.70	9.53	1.80	0.53	0.95
	NIPA/Acn	10.60	139.00	13.10	1.30	0.34	0.40

Table 5. Encapsulated cations in hydrogels consisting of copoy[NIPA(1*x*)/ functional-monomer(*x*)] networks (shrunken state)

				Mean Field	Field	Perturbation	
ion	polymer	cation	Amount	Number	Efficiency	Number	Ratio
	netorks	in gels	of polymer		versus	of minor	minor vs.
		µmol	µmol	per cation	NIPA	per cation	NIPA
	NIPA	31.70	133.00	4.22	1.00	0.00	1.00
Cr3+	NIPA/NaAc	11.90	55.30	4.66	0.91	0.14	0.10
	NIPA/Aal	8.78	23.20	2.66	1.60	1.80	0.82
	NIPA/Acn	18.30	77.90	4.26	0.99	0.00	----
	NIPA	13.70	125.00	9.10	1.00	0.00	1.00
Co2+	NIPA/NaAc	3.54	40.80	11.50	0.79	0.00	----
	NIPA/Aal	3.25	61.20	18.80	0.48	0.00	----
	NIPA/Acn	24.00	113.00	4.72	1.93	1.80	1.10
	NIPA	9.82	119.00	12.10	1.00	0.00	1.00
Cu2+	NIPA/NaAc	4.21	24.50	5.82	2.08	0.67	1.50
	NIPA/Aal	1.31	64.00	48.70	0.25	~ 0	~ 0
	NIPA/Acn	3.96	104.00	26.30	0.46	~ 0	~ 0
	NIPA	0.04	115.00	3291.00	1.00	0.00	1.00
Ni2+	NIPA/NaAc	0.17	58.10	348.00	9.46	0.02	11.00
	NIPA/Aal	0.26	33.40	131.00	25.10	0.08	2.80
	NIPA/Acn	0.30	121.00	403.00	8.17	0.04	7.90
	NIPA	2.90	120.00	41.50	1.00	0.00	1.00
Eu3+	NIPA/NaAc	17.30	156.00	9.00	4.61	0.59	4.50
	NIPA/Aal	11.30	88.10	7.83	5.30	1.09	4.90
	NIPA/Acn	7.78	95.10	12.20	3.40	0.99	2.00
	NIPA	5.68	101.00	17.80	1.00	~ 0	1.00
Tb3+	NIPA/NaAc	4.35	107.00	24.60	0.72	~ 0	~ 1.0
	NIPA/Aal	0.33	51.00	156.00	0.11	~ 0	~ 1.0
	NIPA/Acn	1.67	87.00	52.00	0.34	~ 0	~ 1.0
	NIPA	1.00	92.80	93.00	1.00	0.00	1.00
Ho3+	NIPA/NaAc	3.80	130.00	34.10	2.72	1.84	21.00
	NIPA/Aal	1.15	60.30	52.40	1.77	0.10	1.00
	NIPA/Acn	3.41	69.70	20.50	4.54	0.73	4.30

x)/functional-monomer(*x*)] network systems are evaluated. The results are summarized in 1st column through 6th in **Tables 4** and **5**, respectively. They were interpreted as follows. If values listed in 6th column are less than unity, the specific functional groups were more efficient than the amide group for capturing or encapsulating cations. Thus, the use of Eq. (2) was correct in expressing amount of polymer networks with a given composition *x*. However, there is the implication that copoly[NIPA(1-x)/functional-monomer (x)] networks are made of *mean* residues. Namely, every polymeric residue is a NIPA residue, but somewhat modified by the character of the functional-polymeric residue, by the amount *x*. This is the interpretation based on mean field theory. These '*mean*' polymeric networks are different from possible real network structures where NIPA and functional-polymeric residues are randomly bonded in 3D space; in reality, individual NIPA and functional group residues are recognized. As the major polymeric component, NIPA, also participates in capture and encapsulation of cations, the number of functional-polymeric residues per a single cation (5th column) cannot purely be assigned to a functional-group. In fact, it includes contributions from NIPA residues near a functional-residue. Thus the difference between that calculated by MF theory and possibly the *bona fide* value assigned exclusively to the respective functional group arises from the following: 1) one assumes a completely random distribution of functional groups made in MFT, 2) a non-crystalline nature of polymer networks, and 3) the absence of cooperative behavior of two different functional groups. In other words, the configuration of networks is not the same in all cases. We must thus exercise caution in consideration of differences.

(b) First-order thermodynamic perturbation theory (FOTHPER)

As the major NIPA component is not extensively replaced by functional groups (**Table 2**), it is a good approximation to regard the functional-polymeric groups as a perturbing element of the unperturbed poly(NIPA) networks. We could then directly apply the fundamental principles of FOTHPER9, 10, 32) theory to evaluate both metal binding capability and retainability of respective functional groups. The difference in the experimental values for cation amounts, between perturbed and unperturbed systems, logically arise from the contribution from functional-polymeric residues (7th column). As we have presented in our previous works9, 10), the cation amounts solely captured or encapsulated per a single NIPA residue in the unperturbed poly(NIPA) networks were easily obtained by using values listed in 3rd and 4th columns. Cation amounts caught by all NIPA residues in copoly[NIPA(1-*x*)/functional-monomer(*x*)] (the perturbed system) were evaluated by applying the difference in respective chemical compositions. Values listed in the 8th column were obtained by taking the ratio of these values in perturbed systems *versus* to those in unperturbed systems with respect to specific cations. Therefore, this value may be regarded as describing the efficiency of capture and retention apability of the respective functional group, in reference to the amide group in the NIPA residue. The same argument described for MFT should be applied to the physical meaning of number of functional-polymeric residues per a single cation (7th column). In FOTHPER theory, the interactions of cations and functional groups occur as if functional groups occupy (randomly) the non-interacting NIPA residues. In contradt to MFT, the values in 7th column do not contain contributions from neighboring NIPA residues, if cooperative influence of captured/encapsulated cations by functional and amide groups exist. Again, the calculated results must be considered as a virtual situation.

4. Metal binding capability of functional groups for transition metal cations

A total of sixteen (16) gel samples were subjected to Step 1) experiments. The results for cations are tabulated in **Table 4**. Here, we focused on the relationship between the amount of cation and that of minor polymer component, as indicated in the 3rd and 4th columns. The results obtained from MFT are shown in the 5th and 6th columns. In considering the scientific significance expressed under MF Theory, we can state that: values in the 5th column indicated that the amide group for NIPA residue was quite effective in the capture of Cr^{3+}, Co^{2+} and Cu^{2+}; but not Ni^{2+}. Further all functional groups were relatively ineffective in capture of Ni^{2+}. This is well supported by the FOTHPER approach. The hydroxyl group was totally ineffective for capturing Cr^{3+}, while other groups were effective for Cr^{3+} in the increasing order of amide, carboxylic, and cyanide groups (values noted in 6th column). All functional groups were marginally effective in capturing Co^{2+} and Cu^{2+}. However, the results for cyanide group for both Cr^{3+} and Co^{2+}, as well as hydroxyl group for Co^{2+} suggested another important factor; namely, the proximity of functional groups. In considering the arguments developed in consideration of MF and FOTHPER approaches, the values shown in the 5th and 7th columns reflected the ineffectiveness of cation capture if multiple functional groups are available.

5. Retaining capability of functional groups: Encapsulation of transition metal cations

The results shown in **Table 5** exhibited substantial differences from the corresponding trends found for capturing cations. All functional groups were ineffective in capturing and encapsulating Ni^{2+}. The results from both MFT and FOTHPER approaches indicated that both carboxylic and hydroxyl groups effectively encapsulated Cr^{3+} and the former, selectively encapsulated Cu^{2+}. The cyanide group is the only functional group that successfully encapsulated Co^{+}, even though all functional groups effectively capture Co^{2+}. Chromium tri-valent cation offered an important case that reveals the difference between capture and encapsulation processes. The proximity of multiple functional groups seemed to play an important role in the latter process as exemplified by the hydroxyl group.

6. Metal binding capability of functional groups for rare-earth cations

Experimental results for three lanthanide, tri-valent cations, Eu^{3+}, Tb^{3+}, and Ho^{3+} are given in **Table 4**. In contrast to transition metal cations, the amide group was in general ineffective in capturing lanthanide cations. The carboxylic group was basically a good extractant for all lanthanide cations; however, the hydroxyl group acted selectively, being best for Eu^{3+}. Further, the cyanide group was quite effective in capturing both Tb^{3+} and Ho^{3+} but, not Eu^{3+}. As the functional group was well separated (**Table 2**) and surrounded by NIPA residues, the smaller values shown for the functional group of NIPA residue (7th column of **Table 4**) reflected high affinity *via* the sole functional group rather than 'collective affinity', as exhibited by NIPA groups. This suggests that increase of mol fraction (minor group) was also an important factor for effective capture of lanthanide cations.

7. Retaining capability of functional groups: Encapsulation of rare-earth cations

Experimental results for encapsulation are given in **Table 5**. The results by MF Theory clearly showed selective encapsulation of cations by specific functional groups. Namely, all functional groups were ineffective for Tb^{3+}. In contrast, carboxylic, hydroxyl, and cyanide groups were relatively more effective for Eu^{3+} and Ho^{3+}. This result was also supported by the results obtained by FOTHPER. Terbium cation distinctly exhibited a difference between the capture and encapsulation processes.

It is worthwhile to briefly compare the preceding results with hard-soft acid-base theory[34.] which is more qualitative than quantitative in nature. Among the cations we examined Cr^{3+} is regarded as a hard acid and Co^{2+} lies at the border. Among functional groups, carboxylic acid is referred to as a hard base. On the basis of hard-soft acid-base theory, hard acids react faster and form stronger bonds with hard bases. This assertion seemed to hold very well between Cr^{3+} (as well as Co^{2+}) and carboxylic acid, as supported by both MFT and FOTHPER approaches. As well, it seemed correct for the cyanide group.

It is well known that rare earth tri-valent ions form salts with oxalic acid. According to hard-soft acid-base theory, all rare earth tri-valent ions must be regarded as hard acids and this concorded with their observed affinity for hard base. However, another hard base, the hydroxyl showed selective affinity for the three cations as revealed by both MFT and FOTHPER approaches..

IV. CONCLUSION

Although the long-term storage of spent nuclear fuel in the U.S. is again under reconsideration, three constant objectives are that the U.S. recycle spent nuclear fuel in order to minimize waste. while concurrently assuring the maximum energy recovery via longer burn-up of fuel. Science-based R&D to possibly eliminate the need for geologic waste repositories continues to be needed. Here, we investigated the selective capture and encapsulation of metallic cations dissolved in water by hydrogels, consisting of functionalized, thermo-sensitive copoly[*N*-isopropylacrylamide(1-*x*)/*functional-monomer(x)*]. It is a feasible means for cation removal from aqueous medium. The *functional-monomer (x)* stands for carboxylic, hydroxyl, and cyanide groups with the corresponding mol fraction $x = 0.154$, 0.097 and 0.060, respectively. Our results indicated mildly selective process; the amide group's associative property was noticeable for all cations examined in this study. The carboxylic group also acted as a good extractant for Cr^{3+}, Cu^{2+}, Eu^{3+}, and Ho^{3+}. Significant selective numbers of encapsulations are primarily noted for Cr^{3+}, Cu^{2+}, and Co^{2+} by hydroxyl, carboxylic and cyanide groups, respectively. Finally, among functional groups examined for three representative lanthanide cations, the hydroxyl group exhibited the highest selectivity for Eu^{3+}.

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