

**DOE-IIPS PROPOSAL
Grant DE-FG07-04ID14592
Nuclear Engineering Education Research (NEER) Program**

FINAL TECHNICAL REPORT

On

Radiolytically-induced novel materials and their application to waste processing

By:

**Akira T. Tokuhira¹
Assistant Professor of Nuclear Engineering
Director, University of Missouri-Rolla Research Reactor**

**Massimo Bertino²
Assistant Professor of Physics**

and

**Tadashi Tokuhira
Adjunct Professor of Chemistry**

**University of Missouri-Rolla
Rolla, Missouri 65409-0170**

Submitted to:

**U.S. Department of Energy,
Idaho Operations Office
c/o Mr. Seb Klein,
Grant Officer
kleinsm@id.doe.gov**

¹ At time of original proposal submission at University of Missouri-Rolla

² At time of original proposal submission at University of Missouri-Rolla

SUMMARY

In the present NEER project we investigated two different types of gel materials with respect to potential applications in environmental remediation, including mixed waste generated from the nuclear fuel cycles. The materials under study were: 1) silica-polymer based aerogel composites into which specific metallic cations diffuse into and remain, and 2) polymer gels made of thermo-sensitive polymer networks, whose functional groups can be ‘tailored’ to have a preferred affinity for specific cations, again diffusing into and remaining in the network under a volumetrically, contractive phase-transition. The molecular, diffusion of specific cations, including those of concern in low-level waste streams, into the gel materials studied here indicates that a scaled, engineered system can be designed so that it is passive; that is, minimal (human) intervention and risk would be involved in encapsulating LLW species. In addition, the gel materials hold potential significance in environmental remediation of and recovery of metallic cations identified in respective domains and physico-chemical processes.

In brief, silica gels start as aqueous/liquid solutions of base catalyzed silica hydrogels and metal ions (targeted species), such as silver. The metal ions are reduced radiolytically and migrate through the solution to form clusters. Upon post-irradiation processing, aerogel monoliths, extremely lightweight but mechanically strong, that encapsulate the metals are produced. Interestingly the radiolytic or photonic source can be gamma-rays and/or other rays from ‘artificial sources’, such as reactors, or ‘inherent sources’ like those characterizing mixed waste.

Polymer gels, in contrast exhibit thermally-induced volumetric contraction at 20°-50°C by expelling water from the gels’ physical state. Further, some functional groups that capture di- or tri-valent cations from aqueous solutions can be incorporated into the polymer networks on synthesis, including by radiolytic means. These polymer gels retain cations after volumetric contraction and have the ability to trap solid particulates in liquid waste streams. With both silica and polymer gels, functional design of a prototypic ‘recovery’ systems, such as by natural convection in a rectangular cell, appears possible.

Additional and specific details are provided in the rest of this Final Report.

Student Participation

The present NEER project attracted an unexpected number of students who contributed to the success of the project. Table 1 provides a list of students who participated. Many were supported in some form from the grant or via additional funds leveraged with the grant.

Table 1. Students supported

#	First, Last Name	Degree, Major, Year	Supervisor
1	Izumi Hagiwara	MS (under NEER), NE, 2004	A. Tokuhiro
2	Sita S. Akella	MS (under NEER), ChE, 2006	T. Tokuhiro/A.Tokuhiro/K. Henthorn
3	Rolanda. M. Reed	BS05-ChE	T. Tokuhiro
4	Josh W. Carey	BS06-Chem., MS	T. Tokuhiro
5	Lisa Wulff	BS03-CE	M. Fitch, A. Tokuhiro
6	Arish Labroo	MS-CS.	T. Tokuhiro
7	Ryan Hupe	BS08-Physics	M. Bertino
8	Lane Martin	BS08-Physics	M. Bertino
9	Lauren Rich	BS08-Physics	M. Bertino
10	Julie Portman	BS08-ChE	M. Bertino, A. Tokuhiro
11	Emma Schmittzehe	BS-Chemistry	T. Tokuhiro
12	Jaime Arrocha Anino	BS-ChE	T. Tokuhiro
13	David Bash	BS06-Env. Eng.	M. Fitch

14	Brian Heckman	BS06-Physics; MS07 (under NEER)-Physics	M. Bertino
15	Riteshkumar Jain	Post-doc, ChE	T. Tokuhiko
16	David Kimzey	BS09-Physics	M. Bertino
17	Amitabh Mohan	PhD(UMC)	M. Bertino, A. Tokuhiko
18	Arumugam Thangavel	PhD-Chemistry	M. Bertino, N. Leventis
19	Naveen Chandrasekaran	PhD-Chemistry	M. Bertino, N. Leventis
20	Raghuveer Gadipalli	PhD-Physics	M. Bertino
21	Sudhir Mulik	PhD-Chemistry	M. Bertino, N. Leventis
22	Vishal Patel	PhD-Chemistry	M. Bertino, N. Leventis
23	Travis Rohfling	BS-ME(Kansas St. U.)	A. Tokuhiko

Theses Completed

The following Master's theses that were directly related to the project were completed.

- 1) Izumi Hagiwara, University of Missouri-Rolla, 2004
- 2) Sita S. Akella, University of Missouri-Rolla, 2006
- 3) Brian Heckman, University of Missouri-Rolla, 2006

Publications

M. F. Bertino, J. F. Hund*, J. Sosa, G. Zhang, C. Sotiriou-Leventis, N. Leventis, A. T. Tokuhiko, and J. Terry, "High resolution patterning of silica aerogels", published as a letter in *J. of Non-Cryst. Solids* **333**, 108 (2004).

M. F. Bertino, R. R. Gadipalli*, J. G. Story, C. G. Williams, G. Zhang, C. Sotiriou-Leventis, A. T. Tokuhiko, S. Guha, and N. Leventis, "Laser Writing of Semiconductor Nanoparticles and Quantum Dots", *Appl. Phys. Lett.* **85**, 6007 (2004). The article was also published on "Virtual Journal of Nanoscale Science & Technology" (Dec. 20, 2004 issue), and was reviewed by "Micro/Nano Newsletter" (January 2005 issue), by "MRS Bulletin" (Feb. 2005 issue), and by "Nanotechwire.com" (<http://nanotechwire.com/news.asp?nid=1385>).

D. Lahiri, B. Bunker, B. Mishra, Z. Zhang, D. Meisel, C. M. Doudna*, M.F. Bertino, F.D. Blum, A. T. Tokuhiko, S. Chattopadhyay, T. Shibata and J. Terry, "Bimetallic Pt/Ag and Pd/Ag nanoparticles", *J. Appl. Phys.* **97**, 094304 (2005).

D. Lahiri, S. Chattopadhyay, B.A. Bunker, C.M. Doudna*, M.F. Bertino, F. D. Blum, A. T. Tokuhiko and J. Terry, "EXAFS studies of bimetallic Ag-Pt and Ag-Pd nanofibers", *Physica Scripta*, T115, 776 (2005).

S. K. Pillalamarri*, F. D. Blum, A. T. Tokuhiko, J. G. Story and M. F. Bertino, "Radiolytic Synthesis of Polyaniline Nanofibers: A New Templateless Pathway", *Chem. Mater.* **17**, 227 (2005).

S. K. Pillalamarri*, F. D. Blum, A. T. Tokuhiko, and M. F. Bertino, "One-pot synthesis of polyaniline-metal nanocomposites", *Chem. Mater.*, **17**, 5941 (2005).

T. Tokuhiko and A. Tokuhiko, Temperature Dependence of Density of Polymer Gels 3. Effects of Ionizable Group in Copoly(*N*-isopropylacrylamide/Acrylic Acid or Sodium Acrylate) - Water Systems, *J. Polymer Sci.*, accepted, to appear, 2007.

R.R.Gadipalli, L.A.Martin, B. Heckman, J.G.Story, M.F.Bertino, N.Leventis, P. Fraundorf, and S.Guha, "Patterning porous matrices and planar substrates with quantum dots", *J Sol-Gel Sci Techn.* **39**, 299 (2006).

R.R.Gadipalli, L.A.Martin, B. Heckman, J.G.Story, M.F.Bertino, N.Leventis, P. Fraundorf, and S.Guha, "Infra Red Quantum Dot Photolithography", *J Sol-Gel Sci Techn.* **40**, 101 (2006).

M. F. Bertino, R.R. Gadipalli, L. A. Martin, L. E. Rich, A. Yamilov, B. R. Heckman, N. Leventis, S. Guha, J. Katsoudas, R. Divan and D. C. Mancini, "Quantum dots by ultraviolet and X-ray lithography", *Nanotechnology* **18**, 315603 (2007).

M. F. Bertino, R. R. Gadipalli, B. Heckman, L. Martin, N. Leventis, and A. T. Tokuhiko, "Sol-gel Materials for High Capacity, Rapid Removal of Metal Contaminants", *Separation Science and Technology*, manuscript #3232, submitted.

M. F. Bertino, A. Nanni, M. Hoffmann, N. Leventis, and A. T. Tokuhiko, "Interaction of quantum dots with ionizing radiation" *Langmuir*, manuscript # la-2007-031847, submitted.

M. F. Bertino, N. Leventis, R. R. Gadipalli, L. Rich, L. Martin, J. G. Story, A. Yamilov, S. Guha, B. Heckman, "Three-dimensional semiconductor patterning by multiphoton ionization", *Chemistry of materials*, manuscript #cm-2007-03031q, submitted.

Conference Presentations

A. Tokuhiko, M. Bertino and T. Tokuhiko, Results to date on radiolytic processing of solid particulate waste using polymer and silica gel materials, ANS Winter Meeting, Washington DC, November, 2005

T. Tokuhiko, A. T. Tokuhiko, S. S. Akella*, J. W. Carey*. Metal binding capability of functionalized thermo-sensitive polymer networks and application hydrogels to low-level radioactive waste processing, ICONE-15, Nagoya, Japan, April 22-26, 2007.

N. Leventis, R. Gadipalli, M. Bertino, C. Segre, D. Mancini, "Quantum Dot Photolithography", talk presented at EIPBN conference, Denver, Colorado, May 2007.

J. W. Carey, T. Tokuhiko, M. Bertino, A. Tokuhiko, The potential application of metal binding hydro- and silica-gels in low-level radioactive waster processing, ICONE-16, Orlando, USA, May 11-15, 2007.

Section I. Silica gels to capture metallic constituents (M. Bertino) Final Report

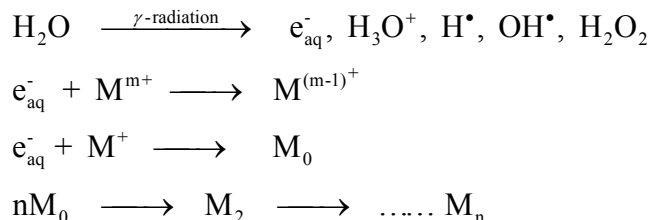
The overall goal of this part of the project was to demonstrate that nuclear waste could be encapsulated radiolytically inside sol-gel materials. The goal has been attained and exceeded.

We have demonstrated that i) noble and transition metals, including lanthanides, can be encapsulated in large concentrations inside sol-gel materials by radiolysis, ii) that sol-gel materials can be used as large-capacity filter septa, iii) that mechanically stable, macroporous sol-gel materials monoliths and powders can be fabricated in large quantities and iv) that the filtration speed with these macroporous gels is increased by almost an order of magnitude. Results originating from the research activity have originated four manuscripts published in international journals, plus another three submitted, and in participation to three conferences. Five undergraduates have been involved in the research and a M.S. student has graduated (with thesis) in 2006. We will now describe the achievements in more detail.

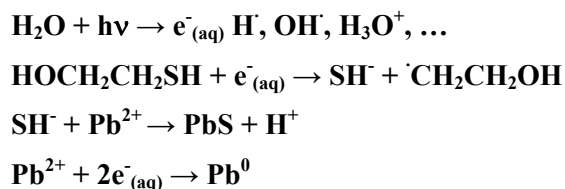
Investigation of Encapsulation of metals by radiolysis

The procedure for encapsulation of noble and transition metals has been described in work published prior and during the funding period by our group [1-9]. In brief, the solvent of sol-gel materials, typically silica gels, is exchanged with a solution of precursors, and irradiated. For noble and transition metals, the precursor can be as simple as a water-soluble metal salt like Ag nitrate. The noble metal ions are reduced by the solvated electrons and other reducing radicals that are liberated when gamma rays interact with water. The reduced metal atoms diffuse then through the material and form small metal aggregates, as described in scheme 1 below.

Scheme I.1. Radiolytic formation of metal aggregates.



For metals like lanthanides, which are a typical by-product of fission, the scheme above could also be employed, since these metals have a highly negative reduction potential, around -2.2 eV, which is higher than the reduction potential of solvated electrons, which is on the order of -2.7 eV [10]. However, all attempts to reduce lanthanides in this way were unsuccessful, regardless of the presence of oxygen or radical scavengers in the parent solution. Therefore, radiolytic formation of non-soluble species such as sulfides was investigated. It is in fact known that compounds such as 2-mercaptoethanol can scavenge water radiolysis by-products such as solvated electrons. Scavenging leads to dissociation of the organic molecules and liberation of SH- which, in turn, react with metal to form sulfides, as shown in scheme 2 [11,12]. Radiolysis of mercaptoethanol has been used in the past to form metal chalcogenides, e.g., CdS and PbS. In this work, radiolytic formation of chalcogenides was revisited and extended to lanthanides such as Nd and Eu [6,7].



Scheme I.2. Radiolytic dissociation of thiols and formation of chalcogenide aggregates.

As for the structural properties of the particles, we found that both metal and chalcogenide particles could be produced with a size ranging from a few nanometers to a few microns, depending on precursor concentration, radiation flux, and addition of surfactants. To characterize the structure and chemical composition of the particles, an array of analytical techniques was employed, ranging from transmission and scanning electron microscopy to X-ray diffraction, selected area diffraction, X-ray photoemission spectroscopy, UV-VIS absorption spectroscopy, photoluminescence spectroscopy and Raman spectroscopy. All these techniques showed that the particles had the bulk structure and were free of contamination.

Regarding concentrations, we found that the metal ion concentration inside silica hydrogels tended to be higher than the metal ion concentration of the parent solution. This is understandable, since positively charged metal ions adsorb electrostatically to the negatively charged walls of the matrix pores. The amount of metal adsorbed on the pore walls was determined by measuring with atomic absorption spectroscopy the concentration of metal ions in the parent solution before and after solvent exchange. It was found that pore walls could uptake up to $10 \mu\text{mol}\cdot\text{g}^{-1}$ (dry gel) of Cd^{2+} , or Ag^+ . This is a relatively high value for non-derivatized hydrogels, and it means that ANY metal concentration in the parent solution that is below the saturation value of the pore walls will be absorbed by the gels. Because of the concentrating action of the pore walls, metal nanoparticles were formed radiolytically even for very diluted bathing solutions ($< 0.1 \mu\text{mol}\cdot\text{l}^{-1}$). For concentrations below about this limit, no definite statements could be made, since nanoparticles (if present) were so dilute and so small that they could not be distinguished from the silica matrix with TEM.

Experiments were also conducted to determine the maximum amount of metal ions that could be trapped inside the pores in form of metal nanoparticles. In these experiments, a silica hydrogel was soaked inside a solution of a known concentration for several hours. The solution was then decanted and replaced by fresh solution with the same ion concentration for at least four times. Samples were then irradiated with radiation emitted by the fission products entrapped in fuel rods after reactor shutdown. In the case of the reactor available on the UMR campus, the operation power was modest (ca. 200 kW) and the flux was relatively small. The radiation flux in the center of the core decreased from about 800 kRad/h immediately after reactor shutdown to about 0.1 kRad/h 12 hours after shutdown, as shown in figure 4. However, samples could be placed only on the outer rim of the core, where the fluxes were about a factor 4 smaller than in the center. As a consequence, maximum doses on the order of 3-400 kRad were obtained, and this only after exposing the samples for 24-48h.

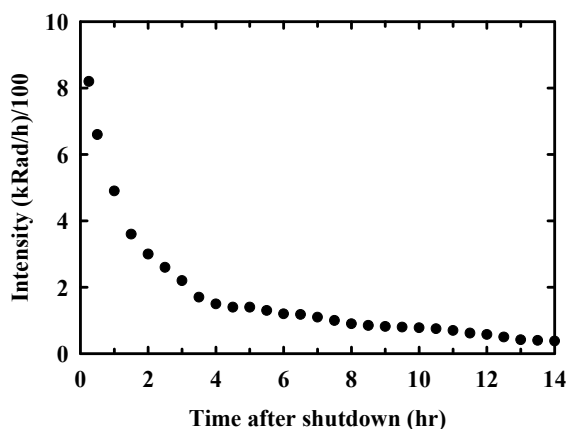


Figure I.4. Gamma-ray decay rate in close proximity of the reactor core. The reactor was run at 180 kW for two hours and then shut down one hour prior to the dose rate measurements.

Now, the efficiency G of generation of reducing radicals by irradiation is on the order of 2-3 per 100 eV of absorbed radiation in pure water, and around 6 when radical scavengers such as 2-propanol (or mercaptoethanol) are added to the parent solution. This means that the maximum concentration of ions that could be reduced by using the nuclear reactor as a gamma ray source was on the order of $1 \text{ mmol}\cdot\text{l}^{-1}$,

or $0.1 \text{ g}\cdot\text{l}^{-1}$ for Ag. This value was attained and measured for both monolithic, macroscopic gels and for micro-gel particles with a diameter of around 50 microns obtained by ball milling of hydrogels. This corresponded to about a 10% weight increase, since hydrogels have a typical skeletal density between 1.1 and $1.3 \text{ g}\cdot\text{l}^{-1}$. To explore if higher loadings were possible, a collaboration was started with the group of Prof. C. Segre, Illinois Institute of Technology. This group operates a beamline (MR-CAT) at Argonne National Laboratory which is equipped with an X-ray beam with an energy tunable between about 5 and 12 keV. X-rays induce the same reactions described in Schemes 1 and 2 when they interact with water and solvents. While the efficiency of X-rays is higher than that of gamma rays, the experiments helped establish the feasibility of entrapment of high metal ion concentrations by gamma ray bombardment. The X-ray experiments showed that Ag concentrations could be reduced that were near the solubility limit, ca. $6 \text{ mol}\cdot\text{l}^{-1}$ (i.e., more than $600 \text{ g}\cdot\text{l}^{-1}$). Similarly, Pb^{2+} in concentrations of up to $1 \text{ mol}\cdot\text{l}^{-1}$ (i.e., more than $200 \text{ g}\cdot\text{l}^{-1}$) could be transformed into PbS by radiolytic dissociation of thiols (scheme 2). Therefore, radiolytic encapsulation of high metal concentrations is possible, provided that intense enough sources (or enough time) are available. Experiments were then carried out to quantify the metal uptake of small hydrogel fragments. In these experiments, small gel fragments were obtained by ball milling or by simply manually crushing a large piece of gel. The gel fragments were soaked into a metal ion solution with a concentration of $10^{-4} \text{ mol}\cdot\text{l}^{-1}$ and then irradiated with a gamma ray dose of $\sim 200 \text{ kRad}$. The intention was to repeat the process several times, each time absorbing metal ions from the parent solution. We noticed, however, that the surfaces of the hydrogels became coated with a silvery film after 2-3 runs. The presence of this coating was unexpected, since colloidal suspensions prepared from a $10^{-4} \text{ mol}\cdot\text{l}^{-1}$ parent solution have usually a brown/yellow color, characteristic of the Ag surface plasmon. A black/silver coloration generally indicates the presence of micron-sized particles, which generally form at high concentrations, e.g., $10^{-2} \text{ mol}\cdot\text{l}^{-1}$. To investigate the origin of the silver coating, e.g., to determine whether pre-formed Ag nanoparticles were catalyzing the reduction of Ag^+ in the parent solution, the same experiments were repeated with a Cd^{2+} /mercaptoethanol solution. In this case, the concentration of the parent solution was monitored with atomic absorption spectroscopy. It was found that the concentration in the parent solution decreased only in the very initial stages, and then remained nearly constant. We suspected that metal chalcogenide nanoparticles were forming on the surface of the silica gel particles, and therefore we decided to conduct a more systematic study of particle formation inside hydrogels. Since we were already conducting an investigation of chemical filtration with gels, we decided to combine the studies and also try to better investigate precursor diffusion into gels. This study also led to the design of a large-scale filtration system, which could be used not only for nuclear waste, but also, potentially, for environmentally sensitive waste.

Investigation of precursor diffusion

In the first part of the granting period, we had started examining chemical precipitation of metals inside gels. The aim of these studies was to get a better understanding of the formation of nanoparticles inside gels and to attempt to fabricate large gels that could be employed as filters. The first attempts proved successful, but filtration was slow. Something was slowing down filtration, as in the case of the radiolysis experiments. We first decided to replicate the radiolysis experiments by replacing the radiation source with a sulfur precursor that slowly dissociates in the presence of high concentrations of metal ions, such as thioacetamide. We prepared filter columns by crushing silica hydrogels to increase the available surface area and to reduce the time necessary for the precursors to diffuse inside the hydrogel fragments. 10 ml of these hydrogel fragments were placed in a PVC tube closed at the bottom. The tube was wrapped with heating tape, as shown in Figure 5. A solution of CdSO_4 and thioacetamide, $\text{C}_2\text{H}_5\text{NS}$, was poured into the gel column and the top of the tube was sealed with paraffin film. High concentration solutions had $[\text{Cd}^{2+}] = 5.4 \text{ g}\cdot\text{l}^{-1}$ (or $4.8 \times 10^{-2} \text{ mol}\cdot\text{l}^{-1}$), while low concentration solutions had $[\text{Cd}^{2+}] = 0.27 \text{ g}\cdot\text{l}^{-1}$ ($2.4 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$). These values correspond roughly to the maximum and minimum concentrations of metal ions in nuclear waste reprocessing solution [13]. The total volume of the precursor solution was 10 ml, and the hydrogels were bathed in the precursor solution for a time between one and two hours.

This time was long enough for complete diffusion through the hydrogel fragments. The velocity of diffusion of Cd^{2+} in silica hydrogels has been measured to be $7.5 \text{ mm}\cdot\text{hr}^{-1}$, and a bathing time longer than one hour is sufficient to ensure diffusion through our hydrogel fragments, which had a radius below 3 mm. [14]. After this time, the solution was drained and collected for characterization.

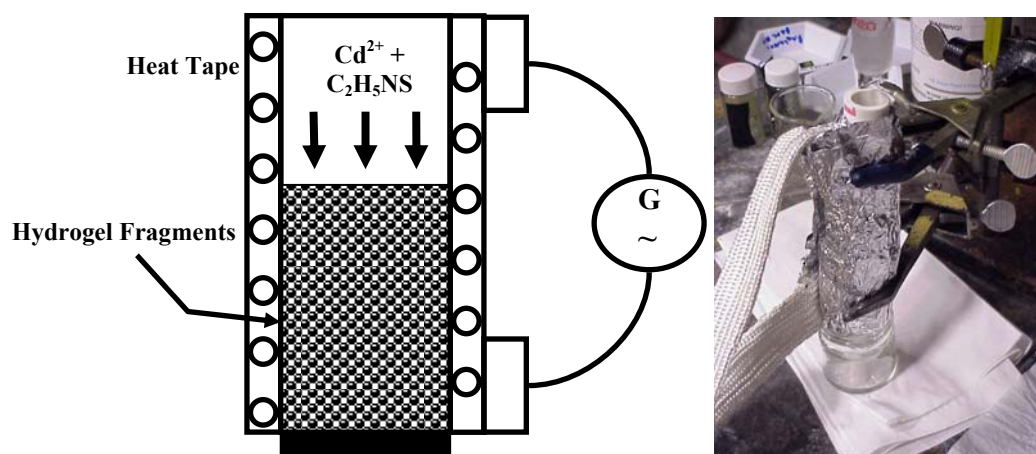


Figure I.5. Schematic cross-section (left) and digital camera image (right) of the set-up used in the gel columns filtration technique.

The exchange-drain-heat cycle just described was repeated several times for each gel column. The Cd^{2+} concentration in the drained solution was measured with atomic absorption. The results, averaged over a series of three experiments, are reported in Figure 6 for the high concentration solution ($[\text{Cd}^{2+}] = 5.4 \text{ g}\cdot\text{l}^{-1}$). The amount of metal absorbed in each run by the gel column decreased rapidly with increasing number of runs. For example, the amount absorbed was on the order of tens of mg per run for the initial 3 runs. The white circles in Figure 6 indicate the total amount of Cd^{2+} absorbed by the gel columns (i.e., the sum of the Cd^{2+} absorbed per each run). The total amount absorbed increases, obviously, with the number of runs, but reaches a plateau very quickly, in agreement with the initial radiolysis experiments. Comparable results were obtained for the lower concentration solution, which are not reported for brevity.

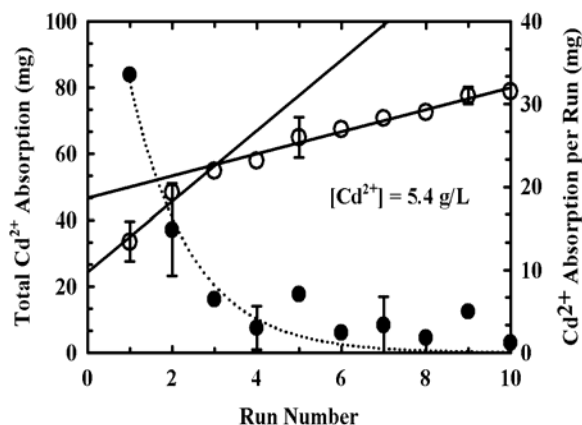


Figure I.6. Average Flame Atomic Absorption Spectroscopy data for high-concentration crushed-gel Cd^{2+} filters. The filters had an initial concentration of $[\text{Cd}^{2+}] = 5.4 \text{ g}\cdot\text{l}^{-1}$. The absorption was relatively linear with a rate of $10.7 \text{ mg}\cdot\text{run}^{-1}$ for the first few points, and $3.33 \text{ mg}\cdot\text{run}^{-1}$ for the remainder.

To investigate the origin of the decrease in the metal absorption with increasing number of cycles, the hydrogel fragments making up the columns were super-critically dried using CO_2 to create aerogels. BET

analysis showed that the aerogels had a surface area of $526 \text{ m}^2 \cdot \text{g}^{-1}$ and an average pore diameter of 5.8 nm. The data coincided, within experimental error, for the columns used for high and low metal concentration. Gels prepared with the same procedure described in the experimental section but that were not used in filter columns had a surface area around $870 \text{ m}^2 \cdot \text{g}^{-1}$ and average pore diameter of 7.7 nm. Thus, porosity and surface area were reduced by about 40% in gel columns used for 10 cycles. The observed reduction in mean pore size and surface area, while relevant, does not account completely for the observed reduction in metal absorption per run reported in Figures 2 and 3. In fact, the absorption capacity is expected to scale with the mean pore volume, that is, with the cube of the pore diameter. A reduction from 7.7 nm to 5.8 nm means a reduction of about 2.3 times of the available pore volume. The pore volume reduction is thus about 3 times lower than the observed reduction of metal absorption between the first and the tenth run, which was about a factor of 10. In addition, pore clogging would not be comparable for the high and low concentration filter columns. Another mechanism must have been at work, and that was likely formation of a dense crust of metal sulfide particles in the outer layers of the hydrogel fragments. In the larger gel fragments, which had a size of 4-5 mm, we often observed inhomogeneities in the coloration. Typically, the outer regions of these gel fragments were darker than the inner regions. Transmission electron microscopy analysis, as shown in Figure 7, also revealed the presence of a large number of sulfide particles with a diameter as large as several microns in all hydrogel fragments that were examined. These larger particles, which probably formed preferentially in the outer layers of gel fragments, impaired diffusion of the precursors towards the inner regions. Thus, the measured porosity was an average between the outer regions (whose pores were mostly clogged by nanoparticles), and the inner, more empty, regions.

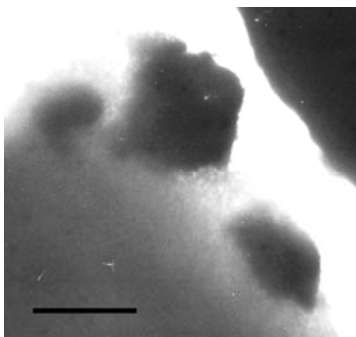


Figure I.7. Bright field TEM micrograph of CdS particles formed within the bulk of silica gel filters (crushed and monolithic). The reference bar represents 200 nm.

Improved diffusion in macro-porous gels

The data from the radiolysis and crushed gel experiments showed therefore that particle formation inside the gels tended to clog the matrix pores and impaired diffusion of fresh precursors inside the matrix. Metals accumulated in the outer layers of the gel particles. Therefore, materials had to be devised that allowed a faster diffusion. Among possible materials, it was decided to prepare gels with macro-pores, which were developed in collaboration with the group of Dr. N. Leventis, University of Missouri-Rolla. The large pores of these gels would be unlikely clogged by particles growing inside them; in addition, the materials could be made mechanically strong by a cross-linking process, and could be turned into micron-sized particles by ball milling. To compare the velocity of diffusion through conventional and macro-porous gels an experiment was designed where a monolithic gel cylinder was interposed as a septum between a waste simulant solution and a precipitant. Septa were fabricated out of silica gels fabricated following conventional recipes and by following the procedure developed by Dr. Leventis. This approach provided two advantages. In the first place, the velocity of absorption of the waste simulant provided indications on the diffusion velocity; in the second place, the gel septa proved so reliable and simple to use that a large-scale application of these materials proved conceivable, independent on radiolysis. In our experiments, a monolithic-gel filter was placed between two L-shaped PVC tubes connected by a clear acrylic tube. The acrylic tube served as a mold for the silica gel and a medium through which to view the resulting precipitations. A schematic and photograph of the apparatus

can be seen in Figure 8. The waste-simulating solution was placed on one side of the U-shaped filter, and the reactant solution was placed on the other side, with the hydrogel between them. Many waste-simulating solutions were attempted, including those containing Cd^{2+} , Sr^{2+} , Eu^{3+} , and Nd^{3+} . Most waste solutions were made in 125 ml of H_2O with concentrations comparable or higher than those typical of waste processing solutions [13]. The waste ion concentrations were $[\text{Cd}^{2+}] = 4.8 \text{ g}\cdot\text{l}^{-1}$, $[\text{Cd}^{2+}] = 0.48 \text{ g}\cdot\text{l}^{-1}$, $[\text{Sr}^{2+}] = 1.3 \text{ g}\cdot\text{l}^{-1}$, $[\text{Eu}^{3+}] = 1.0 \text{ g}\cdot\text{l}^{-1}$, and $[\text{Nd}^{3+}] = 6.0 \text{ g}\cdot\text{l}^{-1}$. All simulated wastes were reacted with a S^{2-} ion source, Na_2S , except Sr^{2+} , which was reacted with a CO_3^{2-} ion source, NaHCO_3 . The concentrations of the reactants were comparable or higher than the metal ion concentrations. The gel monolith served as a porous septum through which the two solutions diffuse. The resulting precipitates are nearly insoluble in water, and therefore remained within the gel. These particles aggregated and became immobilized within the porous structure of the gel. Approximately every 12 hours, a 2 ml sample was collected from the simulant side and saved for characterization.

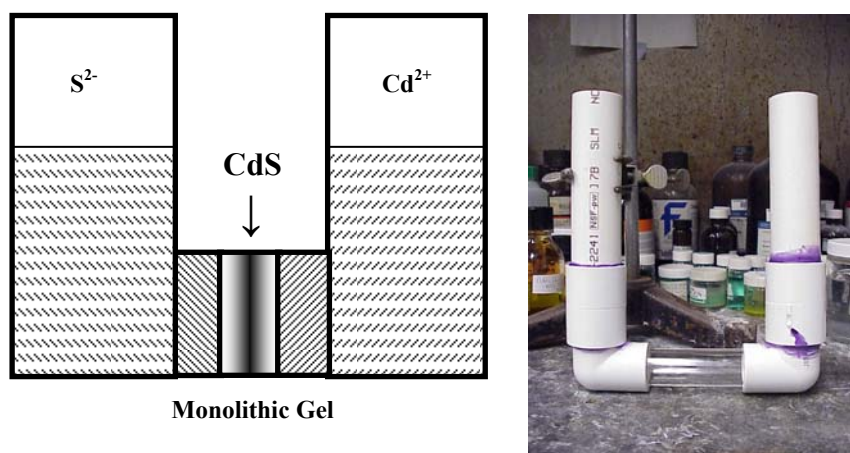


Figure I.8. Schematic (left) and photograph (right) of apparatus used in monolithic-gel filter. The gel monolith is formed in a clear acrylic tube (1.9 cm i.d.) and attached to two PVC pipes (3 cm i.d.) with an elbow converter.

The monolithic-gel method relies on the precipitation reaction between simulated waste salts and reactant solutions. The reactant solutions must therefore be chosen carefully to provide the most efficient precipitation of the waste materials within the gel. For example, both Cd^{2+} and Nd^{3+} ions can be filtered by precipitating as sulfides. Using atomic absorption spectroscopy, a linear relation between the amounts of Cd^{2+} absorption versus elapsed time was determined. The average rate of high $[\text{Cd}^{2+}] = 4.3 \text{ g}\cdot\text{l}^{-1}$ concentration filters was determined to be $442 \mu\text{g}\cdot\text{hr}^{-1}$, and the average rate of low $[\text{Cd}^{2+}] = 0.43 \text{ g}\cdot\text{l}^{-1}$ concentration filters was determined to be $23.7 \mu\text{g}\cdot\text{hr}^{-1}$. These rates are much lower than those for the crushed-gel filters, due to the time needed to diffuse to the center of the gel monolith and decreased surface area of absorption. The average capacities of the gels were calculated to be 1.17 mmole and $71.7 \mu\text{mole Cd}^{2+}$ per gram of dry gel, respectively, with 1 ml of dry gel having a mass of 0.1 g. The high-concentration absorption is 35 times higher than, and the low-concentration was double the amount that is typically obtained by derivatizing pore surfaces. The AA data for Cd^{2+} can be seen in Figure 9, and the neutron activation data for lanthanides and Sr in Figure 10.

The average capacities of the gels were determined to be 1.15 mmole Nd^{3+} , $167 \mu\text{mole Eu}^{3+}$, and $498 \mu\text{mole Sr}^{2+}$ per gram of dry gel, respectively, with 1 ml of dry gel having a mass of 0.1 g. The Nd^{3+} capacity is comparable to the amount absorbed by others [15] using partially sintered gels. It should be noted, however, that the total capacity might be much higher than the values reported here. In fact, gels continued to absorb metal ions for a long time. In addition, the precipitation reaction generally did not occur throughout the entire gel, but only a small ($\sim 25\%$ volume) portion in the center of the gel.

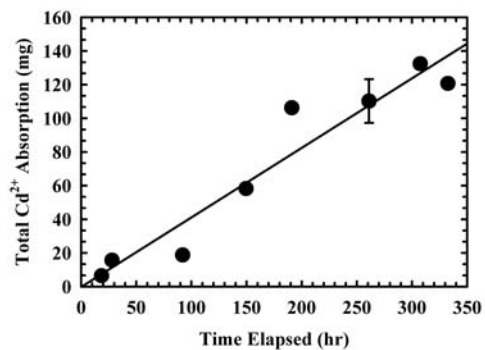


Figure I.9. Average Flame Atomic Absorption Spectroscopy data for microporous monolithic-gel Cd^{2+} filters. The waste simulant solution had an initial concentration of $[\text{Cd}^{2+}] = 4.3 \text{ g}\cdot\text{l}^{-1}$.

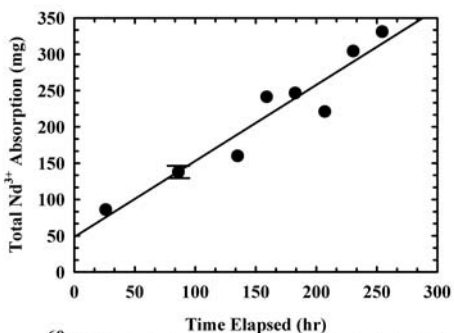
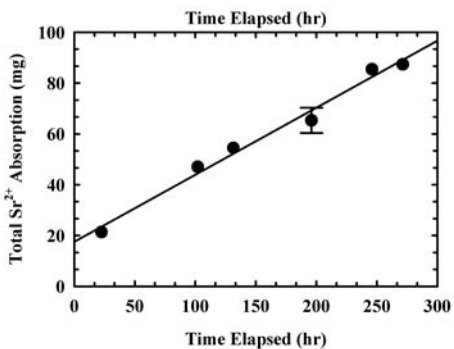
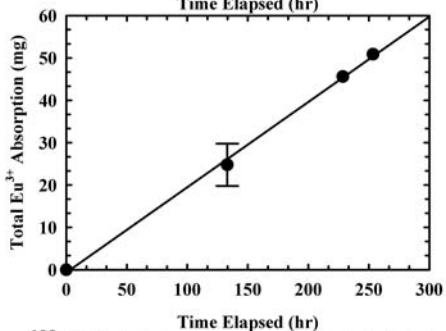


Figure I.10. Absorption rates of nuclear waste simulants by microporous monolithic gel filters. The concentrations of the contaminants were $[\text{Nd}^{3+}] = 6.0 \text{ g}\cdot\text{hr}^{-1}$, $[\text{Eu}^{3+}] = 1.0 \text{ g}\cdot\text{hr}^{-1}$, and respectively $[\text{Sr}^{2+}] = 1.3 \text{ g}\cdot\text{hr}^{-1}$.



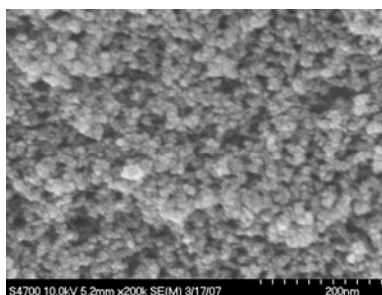
The results presented for microporous gels show that silica monoliths have a high filtration capacity, constant filtration velocity, and can be used to precipitate a wide range of metal ions. However, the filtration velocity is not very large, and the gel filters are mechanically unstable. Filtration (i.e., diffusion) velocity and mechanical stability were crucial for the proposed convection experiments. We decided therefore to fabricate silica gels with large pores to increase the filtration speed, and to cross-link the gels to increase their mechanical stability. For this, a collaboration was initiated with Dr. Nicholas Leventis, also at University of Missouri-Rolla, who has developed a series of sol-gel techniques that allow to attain mechanically strong materials with large pores. An undergraduate student, Lane Martin, was put to work on the project after the graduation of Brian Heckman, and was helped part-time by graduate students working in the group of Dr. Leventis. Mechanically strong, macroporous hydrogels were prepared by modifications of published procedures. Specifically, we based our synthesis on recent work by the Nakanishi group [16], which, in turn, is based on a modification of Stucky's method for SBA-15/MCF materials [17,18]. Nakanishi's approach yields monolithic silica with well-defined periodic macropores by reducing the amount of solvent (aqueous acid) in Stucky's process, thus obtaining gels rather than precipitates. In Nakanishi's method, however, the gelation solvent (water) was removed at 60 °C under ambient pressure, and the templating agent (Pluronic P123 – BASF -) was removed by calcination at 650 °C. Solvent and templating agent removal lead to up to 50 % volume shrinkage, which is not desirable if large, crack-free monoliths are to be prepared. We decided therefore to remove solvents swelling agents and surfactants by repeated washings and Soxhlet extraction [19]. Our extraction procedure minimizes the shrinking and cracking of calcination treatments, and yields large, crack-free monoliths. In a typical synthesis, macroporous gels were prepared by dissolving four grams of P123 in 12 grams of a 1.0 M aqueous solution of nitric acid; to this solution, 3.1 grams of 1,3,5 trimethyl benzene (TMB) were added under vigorous stirring. After about 3 hours, the system was cooled to 0⁰ C in an ice bath, and then 5.15 grams of TMOS were added under stirring. After 10 minutes the solution was poured into a mold. The mold was kept 60⁰ C for 5x the gelation period (roughly 12-15 hours). The gel was then washed twice in ethanol, 8 hours each time. To the washings followed Soxhlet extraction using acetonitrile for two days to remove P123. The gels were then washed 4 times with acetone (8 hours). The mechanical stability of the gels was increased by cross-linking, as previously established by our groups. To cross-link, the macroporous gels were placed in 200 ml of acetone in which 22 grams of Desmodur N3200 (Bayer) had been previously dissolved. After bathing in Desmodur solution for 24 hours, the gels were placed in a sealed container and heated to 55⁰ C for 3 days. The gels were washed 4x in acetone, (8 hours), methanol, and water. Porosity, density, mechanical strength and surface area of the two types of monoliths used in our experiments are reported in Table 1. Notice that the BET surface area of the cross-linked monoliths is more than 100 times smaller than that of microporous monoliths. This is because the cross-linking polymer clogs the nanopores while leaving the micropores nearly unscathed, as shown in figure 11. At the end of the process, the monoliths had a diameter of about 16 mm and a length of up to 55 mm. They were then glued to stainless steel washers which had an inner diameter of 8 mm and an outer diameter of 19 mm. The washers were snugly fit into the same acrylic molds used for the microporous gels, and silicon glue was then employed to waterproof the contact between washers and mold.

The filtering ability of macroporous cross-linked gels was compared to that of the microporous gels by filtering a 4.3 g·l⁻¹ solution of Cd²⁺. The metal absorption rate is reported in figure 12. The data could be well reproduced by a linear fit, from which a rate of 0.692 mg·hr⁻¹ was calculated. This rate is about 1.5 times higher than that of microporous gels, but has to be increased by another 5.6 times to account for the different cross-sections of the filters. Because of shrinking during the templating agent removal process, macroporous gels had a diameter about 2 mm smaller than the molds into which they were formed, and had to be glued to washers which had an inner diameter of 8 mm and an outer diameter equal to the inner diameter of the molds and. Microporous gels did not have any shrinking issues, and therefore the acrylic molds with a diameter of 19 mm into which they were formed could be glued directly to the PVC tubing. Once the different effective diameters (8 vs. 19 mm) of the monoliths are

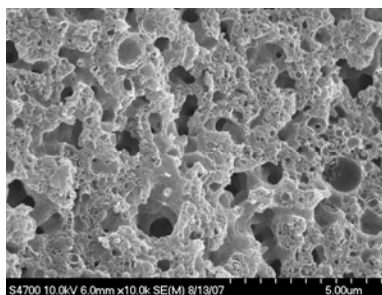
accounted for, we obtain that absorption rates through macroporous gels are a factor 8-9 times higher than through microporous gels.

The higher absorption rate of the macroporous gels is in apparent contrast with the porosity data reported in Table 1. The BET surface area of cross-linked macroporous gels is about 600 times lower than that of microporous gels, and the porosity is a factor 2.5 lower. Thus, one would expect the absorption rate of microporous gels to be higher than that of macroporous gels. This apparent contradiction can be explained by taking into account the interaction of the metal ions with the pore walls. Previous work by the Collinson group [20-24] has shown that the diffusion of chemical species within sol-gel materials depends on the pore size but also on the interaction between the chemicals and the pore walls. The diffusion velocity increases when the pore size is increased and it decreases when the interaction with the pore walls increases. In monoliths with narrow pores, most ions will be near the walls and interact with them. Thus, in microporous systems the interaction with the walls is the limiting factor. In systems with larger pores, the fraction of ions that interact with the walls will be much smaller, and therefore the interaction with the walls will be less important. The difference between micro- and macro-porous gels observed in our experiments can be explained in the same terms. In macroporous gels very large pores are available, a small fraction of the ions interacts with the walls, and diffusion is rapid. In microporous gels the pore density is higher but the pores are very small and diffusion is slow. Thus, the observed differences in absorption rates can be reconciled with the different diffusion velocities, which, in turn, are dictated by pore size and pore wall interactions. We think that the different termination of the pore walls in microporous and macroporous gels did not play a relevant role. In fact, the walls of microporous gels had a OH⁻ termination at the pH values used in our experiments (pH>3 in all our experiments). These negatively charged groups probably interacted strongly with Cd²⁺ and decreased the diffusion velocity. Macroporous gels had a NH₂ termination, which might have also coordinated Cd²⁺. However, the pores of the macroporous gels were so large that the interaction with the walls did not play a relevant role. Collinson, for example, showed that the diffusion coefficient in OH⁻ terminated monoliths was comparable for anions and cations, provided that the pores had a diameter larger than about 20 nm. Thus, the results obtained with macroporous gels are in line with expectations, and show that macroporous cross-linked materials can be used as filter materials.

a)



b)



c)

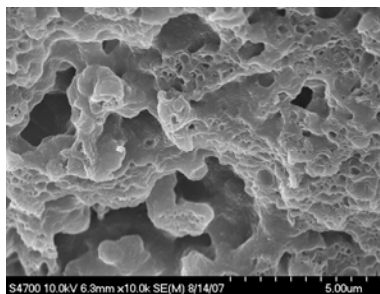


Figure I.11. Scanning electron microscopy images of a) microporous silica gels, b) macroporous gels before cross-linking, and c) macroporous gels after cross-linking.

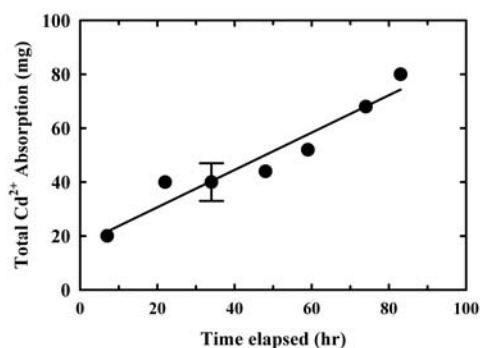


Figure I.12. Absorption rate of Cd^{2+} through a macroporous gel. The contaminant concentration was $4.3 \text{ g}\cdot\text{l}^{-1}$.

Metal Ion	Contaminant Concentration ($\text{g}\cdot\text{l}^{-1}$)	Rate of Absorption ($\text{mg}\cdot\text{hr}^{-1}$)	Minimum Capacity ($\square \text{mole}\cdot\text{g}^{-1}$ dry gel)
Cd^{2+}	4.3	0.442	1171
* Cd^{2+}	*4.3	*3.90	*670
Nd^{3+}	6.0	1.05	1147
Eu^{3+}	1.0	0.201	167
Sr^{2+}	1.3	0.264	498

Table I.1. Summary of results for monolithic gel filters. Notice that the values of the capacity were calculated based on the amount of metal absorbed at the time the experiments were stopped, typically 300 hours. Absorption had not been observed to saturate at that point and therefore the indicated capacities are to be interpreted as minimum values. The asterisk indicates the result obtained with macroporous cross-linked gels.

Conclusions

The results obtained show that silica hydrogels can be used as high-capacity sorbents. Our approach differs from most other approaches, since metals are not adsorbed to the walls of the pores. Instead, nano- and micro-particles of the contaminant are formed inside the pores, thereby allowing to exploit the volume, and not only the surface, of the porous matrix. We have also shown that the entrapment velocity increases by almost an order of magnitude when macro-porous gels are formed. The materials and techniques devised in our experiments could be conceivably employed to i) produce large amounts of gel

microparticles to be used as filtration beads by radiolysis; and ii) to produce large monoliths, to be used for filtration purposes.

Educational Component. A M.S. student graduated with thesis in 2006, Brian Heckman. Brian graduated in record time (one year), and this left time and resources to further proceed with the research. It was decided to use mostly undergraduate students, since the remaining time at disposal for the completion of the project, about one year, was not sufficient for a M.S. thesis. Five undergraduates (Ryan Hupe, Lane Martin, Lauren Rich, Joshua Carey, David Kimzey) were hired to further develop the project, and two of them, Lane Martin and Lauren Rich, proved very skilled and reliable. These students in a very short time mastered the project and fabricated macroporous, cross-linked gels monoliths. Ph.D. candidates (Sudhir Mulik, Vishal Patel, Arumugam Thangavel, and Naveen Chandrasekaran) from the Leventis group were hired part-time for short times (1-2 months) to help complete synthesis and analysis of the macroporous filters. Results originating from the research activity have originated four manuscripts published in international journals, plus another three submitted, and in participation to three conferences. Six of the manuscripts have been published or submitted which include undergraduates as co-authors.

References

1. J. F. Hund, M. F. Bertino, G. Zhang, C. Sotiriou-Leventis, N. Leventis, A. Tokuhiko, and J. Farmer, "Formation and Entrapment of Noble Metal Clusters in Silica Aerogel Monoliths by α -Radiolysis", *J. Phys. Chem. B* **107**, 465 (2003).
2. M. F. Bertino, J. F. Hund, J. Sosa, G. Zhang, C. Sotiriou-Leventis, N. Leventis, A. T. Tokuhiko, and J. Terry, "High resolution patterning of silica aerogels", published as a letter in *J. Non-Cryst. Solids* **333**, 108 (2004).
3. J. F. Hund, M. F. Bertino, G. Zhang, C. Sotiriou-Leventis, N. Leventis, "Synthesis of homogeneous alloy metal clusters in silica aerogels", *J. Non-Cryst. Solids* **350**, 9 (2004).
4. R.R.Gadipalli, L.A.Martin, B. Heckman, J.G.Story, M.F.Bertino, N.Leventis, P. Fraundorf, and S.Guha, "Patterning porous matrices and planar substrates with quantum dots", *J Sol-Gel Sci Techn.* **39**, 299 (2006).
5. R.R.Gadipalli, L.A.Martin, B. Heckman, J.G.Story, M.F.Bertino, N.Leventis, P. Fraundorf, and S.Guha, "Infra Red Quantum Dot Photolithography", *J Sol-Gel Sci Techn.* **40**, 101 (2006).
6. M. F. Bertino, R.R. Gadipalli, L. A. Martin, L. E. Rich, A. Yamilov, B. R. Heckman, N. Leventis, S. Guha, J. Katsoudas, R. Divan and D. C. Mancini, "Quantum dots by ultraviolet and X-ray lithography", *Nanotechnology* **18**, 315603 (2007).
7. M. F. Bertino, R. R. Gadipalli, B. Heckman, L. Martin, N. Leventis, and A. T. Tokuhiko, "Sol-gel Materials for High Capacity, Rapid Removal of Metal Contaminants", *Separation Science and Technology*, manuscript #3232, submitted.
8. M. F. Bertino, A. Nanni, M. Hoffmann, N. Leventis, and A. T. Tokuhiko, "Interaction of quantum dots with ionizing radiation" *Langmuir*, manuscript # la-2007-031847, submitted.
9. M. F. Bertino, N. Leventis, R. R. Gadipalli, L. Rich, L. Martin, J. G. Story, A. Yamilov, S. Guha, B. Heckman, "Three-dimensional semiconductor patterning by multiphoton ionization", *Chemistry of materials*, manuscript #cm-2007-03031q, submitted.
10. A. Henglein, "Estimated Distributions of Electronic Redox Levels in aq/Caq, H⁺/Haq and Some Other Systems", *Ber. Bunsenges. Phys. Chem.* **78**, 1078 (1974).
11. M. Mostafavi, Y.-P. Liu, P. Pernot, J. Belloni, "Dose rate effect on size of CdS clusters induced by irradiation", *Radiation Physics and Chemistry* **59**, 49 (2000).
12. D. Hayes, O. I. Mitit, M. T. Nenadovit, V. Swayambunathan, and D. Meisel, "Radiolytic Production and Properties of Ultrasmall CdS Particles", *J. Phys. Chem.* **93**, 4603 (1989).
13. R. G. Cochran, N. Tsoulfanidis, "The Nuclear Fuel Cycle: Analysis and Management" American Nuclear Society, p. 301, (1999).
14. C. M. Bagnall, J. Zarzycki, "Obtention of CdSe/S precipitates in sol-gel matrices" *SPIE* **1328**, 708 (1990).

15. T. Woignier, J. Reynes, J. Phalippou, J.L. Dussossoy, N. Jacquet-Francillon, "Sintered silica aerogel: a host matrix for long life nuclear wastes", *Journal of non-crystalline solids* **225**, 153 (1998).
16. T. Amatani, K. Nakanishi, K. Hirao, T. Kodaira, *Chem. Mater.* 17 (2005) 2114.
17. D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. Chmelka, G. D. Stucky, *Science* 279 (1998) 548.
18. D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* 120 (1998) 6024.
19. N. Leventis, S. Mulik, X. Wang, A. Dass, V. U. Patil, C. Sotiriou-Leventis, H. Lu, G. Churu, A. Capecelatro, *Jou non-cryst. Solids*, in press.
20. M. M. Collinson, P. J. Zambrano, H. Wang, J. S. Taussig *Langmuir* 15, 662 (1999).
21. M. Kanungo and M. M. Collinson *Langmuir* 21, 827 (2005).
22. A. R. Howells, P. J. Zambrano, and M. M. Collinson *Anal. Chem.* 72, 5265 (2000).
23. M. Kanungo and M. M. Collinson *Anal. Chem.* 75, 6555 (2003).
24. M. M. Collinson and B. Novak *Jou. Sol-Gel Sci.Technol.* 23, 215 (2002).

Section II. Hydrogels made of thermo-sensitive groups to capture and encapsulate metallic cations in aqueous media (T. Tokuhira) Final Report

The overall goal of this part of the project was to establish the fundamental science for capturing and encapsulating metallic cations, major components in low-radioactive waste streams, by functionalized hydrogels consisting of thermo-sensitive polymer networks.

We have demonstrated that: i) while maintaining thermal property of the major polymer component, *N*-isopropylacrylamide (NIPA), some functional groups (minor polymer component) capable of capturing metallic cations were synthetically incorporated into the polymer networks; ii) selective capturing of specific cations by specific functional groups was found; and iii) encapsulation process based on thermal property of hydrogels was successfully achieved. We will describe the achievements more in detail in the following.

A. Synthesis of hydrogels made of thermo-sensitive poly(NIPA) networks containing functional groups capable of capturing metallic cations

A1. Radical polymerization and gelation of copoly[NIPA(*m*)/minor(*n*)] where, minors are sodium acrylate, allyl alcohol, or allyl cyanide while NIPA contains amide group as functional group were successfully carried out by following usual method [1-17]. Here, *m* and *n* stand for mol fractions

A2. A new approach for *in-situ* functionalization of copolymer networks was developed in which an existing functional group in copoly[NIPA(*m*)/minor(*n*)] networks (synthesized in **A1**) is transformed to other functional group by chemical reaction conducted in hydrogels [18]. For example, hydroxyl groups in copoly[NIPA(*m*)/allyl alcohol (*n*)] was successfully converted to [–OPO₃]^{3–} groups covalently bonded to –CH₂– groups. Experimental set-up is shown in Fig. 1.

A3. Experimental determination of chemical composition of copolymer networks

There are subtle differences in reactivity of each monomer in radical polymerization and gelation process and this may consequently lead to different ratio of *n/m* than expected from the original ratio in pre-gel solution. When *n/m* < 0.05, we confirmed that negligibly small discrepancy between them (less than 5 %) did not influence scientific conclusion [18]. However, we intended to incorporate various functional groups at possibly much higher ratio while maintaining thermal property of NIPA component in this project, we must experimentally determine resultant *n/m* ratio. Thus, chemical compositions of all

copolymer networks synthesized were analyzed by elemental analysis to obtain the final stoichiometry (n/m). We found the experimental error ranges for atomic weight percentages of hydrogen, carbon and nitrogen obtained by Perkin-Elmer Model 2400 in five specimens taken from various portions of dried gel is less than $\pm 2\%$, as compared to just below $\pm 1\%$ in re-crystallized NIPA specimens. These facts assure that our dried gel materials are homogeneous in composition. A mathematical procedure (written in "C") was developed for seeking a best-fitted value of n/m by satisfying that all theoretical n/m values obtained for hydrogen, carbon and nitrogen must fall within $\pm 2\%$ in reference to the experimental n/m value.

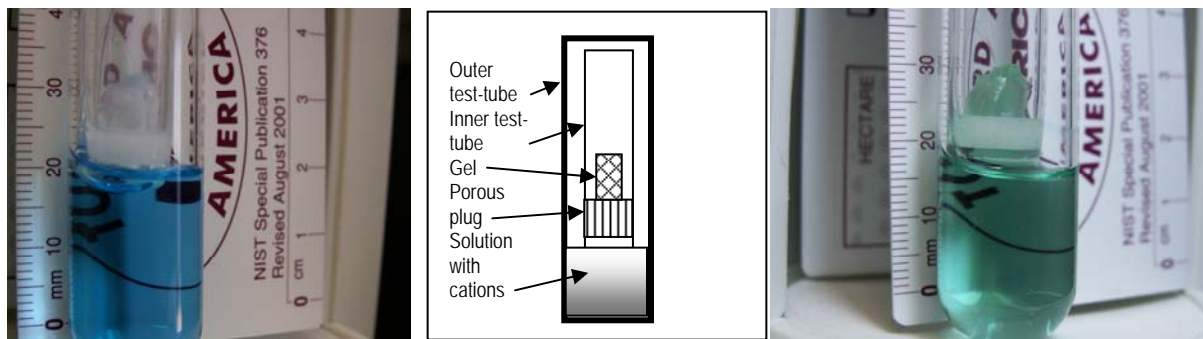


Figure II.1. Set-up of in-situ esterification of $-\text{OH}$ group to $[-\text{OPO}_3]_3-$ by means of micro flow system. A fritted glass “porous plug” filter: 10 mm o.d.; 5 mm thickness; average pore size, 5-8 μm . Blue portion: aqueous solution of phosphoric acid (50 mM) with an indicator. Image at left is on day 1, image at right is some 9 days later. Esterification between OH group and phosphoric acid will occur only within gel piece.

A-4. Experimental Results: Physical property of shrunken gels

A summary of the physical property of gels in the shrunken (sh) state is presented in Table 1. The water content in gels (Column 5) was obtained by subtracting both mp (column 1) and the amount of cations caught in gels from the experimental mass of gels (sh). Taking the ratio of the amount (Column 5) versus mp (Column 2) generates the number of water molecules per a single polymeric residue (Column 6) [14,15]. Table 1 shows the state of hydration varies with the kind of cation and functional group. In general, one polymeric residue is surrounded by approximately 15 water molecules.

Table II.1. Physical property of polymer gels (sh)a

	Column 1	2	3	4	5	6
	Mass of	Amount of	Mass of	Mass of	Amount of	Number of
Polymer	polymer	polymeric	gel (sh)	water	water	water per
network	network	residue (sh)		in gel (sh)	in gel (sh)	polymeric
	[mg]	[10 ⁻⁴ mol] ^b	[mg]	[mg] ^c	[10 ⁻³ mol] ^d	residue ^e
CO²⁺						
NIPA	24.9	2.20	95.9	68.1	3.78	17.2
NIPA/NaAc	25.2	2.33	88.3	59.7	3.31	14.2
NIPA/AAI	25.1	2.53	87.7	59.5	3.30	13.1
NIPA/ACn	25.4	2.50	83.1	54.1	3.00	12.0
Cr³⁺						
NIPA	24.8	2.19	87.7	61.2	3.40	15.5
NIPA/NaAc	25.4	2.34	94.1	66.8	3.71	15.8
NIPA/AAI	24.6	2.48	70.1	43.8	2.43	9.8
NIPA/ACn	24.9	2.45	91.5	64.8	3.60	14.7
Cu²⁺						
NIPA	25.3	2.24	33.1	5.8	0.32	1.4
NIPA/NaAc	24.7	2.28	51.7	24.8	1.38	6.0
NIPA/AAI	25.4	2.56	35.4	8.0	0.45	1.8
NIPA/ACn	24.9	2.45	35.8	8.9	0.49	2.0
Ni²⁺						
NIPA	24.6	2.17	93.3	66.2	3.67	16.9
NIPA/NaAc	25.4	2.34	83.2	54.3	3.01	12.9
NIPA/AAI	25.3	2.55	88.8	60.9	3.38	13.3
NIPA/ACn	24.9	2.45	85.3	58.3	3.24	13.2

a: sh denotes the shrunken state of gel.

b: mass of polymer used in experiment divided by the mean formula mass of copolymer network.

c: equals (mass of gel (sh) - (mass of polymer network) - [mass of cations in gel (sh) (Table 2)])

d: mass of water (c) divided by molecular mass of water 18.015 g.

e: (d) divided by (b).

B. Capturing and encapsulating cations by hydrogels

In order to assess the anticipated dynamic phenomena in *in-situ* waste processing, a static condition was established and taken as the reference case. This permits one 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 encapsulated in polymer gel pieces, the following encapsulating process was performed as follows: Step (1) is designed to determine the metal binding capability of functional groups. Namely, we determine the amount of cations caught in gel pieces. Step (2) evaluates the retainability of functional groups. Here, we determine the quantity of cations remaining in gel pieces after transforming the polymer networks from a swollen state to the (volumetrically) shrunken state. Henceforth, we quantitatively determine the stoichiometric ratio between metallic cation *versus* functional group.

B1. Quantitative determination of cation concentration

Atomic absorption (AA) flame photometry method was used to quantitative determination of cations caught in hydrogels. Relations between absorbance (*A*) and concentration (*C*) of the respective cations were mathematically expressed as:

$A = aC + bC^2 + cC^3$ where $a \gg b \gg c$. Absorbance data were obtained using a Perkin Elmer Model 3200 AA photometer and a , b , and c were established with various concentrations of freshly prepared solutions of respective nitrates. Concentration of the respective cations in specimens was then determined by solving linear, quadratic or cubic equations. The absorption wavelengths for Co^{2+} , Cr^{3+} , Cu^{2+} , Ni^{2+} and Na^+ were 240.7, 357.9, 324.7, 341.5, and 589.0 nm, respectively.

B2. Experimental scheme for capturing cations

In Step (1), a piece of lyophilized polymer networks (*mp*) was weighed in a small plastic bottle (with a tight cap). Then a sufficient amount of deionized water was added and the contents of the bottle left for more than a week at room temperature. After discarding the water, a 200 mL aqueous solution (100 mM) of Cobalt (II), Chromium (III), Copper (II) or Nickel (II) nitrate was added to now swollen gel piece. Sixteen different samples thus prepared were left at $30^\circ \pm 1^\circ\text{C}$ in anticipation of a chemico-physical capturing of the metallic cations. The amount of cations caught in a gel piece was indirectly monitored by taking 1.0 mL of aqueous solution of cations for analysis *via* AA method. The same sampling was repeated everyday to monitor changes in concentration for one full week.

B-3. Experimental scheme for encapsulating cations

In Step (2), upon completion of Step (1), about 90 % volume of the respective solution was removed from the bottle. The remaining, now colored gel piece(s) was/were then transferred carefully to another small vial without physically touching gel piece. The coloration is here an indication of cation uptake. A representative image is shown in Fig. 2. This vial was then immersed in a small, thermo-regulated water bath whose temperature was adjusted to slightly above the respective T_{tr} [19]. As the vial temperature rose above T_{tr} , the small gel piece shrank in volume into a smaller piece within a matter of a few minutes. Water from the gel piece was so released. After removing the dispelled water with a pipette and filter paper, this vial containing a piece of gel (tightly capped) was transferred in a large thermo-regulated water bath (43° or $65^\circ\text{C} \pm 0.1^\circ\text{C}$) and left intact for 3 full days. Further shrinkage of gel pieces produced additional water. After carefully removing the residual solution while maintaining the bath temperature, the vial was quickly removed, still tightly capped and left to acclimate to room temperature. This completed the encapsulation process. Then, each vial was weighed and mass of the piece recorded. The shrunken small gel pieces so produced were deeply colored. Gel pieces were subsequently digested by gentle boiling in concentrated nitric acid in a Kjeldal flask (1 full day). The entire volume of nitric acid solution (about 2 mL) was transferred to a volumetric flask with water and used for AA determination.

B-4. Experimental Results: Evaluation of metal binding capability of functional groups [20]

The AA results in Step 1 indicate the following: (1) that all samples reached in equilibrium within 6 - 7 days; and (2) that different rates of uptake of the respective cations took place in each of the different samples before reaching equilibrium. Since all aqueous solutions of transition metal nitrates are take on color (visible range); that is, Co^{2+} , Cr^{3+} , Cu^{2+} , and Ni^{2+} , respectively appear pink, purple, blue, and green (see Fig. 2), the above gels all assume color when they reached their equilibrium state. In order to further understand the nature of the above process, we sought to reverse the process itself. Namely, all colored (shrunken) gels obtained above were immersed in pure deionized water and left intact at 30°C for one full week. The result was that the colored gel pieces returned to their transparent, uncolored state and water took on the corresponding color. The reversible infusion of cations into hydrogel pieces is thus a simple diffusion of cations in and out of gel phase, and is likely driven by the concentration gradient of cations. However, rate processes can often be different from one another, and thus it is likely that some weak chemical binding by functional groups occurred to a different extent in the uptake of the sampled cations into gel phase.

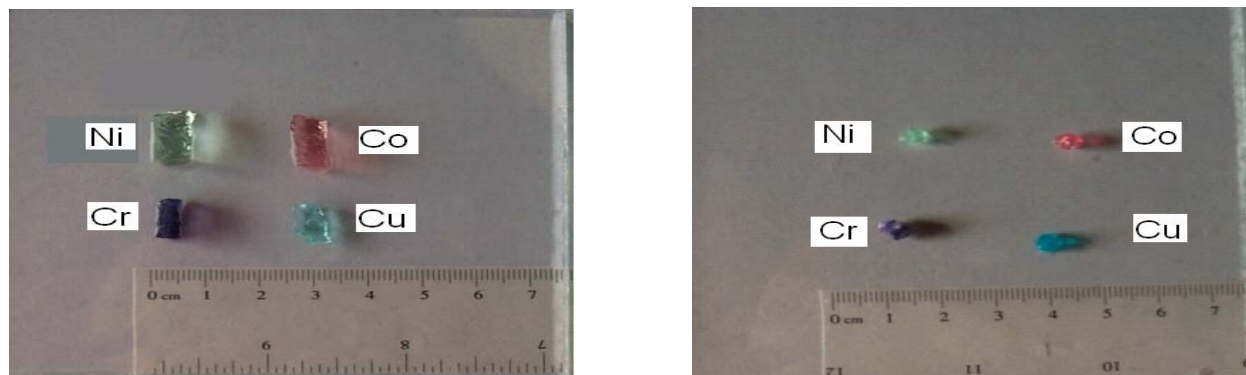


Fig. II.2. Pre-shrunken gels with metallic nitrates (L) and shrunken gels (R)

B-5. Experimental Results: Evaluation of effectiveness of encapsulation

The 16 gel samples prepared in Step 2 were subjected to cation content determination by AA method. Table 2 tabulates the result of the AA in terms of mass of cations in gel (sh) [mg] (Column 2). Further, in order to characterize the effectiveness of encapsulation of cations, as it occurred in the shrunken copolymer networks, we first express the amount of cations caught in gels (sh) (Column 2) in terms of mol (Column 3). Since this amount is nonzero for homo-polymer networks of NIPA, it implies that poly(NIPA) also works as an encapsulating agent. The amount of Poly(NIPA) in three copolymer systems is not the same as shown in Column 4 and therefore, we must evaluate the amount of cations encapsulated by polymeric NIPA residues. By considering the amount of other polymer component in the three copolymer systems as one-third of the polymeric NIPA residues, one may approximately treat the encapsulation ability of the NIPA component (in three copolymer systems stays) equally as in the homo-polymer NIPA system. On this basis, we evaluated the amount of cations encapsulated by polymeric NIPA residues in the three copolymer systems by taking into account the amounts of poly(NIPA) noted in Column 4. This result is shown in Column 5. Then the contribution from the polymeric NIPA residues must be subtracted from the overall cations content shown in Column 3. The remainder must logically be assigned to the contribution from the other polymeric residues. Thus, the amount of cations encapsulated by the other polymeric residues is calculated as shown in Column 6. Finally, we can logically assess how many other polymeric residues, i.e., functional groups, are needed to encapsulate a single cation (Column 7).

Table II.2. Amount of encapsulated cations in polymer gels (sh)^a

Column 1	2	3	4	5	6	7
	Mass of	Amount of	Amount of	Amount of	Amount of	Number of
Polymer network	cations in gel(sh)	cations by in gel(sh)	NIPA polymer	other polymer	cations by other polymer	polymer per cation
	[mg]	[10 ⁻⁵ mol] ^b	[10 ⁻⁵ mol] ^c	[10 ⁻⁵ mol] ^d	[10 ⁻⁵ mol]	[10 ⁻⁵ mol]
			Co²⁺			
NIPA	2.89	4.90	22.4	0	0	[4.5] ^e
NIPA/NaAc	3.39	5.75	17.4	5.81	1.87	3.1
NIPA/AAl	3.14	3.14	18.9	6.31	1.11	5.7
NIPA/ACn	3.63	3.63	18.7	6.25	1.98	3.2
			Cr³⁺^e			
NIPA/NaAc	1.87	3.60	17.6	5.86	1.04	5.6
NIPA/AAl	1.74	3.34	18.6	6.19	0.63	9.8
NIPA/ACn	1.78	3.43	18.4	6.12	0.76	8.1
			Cu²⁺			
NIPA	2.04	3.21	22.3	0	0	[7.0] ^e
NIPA/NaAc	2.18	3.44	17.1	5.7	0.98	5.8
NIPA/AAl	1.98	3.11	19.1	6.39	0.36	18
NIPA/ACn	1.99	3.13	18.4	6.12	0.49	13
			Ni²⁺			
NIPA	2.55	4.34	21.7	0	0	(5.0) ^e
NIPA/NaAc	3.52	5.99	17.6	5.86	2.48	2.4
NIPA/AAl	2.58	4.39	19.0	6.36	0.58	11
NIPA/ACn	2.14	3.64	18.4	6.12	~ 0	

a: sh denotes the shrunken state of gel.

b: values in Column 2 were divided by the respective atomic mass of cation

c: obtained by: amount of polymer residue expressed in mol (column 3 in Table 1) times 0.75 for all copolymers

d: by: amount of polymer residue expressed in mol (column 3 in Table 1) times 0.25 for all copolymers

e: values refer to NIPA.

Thus in summary, the quantity shown in Table 2, Column 6 (also Column 7), represents the encapsulation effectiveness of various cations by different copolymer networks, i.e., functional groups. Specifically, small values in Column 7 indicate that only small number of functional groups is needed to encapsulate a single cation. In other words, it indicates a high affinity for encapsulating cations.

From the values listed in Column 7, we can provisionally conclude as follows: (1) that the thermo-sensitive property arises from the major polymer component, poly(NIPA), while other copolymer components act as modifiers. However, the tabulated values indicate that poly(NIPA) lies in the middle in magnitude and thus, we can (only) regard the NIPA group as one of possible encapsulating groups. It is worth noting that one disadvantage is the lack of specificity for specific cations; (2) that carboxylic group has the most effective encapsulating capability for all cations examined in this study (Co²⁺ and Ni²⁺, in particular); (3) that the allyl alcohol group is the weakest; that is, with nearly zero encapsulating capability for both Cu²⁺ and Ni²⁺; (4) that the allyl cyanide group is very effective specifically for Co²⁺. It selectively encapsulates Co²⁺; and (5) reasoning, the carboxylic group exhibits that numbers do not

indicate a specific relation between the positive charge of cations and the number of possible negative charge on the polymer chain.

With regard to the conclusion (5) above, electrical neutrality within gel must, in principle, be maintained. In the case of NaAc, it might be possible to maintain the electrical neutrality while no such possibility exists for other polar groups and thus, gels must also take in the counter anions (nitrate in this case). One experimental evidence of this is revealed by the absence of Na⁺ in copoly [NIPA(0.75)/NaAc(0.25)] gels with encapsulated cations. We found Na⁺ (determined by AA) in the original aqueous solutions of nitrates of the above four transition metals after the referred to encapsulation process. This means that transition metal cations diffuse into the gel pieces while simultaneously sodium cations diffuse out. However, the values shown in Column 7 may be seen as inconsistent with this concept of electrical neutrality if only a Coulombic interaction is considered. On the contrary, this suggests that a simple Coulombic interaction is not the sole source of chemical interaction between the cation and functional group. This suggests some coordination chemical bonds. A recent study on hydrogels of copoly [NIPA (668mM) / NaAc(32mM)] by Tokuhiko and Tokuhiko (2007) [19] shows that NaAc fully dissociate in aqueous environment and thus, the polymer networks carry negative charges while sodium cations are present near the carboxylic groups as hydrated cations. Since the ionized carboxylic group is a weak base, it exists in chemical equilibrium with the corresponding acid form that is attached to the major polymer chain. This equilibrium significantly shifts toward localizing more ionized (COO⁻) groups near T_{tr} . We think it likely that this accelerates the encapsulation process. Further, this may satisfy part of the electrical neutrality of the gel system as the polymer networks becomes more negatively charged. This will require further investigation.

In order to extend the scope of elements (radioisotopes) amenable to encapsulation by polymer gel networks, we have expanded the above static experiments to encompass other functional groups with 4 rare-earth cations, i.e., Pr, Eu, Tb, and Ho (all tri-valent) instead of transition metal (surrogate) cations. Two manuscripts for the results and analyses are currently in preparation.

C. Effects of γ -ray irradiation on integrity of polymer networks

All experiments for encapsulating metallic cations by hydrogels were conducted by using cations, i.e., non-radioactive elements. This poses a question that how integrity of hydrogels can be maintained in real radioactive disposal streams. Heats generated by low-radioactive wastes (2 watts/L) is counted as one of the factors for assisting volumetric contraction process of hydrogels pieces and thus, promoting encapsulation of cations in a possible processing design by means of natural convection-type cell (see Section III). Since we are not properly equipped for conducting extensive examination of the problem, we investigated effect of the presence of oxygen molecules dissolved in aqueous solutions of poly(vinyl alcohol) (PVA) under γ -ray irradiation. Our experiments confirmed that oxygen molecules acted as scavenger to prevent generation of radicals that lead to cross-linking of PVA and thus forming PVA hydrogels. This may be interpreted as an encouraging sign for possible practical application of our approach for radioactive waste disposal in which integrity of copolymer networks may be maintained.

Conclusion

The results show capturing and encapsulating various metallic cations dissolved in water are scientifically and technically feasible approach and applicable to low-radioactive waste disposal processing. It should be emphasized here that separation of hydrogels containing metallic cations could be achieved by simple method such physical filtration and cations are confined in much smaller volume.

Educational Component. A M.S. student, Sita S. Akella graduated with thesis in Chemical Engineering Program, December, 2006. She engaged in 1) synthesis of various copolymer gels consisting of NIPA and other minor component containing functional groups and 2) investigation of capturing and encapsulating property for metallic cations dissolved in water. Rolanda, M. Reed (B.S. Chemical Engineering, University of Missouri-Rolla, May, 2005 and enrolled in Engineering Management Graduate Program) and Arish Labroo (enrolled in Computer Science Graduate Program) were joined to

engage in research from December, 2006 and January, 2007, respectively until the end of the project (June 30, 2007) on the part-time basis. Rolanda carried out all instrumental operation for elemental analysis of copolymer networks and for measurements of metallic cations by atomic absorption flame photometry (AA). Arish engaged in programming of two "C" softwares for elemental analysis and analysis of AA experimental results. They expect to complete M.S. Program in their respective fields, May, 2008.

Joshua, W. Carey (B.S. Chemistry, University of Missouri-Rolla, May, 2007) engaged in adsorption experiments of cations by hydrogels since September, 2006 as an Undergraduate Research Participant since September, 2006. He is currently enrolled in Chemistry Graduate Program since June, 2007 and continued the research work until the end of the Project. Roland and Joshua are co-authors for the paper presented in the 15th ICONE, April, 2007 (7 pages). They are also co-authors for two manuscripts which will be submitted soon to J. Nucl. Sci. & Tech. regarding the work.

References

1. Hirotsu S, Hirokawa Y, Tanaka T, J. Chem. Phys. 1987;87:1392-5.....
2. Matsuo SE, T. Tanaka, J. Chem. Phys. 1988;89:1695-703.....
3. Hirokawa Y, Tanaka T, J. Chem. Phys. 1984;81:6379-80.
4. Katayama S, Hirokawa Y, Tanaka T, Macromolecules, 1984;17:2641-3.
5. Amiya T, Hirokawa Y, Hirose Y, Li Y, Tanaka T, J. Chem. Phys. 1987;86:2375-9.
6. Hirotsu S, J. Phys. Soc. Jpn, 1987;56:233-42.
7. Hirotsu S, J. Chem. Phys. 1988;88:427-31.
8. Otake K, Inomata K, Saito S, Macromolecules, 1990;23:283-9.
9. Schild HG, Prog. Polym. Sci. 1993;17:163-249 and references therein.
10. Shibayama M, Mizutani S, Nomura S, Macromolecules, 1996;29:2019-24.
11. Yoshida R, Uchida K, Kaneko Y, Sakai K, Kikuchi A, Sakurai Y, Okano T, Nature, 1995;374:240-2.
12. Annaka M, Tanaka C, Nakahira T, Sugiyama M, Aoyagi T, Okano T, Macromolecules, 2002;35:8173-9.
13. Dies Pena E, Quesada L, Fritos P, Barrales-Rienda JM, Macromolecules, 2002; 35:2667-75.
14. Tokuhito T, J. Phys. Chem. B 1999;103:7097-101.
15. Tokuhito T, J. Phys. Chem. B 2001;105:11955-60.
16. Ito K, Ujihara Y, Yamashita T, Horie K, J. Polym. Sci., B. Polym. Phys. 1998; 36:1141-51.
17. Ito K, Ujihara Y, Yamashita Y, Horie K, Polymer 1999;40:4315-23.
18. Tokuhito, T. Tokuhito, A.T. (unpublished data) T_{tr} stands for transition temperature for reversible volumetric phase transition between swollen and shrunken states
19. Tokuhito T, Tokuhito AT, Akella SS, Carey JW, Proc. 15th Int'l. Conf. Nucl. Engineering (Nagoya, Japan) April, 2007, paper#:15-10163 (8 pages).
20. Tokuhito, T, Tokuhito, A.T. Polymer, 2007, Vol. 28. (accepted for publication)

Section III. Natural Convection with Gel Particles (A. Tokuhira) Final Report

Ultrasonic Doppler Velocimetry

The principles of ultrasonic Doppler velocimetry (UDV) were described in the original proposal (see Appendix A). Although UDV can be used with gases, as the acoustic velocity in gas is roughly $\sim 300\text{m/s}$ versus $>1500\text{m/s}$ in liquids, UDV can be used as a quasi-live velocimetric “tool” in liquids. That is, it provides spatial velocity information (distribution) along its acoustic beamline can be derived by measuring and sufficiently sampling the Doppler shift (per channel) at the time of echo detection (thus requiring ‘seeding’ of some sort), and temporal velocity information as the ultrasonic burst and echo reception (Doppler shift measurement) is rapidly (electronically) cycled. Thus spatio-temporal velocimetric information is acquired much like a laser-based velocimetry methods (laser Doppler, particle image, etc.). Additional results and details are available in Appendix A and specifics about the Met-Flow Ultrasonic Velocity Profile (UVP) monitor used here can be found at www.met-flow.com [1]. The UVP was procured using leverage funds.

Heat Transfer Results

Single-phase, natural convection heat transfer is well documented in many texts and publications. Many of the classic references are noted in Tokuhira [2]. With the addition of a buoyant (discrete) gas bubbles of sufficient volumetric fraction near the (vertical) thermal and momentum boundary layers in natural convection, sufficient ‘mixing’ or turbulence is introduced such that heat transfer is enhanced relative to the single phase result. Tamari and Nishikawa [3] and Wachowiak [4] showed in fact that the enhancement is at least twice that of the single-phase results. These results generally hold true, whether if the heated plate is immersed in a large pool (infinite pool configuration) or in a tall enclosure or ‘cell’ wherein the dimension of the heated and cooled vertical surfaces is larger than their separation distance.

Here with the addition of porous gel or gel-like particles into the natural convective flow, the particles are essentially hydrophilic in that solid phase occupies a minor fraction of the ‘particle’. Thus, only when the density of the solid phase is larger than that of water and/or combined density of the water-saturated particle, including its solid phase, is ‘heavier’ than water, the hydrophilic, ‘swollen’, particle is expected to sink (be non-buoyant) relative to say the rising convective flow along a heated wall. Thus, if the swollen particles are buoyant and small relative to the thermal and momentum boundary layers, it is possible to again enhance the heat transfer by the following mechanisms: by generating turbulence near the heated wall and by capacitative transport of heat away from the heated wall and across to the cold wall.

Briefly, in the current work, we observed both heat transfer enhancement and de-enhancement depending primarily on the buoyancy-driven force (the local ΔT_y [y is along the wall] and that across hot-to-cold wall, ΔT_{HC}) and the buoyancy of the swollen particle. The latter was largely determined by the size of the particle; that is, larger particles (non-buoyant) sedimented out of the convectively circulating flow in the natural convection cell and collected at the bottom. In fact, particles that became locally heavier at any time, began to decelerate and sink toward the bottom of the cell. In fact, the sedimented particle layer that developed at the bottom increasingly became conduction dominated and changed the starting length (from the bottom) of the natural convective flow (see Figure 1). In fact, in Figure 2 one can see that the temperature profile is more ‘conduction-like’ than ‘convection-like’ for the nominal particle size ($134\mu\text{m}$) and weight loading shown (0.518%). The local deceleration and reversal of direction of particles changed the local velocity profile of the convective flow near the hot wall. This qualitatively summarizes the heat transfer results. Further details and heat transfer plots are given in Hagiwara.

Velocimetry and Particle Motion in Cell

Five 4MHz ultrasonic transducers were positioned side-by-side, as in Figure 3, to measure the vertical velocity component along the heated wall of the natural convection cell. The transducers had an active diameter of 5mm, a casing diameter of ~7mm; thus, velocity data was acquired in increments as the transducers were traversed in unison outward from the wall. A representative UVP-acquired velocity profile is shown in Figure 4, for temperature difference of 10°C and 20°C, weight loading of 0.26% and average particle diameter of 134µm. One can conclude from this and similar data for the ‘smaller’, nominal size of particles, there is relatively little difference between the single and two-phase results. That is, the particles are buoyant and are convected along with the continuous, liquid phase. In contrast, the larger particles, nominally 230µm, are only partially to non-buoyant and sedimented out of the prevailing, upward convective flow along the heated wall. This deceleration and reversal in trajectory changed the local, measured velocity profile. A representative comparison is shown in Figure 5.

Conclusion and Future Work

The results as summarized above indicate that it is possible to use a natural convection cell to passively capture targeted cations by thermally-sensitive polymer gels such that the ‘encapsulated’ species sediment out of the circulating flow at the bottom of the ‘cell’. It is further conceivable to design a cell that siphons or drains the sedimented, loaded gels. Ideally if the solid phase density of the dry-state polymer gel is greater than the density of water, the nominal particle size of the swollen gels should be less than approximately 100-130 µm so that they are convected with the natural convective flow. The fact that both gel and continuous phase circulate provides ‘residency’ time so that the cations diffuse into the polymer network. It may also be possible to directly extract targeted species by a double-walled, cylindrical channel with the inner channel containing a porous ‘plug’ that provides a means for capillary flow to a prepared, unloaded gel piece located on top of the plug. As shown in Figure 1 (T. Tokuhira’s section), the cations diffuse upward into the gel over diffusive clock-time.

Detailed design of the convection cell to optimize the residency time of polymer gels with respect to the targeted species loading will require testing with a finer control of particle sizes than two nominal size groups tested here. The 100-130µm nominal particle size range however seems to be appropriate balance between buoyancy and gravitational forces. Finally, any contribution by heat of decay of radioactive cations (particulates) should facilitate the local, particle phase transition from swollen to shrunken states. It remains to be seen if the particles (α , β , γ other) are energetic enough to damage the polymer gel network or to promote cross-linking as the literature indicates. Lastly, the fact that these polymer gels undergo a reversible phase transition indicate that the shrunken form with the encapsulated species is not suitable as a final, disposition form unless dry, environmental conditions can be assured.

As for waste processing scheme using the herein reported silica gel materials, a simple U-tube type ‘exchange’ column (see Figure 8, M. Bertino’s section) was demonstrated. This arrangement can be modified into one rectangular cell with two vertical porous partitions separating the positive and negative ionic species, in the right and left chambers, while the monolithic gel is located in the center. A temperature gradient maintained at the right and left walls, with respect to the partition can establish a naturally circulating flow of the ionic species, relative to the partition. The chamber contain a remotely controlled means (i.e. gravity-driven) to replace the loaded silica gel by an unloaded gel. This will be pursue as opportunity arises.

Educational Component. Izumi Hagiwara graduated with MS thesis in Nuclear Engineering. She did the majority of the heat transfer and velocimetric experiments in single- and two-phase, the latter with hydrophilic particles. Lisa Wulff, in (UMR’s) Civil Engineering, Environmental Engineering program followed and was tasked with determining the characteristic time of diffusion into polymer gels relative to the typical circulation time in the convection cell. However, she did not complete this scope of work.

Sedimentation of Particles

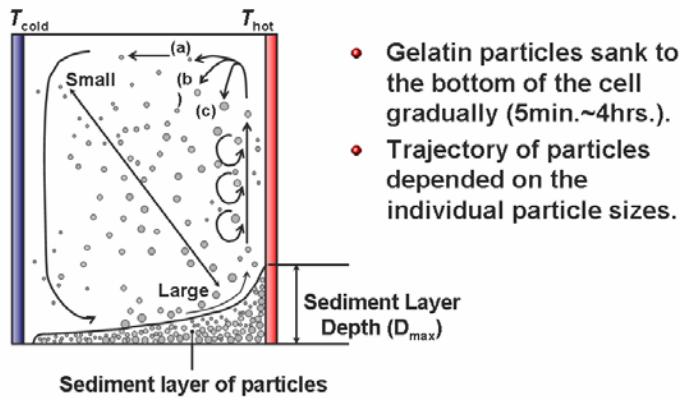
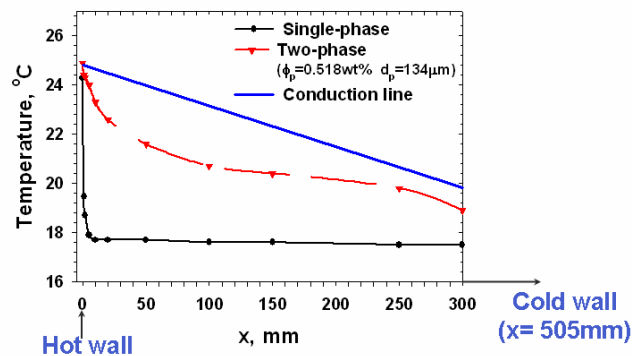


Figure III.1 Schematic of hydrophilic gel particle dynamics, convection and sedimentation in convection cell

Heat transfer De-enhancement at the Bottom of the Cell



- Temperature profiles at 3.0cm from the bottom of the cell.
- The two-phase profile decreases towards the cold wall.
- Heat transfer within the sediment layer is more “conductive”.

Figure III.2. Comparison of temperature profile across the cell for single- and two-phase (with gel particles added). Particle sedimentation changes profile toward strictly conductive in trend.

Velocity Measurement Method ~Ultrasound Doppler Velocimetry (UDV)~

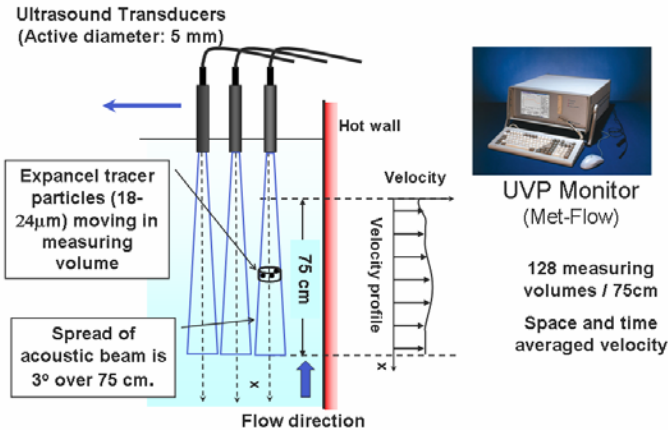
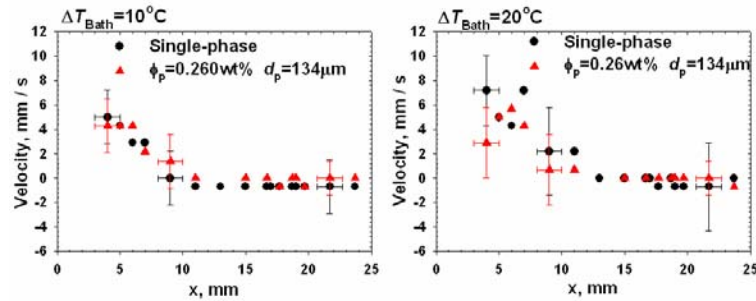


Figure III.3. Schematic of UVP transducer configuration and instrument used in project.

Velocity Profile at $y/H = 0.944$ (turbulent region)

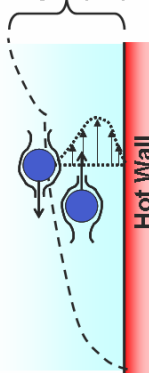


- No data was obtained in the range of $0 < x < 4\text{mm}$.
- No significant difference between single- and two-phase cases as measured by the UVP.

Figure III.4. UVP acquired average velocity profile for single- and two-phase (with particles, 134 μ m nominal diameter) at two ΔT_{bath}

Effect of the Settling Motion of Particles

Boundary Layer (BL)



- Settling particle reduces the rise velocity inside the BL.
- Velocity reduction in the BL leads to heat transfer de-enhancement.

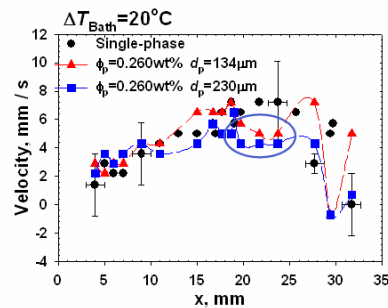


Figure III.5. UVP acquired velocity profiles for single- and two-phase, for two nominal particle sizes and given ΔT_{bath} ; schematic of particles with opposite trajectories in BL.

References

1. Met-Flow SA, www.met-flow.com
2. Tokuhiko, A., Natural convection heat transfer enhancement in mercury with gas injection and in the presence of a transverse magnetic field, Ph.D. Thesis, Purdue University, 1991.
3. Tamari, M., Nishikawa, K., The stirring effect of bubbles upon the heat transfer to liquids, Jap. Res. Heat Transfer, 5(2), 31-43, 1976.
4. Wachowiak, R.M., The enhancement of natural convection by rising bubbles, M.S. Thesis, Purdue University, 1986.

APPENDIX A --- ORIGINAL PROPOSAL

ABSTRACT (original)

Principal Investigator: Akira Thomas Tokuhira (now at tokuhira@uidaho.edu)

Phone: 573-341-4746 FAX: 573-341-6309 e-mail: tokuhira@umr.edu

Co-principal Investigator: Massimo Bertino (now at mfbertino@vcu.edu)

Phone: 573-341-6221 FAX: 573-341-4715 e-mail: massimo@umr.edu

Co-principal Investigator: Tadashi Tokuhira

Phone: 573-341-6027 FAX: 573-341-6033 e-mail: tadashi@umr.edu

Co-principal Investigators: _____

Phone: _____ FAX: _____ e-mail: _____

Project Title: Radiolytically-induced novel materials and their application to waste processing

College/University/Campus University of Missouri-Rolla, Department of Nuclear Engineering

Abstract (less than 200 words, and approved for public release):

The proposed project concerns experimental studies on the potential application of two material processes based on radiolytic reactions using the UMR Reactor facility as follows: 1) silica-polymer based aerogel composites that encapsulate cluster of specific metals and 2) polymer gels made of thermo-sensitive polymer networks for encapsulating LLW particulates. The former start as aqueous/liquid solutions of based catalyzed silica hydrogels and metal ions, such as silver. The metal ions are reduced radiolytically and migrate through the solution to form clusters. Upon post-irradiation processing, aerogel monoliths, extremely lightweight but mechanically strong, that encapsulate the metals are produced. The latter gels exhibit thermally induced volumetric contraction at 20°-50° C by expelling water from the gels' physical state. Further, some functional groups that capture di- or tri-valent cations from aqueous solutions can be incorporated into the polymer networks on synthesis, including by radiolytic means. These polymer gels retain cations after volumetric contraction and have the ability to trap solid particulates in liquid waste streams. The study will see if the radioactive decay heat of isotopic particulates can self-induced the concentration of radioactive cations. Finally, the functional design of a prototypic natural convection cell to process liquid waste streams will be tested.

YES NO

- Does your college or university have a nuclear engineering degree program or option?
 Does the principal investigator with the most significant time commitment to the project have less than 10 years of faculty experience following completion of their education?

3. PROJECT DESCRIPTION

Radiolytically-induced novel materials and their application to waste processing³

3.1 Statement of Objectives

Proposal – 2-year total: \$198,487

Overall Goal:

To investigate, assess and demonstrate two radiolytically-induced material processes that have potential to capture and encapsulate metallic cations in radioactive and non-radioactive liquid mixed waste streams. The research teams three co-PIs with similar scientific interests on a engineering project with the following goals: 1) to further refine understanding of the physical properties of new hydrogels specifically tailored for adsorption of metallic cations in wastewater; foremost mixed liquid waste streams containing radioactive particulates, 2) to radiolytically load with metal clusters mechanically strong aerogel composites as a wet-to-dry encapsulated wasteform, and 3) conduct smaller-scale prototypic natural convection scoping experiments in an enclosure that will serve as a dynamic processing cell for particulate-laden liquid waste.

Year 1 Deliverables (June 2004- May 2005- \$99,930)

- A. (co-PI, T. Tokuhiko) Synthesis of hydrogels of poly(*N*-isopropylacrylamide) modified with sodium acrylate and allyl-carbonate, allyl-cyanide and others will be carried out. Determination of various physical properties will be pursued by the pycnometry method, DSC and proton NMR. Optimization of stoichiometry will be made according to the adsorption experiments of lanthanide tri-valent cations. Preparation of flow experiments at the laboratory scale using mostly glasswares will be done concurrently with A. Tokuhiko's experiments. Preparation of the sub-sections to the Year 1 team report will contain the results obtained in the synthesis and characterization of property. One Master's theses student should be recruited and underway in terms of research.
- B. (co-PI, M. Bertino) Quantitative characterization of the fraction of metals retained inside a silica gels. This characterization will be carried out as a function of the initial metal concentration, and as a function of the metal. Determination of the minimum metal concentration that can be retained inside a silica gel. Extension of the limit towards lower concentrations by addition of pre-formed Ag clusters. Investigation of the range of application and physical state of captured metals by TEM, XRD, XPS and optical spectroscopies. Preparation of the sub-sections to the Year 1 team report. One Master's theses student should be recruited and underway in terms of research.
- C. (co-PI- A. Tokuhiko) Initial experimental results using selected loadings of hydrophilic and hydrogels of type "1)" as above with selected loadings of expected range and types of solids in the prototypic natural convection cell. Hydrophilic particles that do not possess the thermally-induced expansion/contraction properties of hydrogels will serve as the reference case in their ability to attract (but not encapsulate) solid particles. A review of the mixed radioactive (and some non-radioactive) liquid waste streams will be performed with goal of characterizing the range and type of particles able to be processed with the available cell. Consideration will also be given to a mixed convective flow arrangement. A Year 1 Report will provide experimental and

³ NOTE: the order of the co-PIs has been changed since the Notice of Intent. NOI order of co-PIs was Tadashi Tokuhiko, Massimo Bertino and Akira Tokuhiko. In the full proposal submitted here is Akira Tokuhiko, Massimo Bertino and Tadashi Tokuhiko

surveyed results in preparation for further experiments in Year 2. One Master's theses student should be recruited and underway in terms of research.

Year 2 Deliverables (June 2005- May 2006- \$98,557)

- A. (co-PI, T. Tokuhiko) Synthesis of hydrogels of poly(*N-n*-propylacrylamide) modified with sodium acrylate and allyl-carbonate, allyl-cyanide and others will be carried out. Determination of various physical properties will be pursued by the pycnometry method, DSC and proton NMR. Optimization of stoichiometry will be made according to the adsorption experiments of lanthanide tri-valent cations. Laboratory scale flow experiments for the dynamic filtering system will be carried out concurrently with A. Tokuhiko's experiments. Preparation of the sub-sections to the Year 2 team report will contain all aspects of the research. A Master's thesis should be completed.
- B. (co-PI, M. Bertino) Synthesis and characterization of colloidal suspensions of rare earths, synthesized radiolytically. Trials with shorter lived radioisotopes and dilute samples will be conducted to assess safe handling procedures, followed by more relevant radioisotopes and concentrations. Further investigate range of application and physical state of captured metals by TEM, XRD, XPS and optical spectroscopies. Preparation of the sub-sections to the Year 2 team report. A Master's thesis should be completed.
- C. (co-PI, A. Tokuhiko) Completion of the experimental test matrix using selected loadings of several types of "1" hydrogels as above with selected loadings of range and types of solid particles in the prototypic natural and/or mixed convection cell. Limited trials with particles such as irradiated aluminum will be conducted. A measure of the effectiveness of the encapsulation and extraction will be proposed and given. A Year 2 Report will provide experimental results and recommendations for further work. A Master's thesis should be completed.

3.2 Detailed Research Scope

3.2.1. Introduction: National Scope

The U.S. government's weapons associated nuclear research programs since the early 1940's have left a legacy of nuclear, radioactive waste. The Department of Energy (DOE) has inherited the task of safely disposing this waste. A part of this legacy is high-level waste (HLW) produced from handling radiation-laden materials. In fact, 282 underground tanks containing millions of gallons of radioactive HLW, transuranic and mixed waste and 7 additional calcine vaults are located at five federal sites. The tanks range in capacity ranging from 13,000 to 1,000,000 gallons. Sixty-eight of the tanks are known or suspected to have leaked waste to the surrounding soils at the Hanford Site (67 tanks) and Savannah River Site (1 tank). These and many other tanks are nearing the end of their design life. The DOE must retrieve, process, treat and close the tanks while minimizing the risk of waste migration and/or exposure to workers, the public and the environment. These tasks must be in compliance with current regulations.

The Tank Focus Area (TFA) was created in 1994 to develop tank waste remediation technologies for the Department of Energy's (DOE) Office of Environmental Management. The TFA brings together users and technical experts to define and execute a program that contains integrated technical approaches and solutions to waste remediation. The focus area integrates work across the following five sites: Hanford Site, Idaho National Engineering and Environmental Laboratory, Oak Ridge Reservation, Savannah River Site and West Valley Demonstration Project. The final long-term management challenge in the TFA for DOE is the safe and economic closure of underground tanks across the complex that was previously used to house HLW.

It is evident from the brief summary above on just high-level "legacy" waste that the scale of the waste management tasks in terms of disposition and remediation is enormous. Equally, if we consider the waste streams produced by the civilian nuclear power industry over the past 40+ years (front-end to back-end), it is reasonable to assume that the low-level waste (LLW) stream is at least of the same order of magnitude as HLW. If we, as a nation, are to further utilize nuclear power and revitalize this country's commitment to nuclear energy as a part of the economic and energy sustainability and security, it seems evident that some innovations in waste processing science and engineering are called for in the near term.

3.2.2. Introduction: Research Scope

Within the management of radioactive waste, we will focus on the development of a new approach to remedy radioactive hazardous waste in water (low-level waste; LLW) as a part of the effort to improve the environmental quality of federal and commercial sites. Low-level radioactive (liquid) waste is currently stored as diluted aqueous solutions of radioactive elements and contained in storage containers. 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. Among various goals in processing liquid LLW laden in particular with solid radioisotopic particulates, two of the technical objectives are: 1) to separate/extract the radioisotopes from the rest of the mixed constituents, and 2) to produce stable solidified forms encasing radioactive elements. From basic research in the chemistry and physics of gel materials, the three co-PIS have recognized a promising approach to simultaneously achieve the above objectives. That is, by utilizing the physicochemical properties of various hydrogels at the nanoscale, we are able to produce a process by which to encapsulate particular chemical species at the laboratory scale. Via further refinements in the physicochemical property of hydrogels under the present proposal, we will be able to demonstrate at engineering scales a processing methodology for liquid LLW. In fact, investigation of the radiation effects on hydrogels will determine the prototypic design and range of possibilities of the waste processing. We note the unique nature of this research proposal in that it integrates research and approaches from two different disciplines, i.e., basic physical science of polymer gels and basic engineering on multiphase, multi-component flows.

3.2.3. Polymer Gel Basics

Polymer gels are two-component systems consisting of three-dimensional polymer networks and solvent(s) and form different phases than the components. The polymer component can be either natural or synthetic. Three-dimensional polymer networks and water can form soft and bouncy materials (hydrogels). Recent advances in the basic science of polymer gels at both macroscopic and microscopic levels have brought to light several promising engineering applications. Some hydrogels exhibit the capability of catching and binding di- or tri-valent inorganic cations dissolved in water. Since hydrogels form different phases from water, they can be separated by a simple process such as physical filtration. In order to remove water from hydrogels, we can use one of their unique physical properties. Namely, when the polymer component is of the thermally sensitive class of polymers, specific volumetric contraction of gels with increasing temperature accompanies the loss of water (Tokuhiko, 1999; Tokuhiko, 2001). When hydrogels are in thermal equilibrium in excess water however, gels assume maximum volumes at the respective (surrounding) temperatures. In this thermodynamically stable state, referred to as the "swollen

state”, polymer networks evidently assume expanded (stretched) conformations (Tokuhiro, et al, 1991). In contrast with increasing temperature, the gels gradually shrink and at a specific temperature (transition temperature) the polymer networks change completely to another conformation (shrunken state). The process is reversible and an endothermic process with increasing temperature. Various transition temperatures are associated with a class of hydrogels made of thermally sensitive polymer networks (Hirose, et al, 1987; Schild, 1992 and references therein) and the transition temperatures extend from room temperature (20°C) to about 50°C. They depend on the chemical composition of polymer networks.

One of Co-PI's (T.T.) has been concentrating on the study of physical properties of various polymer gels made of thermally sensitive polymer networks over the past several years. An overwhelming majority of studies on polymer gels has been carried out at the macroscopic level. Namely, they have studied the volumetric changes of gel pieces in the presence of excess solvent by measuring diameters of gel pieces and expressed as the relative diameter (or volume) in reference to some standard (conventional swelling experiment) (Hirose, et al, 1987). It is apparent that the absolute value of the total volume of a chosen gel system cannot be determined in this practice. The Co-PI (T.T.) has developed a new approach for the determination of the *absolute* values of 1) the total volume, 2) densities of the polymer and solvent components, and 3) the stoichiometry of gels. The approach has been applied to various polymer gels (T. Tokuhiro, 1999; T. Tokuhiro, 2001). This new approach can presents results at the nanoscale and thus can compare the physical property of any gel systems composed of *different kinds* of polymer and/or solvent (T. Tokuhiro, 2001; T. Tokuhiro, unpublished-1). We can obtain the absolute values for $v_{sp}(\text{gel})$, $N_s(\text{gel})$, and the stoichiometry of gels. Here, $v_{sp}(\text{gel})$ and $N_s(\text{gel})$ are the volume occupied by a single polymeric residue and associated water molecules and number of water molecules per a single polymeric residue, respectively. These studies have yielded the following results, namely that: 1) the volumetric contraction of gels with increasing temperature arise from the loss of water in gels and 2) the transition from the swollen to shrunken state is the result from the loss of water and the conformational changes in the polymer component (T. Tokuhiro, 1999; T. Tokuhiro, et al, 1991). Our DSC results for various hydrogels of poly[*N*-isopropylacrylamide (NIPA)] indicates that the above transition is an endothermic process with raising temperature (T. Tokuhiro, unpublished-2).

The physical property of a particular functional group incorporated into the major polymer component has also been studied by using the above method together with the use of Nuclear Magnetic Resonance (NMR) relaxation phenomena (T. Tokuhiro, unpublished-1; unpublished-3). Using NMR, we can determine the structural and dynamical characteristics of a particular polymer and of solvent components in polymer gel systems at the nanoscale. These studies provide a fundamental basis for the synthesis of new polymer gels having some desirable functionality. If one specific functional group is incorporated into the major polymer chains, the corresponding polymer gels exhibit the capability of binding and retaining metallic cations. Thus, when a thermally sensitive polymer containing the above functional groups as the minor constituent is used to synthesize polymer networks, the corresponding hydrogels exhibit a volumetric changes with varying temperature without losing cations that bound to the above functional groups. One of the physical evidence (obtained in our laboratory) of lanthanide cation retention in gels is shown by the fluorescence spectrum of terbium tri-valent cations bound to poly[NIPA(1-*x*)/NaAc(*x*)] hydrogel where the mol fraction *x* is 0.0417. Here, NaAc stands for sodium acrylate. It is apparent that carboxylic group is binding terbium ions.

3.2.3.1 Polymer Gel Objectives (co-PI, T.Tokuhiro)

The present work will focus on the development of a new approach to process low-level radioactive particulates in liquid waste streams. The low-level radioactive wastes are considered to be aqueous solutions of radioactive elements and defined as radiation that exceeds federal radiological threshold level; that is, radiation that generates heat of radioactive decay is lower than 2 kW/K-liters (2 W/liter).

This means that 4.780×10^{-4} cal/(sec·cm³) of heat is generated. In short we would like to find an “efficient, effective, inexpensive and reliable way to remove radioactive elements from the low-level wastes (aqueous solution)”. We have found one promising way to realize this major objective by utilizing the physical property of hydrogels at the laboratory scale. Some details will follow.

Thermally sensitive class of hydrogels as described can be used to extract metallic cations dissolved in water and thus used to process particulate-laden mixed liquid wastestreams. Physicochemical properties of various hydrogels that are suitable for the above purpose can be designed by focusing on the property of hydrogels at the nanoscale. Further refinements in the physicochemical property are needed for being able to maintain the above property throughout various engineering processes in a reliable and safe fashion. Basic studies on various flows will now make an important contribution to our design in the actual engineering processes of the low-level radio-active wastes (dynamic filtering system below). Direct radiation effects on and heat generated by the radioactive decay inside hydrogels will make the system very unique. It must be emphasized here that the uniqueness of this research proposal is based on integrated thoughts and plans covering two different disciplines, i.e., basic physical science of polymer gels and basic engineering on multi-phase flow, convective and gravity driven flow.

3.2.4. Aerogel Basics (co-PI, M. Bertino)

For brevity, interesting aspects of aerogels such as that by Fricke (1986, 2003), Buscal and Goodwin (1995) are omitted. We directly present the potential for entrapment/encapsulation of radioactive and chemical residues in mixed liquid waste streams inside aerogels.

3.2.4-A Incorporation of radioactive and chemical waste inside aerogels.

In this part of the proposal, we report preliminary results and discuss the possibility of encapsulating chemical and radioactive waste inside silica aerogels.

In a series of recent works, our groups have shown (Hund et al, 2003a; Hund et al., 2003b, Bertino et al., 2003a, Pandit et al., 2003, Bertino et al, 2003b, Bertino et al. 2003c) that metal ions can be removed from a solution and incorporated into silica aerogels. In our technique, we first synthesize silica gels with a base-catalyzed route (Pierre and Pajonk, 2002; Schneider and Baiker, 1995; Leventis et al., 2002) and then exchange the solvent with an aqueous solution containing ions of the target metal. The solution is eventually irradiated with ionizing radiation, such as gamma rays (Hund et al., 2003a &b, Bertino et al. 2003b), or X-Rays, or UV light (Bertino et al., 2003a). Metal ions are reduced by the solvated electrons and the reducing radicals generated by irradiation of the solvent. Metal atoms eventually diffuse through the solution (or the gel) and form metal clusters. Most importantly, the clusters, once formed, are not leached out of the gel monolith, and can withstand several cycles of washing, and even supercritical drying, without being washed out of the monolith. The gels can be vacuum dried, to yield xerogels, or supercritically dried, to yield aerogels. In either case, the dried gels can be vitrified without any leaching of the encapsulated clusters, as reported in the literature (Pierre and Pajonk, 2002; Schneider and Baiker, 1995).

We will now show that the radiation levels normally present in high (and, possibly, low-high level) waste is sufficient to encapsulate a large fraction of nuisance metals present in the waste, and that many metals relevant in waste treatment processes are accessible to the technique.

3.2.4.1 Aerogels Objectives (co-PI, M. Bertino)

3.2.4.1-A Metals accessible to the technique.

The proposed radiolytic technique employs solvated electrons and reducing radicals, all of which have a reduction potential between -1.1 and -2.7 eV, and thus can reduce a wide array of transition metals. Previously reported work has shown that metals with a potential as negative as Cd can be reduced with this technique. Our group showed that colloidal suspensions of metals such as Ti, and Al, can be produced by irradiating de-aerated organic solvent solutions (Pandit et al., 2003). We are planning extension to the case of rare earths, whose reduction potential is around -2.3 eV, and are thus theoretically accessible to the technique. We point out, furthermore, that toxic metals such as Hg, and Pb, can be routinely reduced by the technique, and that silica gels entrapping these metals have already been produced by our group. In addition, we point out that we recently achieved reduction of metals inside silica gels with conventional reducing agents, such as formaldehyde, or sodium borohydride (Bertino et al., 2003). Chemical reduction would be used to complement radiolytic reduction, in case the level of activity of the waste were too low to ensure quick reduction of the radioactive waste.

3.2.4.1-B Efficiency of the technique and flux issues

Typical yields of reducing species are of the order of 6 reducing species/100 eV of energy deposited in the material. Thus, it is possible to reduce about 2×10^{-3} mol/l of monovalent ions with an exposure to 3.5 kGy. Dose rates as low as 0.1 kGy/h have been successfully employed to reduce ions and form clusters (Hund et al., 2003a & b). We point out that typical concentrations of nuisance metals in radioactive waste processing are of the order of g/l, i.e., millimolar for elements heavier than about 100 amu (EPA, 2003). Most noteworthy, the required gamma ray doses, of the order of kGy, are produced by the radioactive waste itself. It appears that up to 3 kGy/h can be delivered by a material which is still classified as a low-level radioactive waste. If this were the case, it is possible to exchange a low-level radioactive waste in a gel, and eliminate radioactive isotopes and toxic metals as electronegative as Cd, by simply waiting a few hours. For materials of low radioactivity, we plan to help cluster formation either by UV irradiation, or by addition of a reducing agent such as sodium borohydride.

3.2.4-C Post irradiation treatment

Once metal clusters are formed, the water in the gel can be exchanged with more contaminated water, and the process repeated, or the gel can be washed with clean water, desiccated, and eventually processed at high temperature to produce a glass pellet. It has been shown (Pierre and Pajonk, 2002; Schneider and Baiker, 1995) that, once metal clusters are formed inside xerogels, or aerogels, the metals do not leach out during high temperature treatment.

3.2.5 Convective Flow Basics (co-PI, A. Tokuhira)

3.2.5.1 Natural Convection of Single-Phase Flow

In order to process larger quantities of radioactive particle-laden mixed liquid waste, one can adopt an “active” device such that through a defined volume a pump forces waste streams through the device, or on the other hand adopt a “passive” device such that within a defined volume waste streams are processed via natural means such as by gravity or gradients (density, concentration). The advantages of the latter option which we recognize and prefer are as follows: 1) no active devices (pumps, etc.) simplifies the design and thereby reduces costs in terms of operation and maintenance, 2) no active devices eliminates failure mode via the active element and 3) adoption of a passive system still provides the option for an active system to serve as an auxiliary or back-up. Thus in the present project, we have adopted to begin with a prototypic natural convection enclosure that will hold the waste stream.

Within the scope of a natural convection-driven enclosure to process radioactive particle-laden mixed liquid waste streams, we first note that the literature on single-phase natural convection and specifically in enclosure is well-documented. Specifically, we focus on aqueous systems wherein thermal energy input induces density gradients in a gravitational field such that the flow in the enclosure is buoyancy-driven. The literature in this area is particularly well-documented in texts such as that by Bejan (1984) and also in the co-PI's work (A. Tokuhira, 1991), as well as by Hagiwara (2003). For brevity we will take natural convection as well understood.

3.2.5.2 Natural Convection with Particles

Only a few noted studies on natural convective flows with particles in our range of interest, mainly 1-100 μm , and none to date have been found with hydrophilic particles and a transverse temperature difference in a vertical enclosure. The few existing works can be attributed to Okada (1996, 1997, 1998a, 1998b, 1999) and his co-workers, Chen (1998), Suzuki (1996), Kang (2001a, 2001b), Hattori (2001) and Mikami (2001). They performed a natural convection experiments in an (initial) suspension of water-fine particles in a rectangular vessel heated from below and with both vertical walls cooled. The overall phenomena was described as a competition of two types of density distributions and thus presented itself as a double-diffusion problem. Namely, the competing mechanisms are: 1) the thermally-induced unstable density distribution of liquid due to the thermal energy input, and 2) the sedimentation mechanism of particles (heavier than water) with a distribution of sizes. Okada and co-workers found using particle flow visualization (particle tracking velocimetry) and heat transfer measurements that various thermal configurations produced multiple horizontal layers consisting of natural convection cells and particle concentrations. In fact even for a narrow distribution of particle sizes, particle concentration gradients still were prevalent.

Sedimentation and suspension flows (in concurrent with natural convection) are of importance in solid-liquid separations in the chemical, mining, pulp and paper, wastewater, food, pharmaceutical and related industries. Although intensively studied for many years, the investigation of sedimentation and suspension flows is still far from complete. Unlike single-phase flow, flow of suspensions introduces additional considerations, including properties of suspensions (rheology, particle size and shape, particle-particle interaction, surface characteristics, yield stress, concentration, viscosity), individual particles (orientation and surfactants), and characteristics of sediments (permeability, porosity and compressibility).

3.2.5.4 Convective Flow Objectives (co-PI, A. Tokuhira)

As noted, a natural convection cell can potentially serve as a dynamic "filtration" system for radioactive and other solid particulates in mixed liquid waste streams. Effective extraction of these particles from the liquid "host" is potentially significance because it removes a major source of the mixed waste. Furthermore, if long-lived isotopes could be removed from a liquid waste stream, the storage and handling of "dry" waste form is seemingly more straightforward.

Polymer gels have the capacity to absorb as much as 1000 times the weight of itself with water (or other liquid). The specific class of gels of interest undergo a volumetric phase transition, between the swollen and shrunken states in response external stimuli, e.g., temperature (20°-50°C), solvent composition, pH, ionic strength, light,] and electric field (Amiya et al, 1987; Hirokawa et al, 1984; Hirotsu et al, 1984; Hirose et al, 1987). At present we are interested in thermally sensitive polymer gels with a lower critical solution temperature (LCST). That is, when thermally sensitive polymer gels are synthesized, the gels exhibit the volumetric contraction with increasing temperature and shrink significantly over a relatively narrow temperature range. For simplicity, this particular temperature may be called volumetric phase

transition temperature (VPTT). The gels lose water throughout this process in a reversible manner (on heating and cooling). These principles are illustrated in Figure 1.

In conjunction with Hagiwara (2003), the co-PI (A. Tokuhira) have experimentally investigated the natural convection heat transfer in a vertical enclosure of hydrophilic gelatin particles (45-125 μm in chord length) in water. The sedimentation dynamics of two particle size groups, roughly 45-75 μm and 75-125 μm , and the convected liquid velocity were measured using ultrasound Doppler velocimetry (UDV). The results show in brief that particles are naturally convected with the flow but sediment as they cluster and become heavier than water. A sedimentation layer dominated by conduction heat transfer gradually forms at the bottom of the cell and changes the aspect ratio of the naturally convective flow. The co-PI has two cells, 107cm (H) x 50cm (W) x 2.54 (D) operational with constant-temperature bath controlled hot and cold walls. Besides temperature measurements using thermocouples, UDV has been used to measure both the liquid and particle velocities. The principles of UDV as well as the co-PI's experience using UDV are noted in Facilities and Resources. The co-PI also has available a Particle

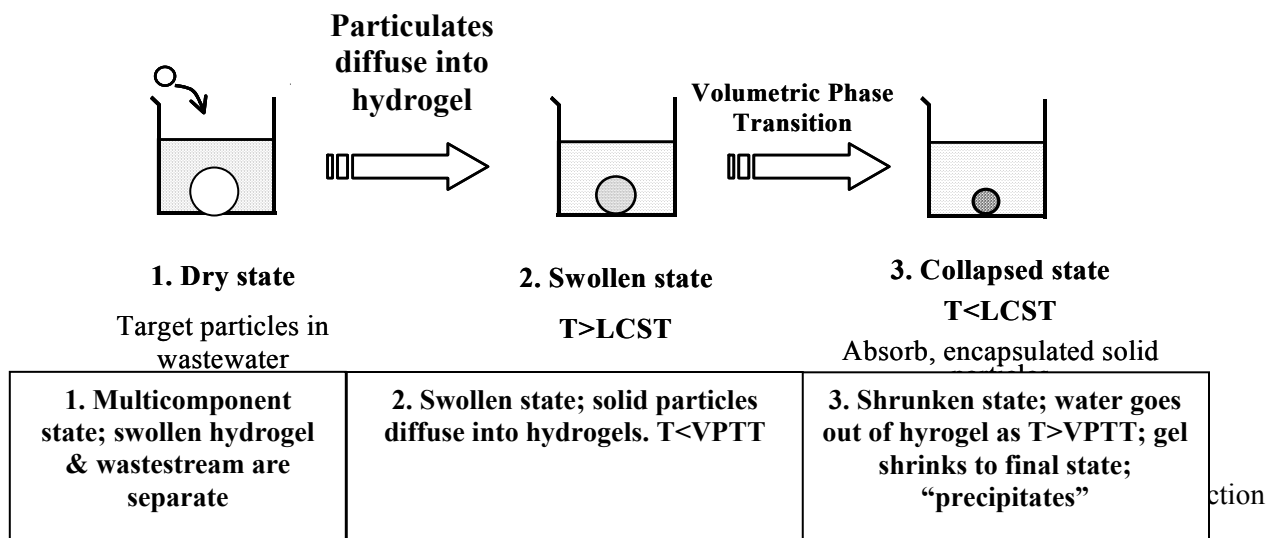


Image Velocimeter, also explained in Facilities and Resources. Based on this preliminary work we have the following objectives:

- 1) to quantify the baseline effectiveness of extracting various solid particle size distributions using hydrophilic gelatin. The solid particles should be representative of expected particles. Since the gelatin does not undergo the desired transitional properties, it is not expected to be effective.
- 2) to demonstrate and quantify the dynamic entrapment of various solid particle size distributions using thermally sensitive hydrogels that undergo volumetric transitions. The transition will first be imposed by controlling the thermal input into the cell.
- 3) to demonstrate and quantify the dynamic entrapment of selected short-lived radioactive solid particles (such as ^{28}Al) using thermally sensitive hydrogels that undergo volumetric transitions. The transition will first be imposed by controlling the thermal input into the cell and then investigated by self-induced decay heat.
- 4) to investigate the potential operating range of the combined imposed and self-induced thermal heat input into the hydrogels of interest.

3.3 Research Plan: Organization

In order to achieve the above objectives, our proposal is composed of three detailed plans. Although the three are presented separately as below, it will be the overall goal of the co-PIs to coordinate and integrate the developments into a prototypic demonstration at the engineered scale. The three research plans are organized as follows:

- 3.3.1 Synthesis and characterization of new hydrogels capable of extracting and retaining lanthanide cations from the low-level radio-active wastes.
- 3.3.2 Experimental investigation of trapping metals in aerogels
- 3.3.3 Convective flow experiments

3.3.1 Synthesis and characterization of new hydrogels capable of extracting and retaining lanthanide cations from the low-level radioactive wastes (co-PI, T. Tokuhiko)

3.3.1.1 Tailoring hydrogels for efficient extraction and retention of lanthanide cations from aqueous solutions.

We have known that some polymer gels have specific capability of extracting and retaining various di- or tri-valent transition metal cations. This certainly indicates that the above hydrogels can extract lanthanide cations in the same way as for the transition metal cations as just mentioned above. The above specific capability of gels stems from the physicochemical property of a functional group. So, we will synthesize modified poly(NIPA) including a functional group such as $-\text{COOH}$, $-\text{C}=\text{O}$, $-\text{P}=\text{O}$, $-\text{C}\equiv\text{N}$ and others. Among functional groups, carboxylic (Hirotsu, et al, 1984), carbonyl (Sano, et al, 1998) and phosphoryl (Sano, et al, 1998) are known to bind the metallic cations. This search will be done for lanthanide cations in a systematic way by which we can find an optimum composition for each functional group. Optimization of the chemical composition will be carried out by considering the following two factors. They are: 1) the ratio of functional groups vs NIPA (the major polymer component); and 2) transition temperature of hydrogels made of newly synthesized polymer networks.

With regard to other thermally sensitive polymers, *N*-alkylmethacrylamides will not be considered here because of higher transition temperatures (Numajiri, et al, 1997) in general than the corresponding acrylamides. Among other acrylamides, for example, the transition temperature of poly[*N*-*n*-propylacrylamide(*Nn*PA)] hydrogel is around 22° C (Numajiri, et al, 1997) instead of 33.8° C for poly(NIPA) gels. The elasticity of the former hydrogel is greater than that of the latter hydrogels. Thus, it is worthwhile to synthesize various modified poly(*Nn*PA) in the same way as poly(NIPA). A larger *N*-alkyl group has also a significant effect on the transition temperature just opposite to the ionizable or acidic groups, as well as on the physical property. When a part of NIPA is replaced by *t*-butyl group, the transition temperature of hydrogels decreases with increasing content of *t*-butyl group (Ito, et al, 1998). Synthesis of hydrogels made of modified poly(NIPA) where a part of NIPA was replaced by two different functional groups having the opposite effect (as the minor components) has never been attempted. We think that a possibility exists for synthesizing such hydrogels that have high capacity of extracting and retaining lanthanide cations per unit volume of hydrogels while maintaining low transition temperature. This may be materialized by three-polymer components in the networks. We will attempt this kind of synthesis once effect of the individual functional group is characterized. All synthesis of hydrogels will be carried out by radical polymerization and gelation at a temperature lower than room temperature as described elsewhere (Tokuhiko, et al, 1998).

One of Co-PI's (T.T.) collaborator has developed a micellar polymerization method (Ito, et al, 1999). They confirmed the polymerization occurred within micelles. Gel beads thus synthesized were of about a few 100 nm in diameter with very narrow distribution of diameters. This method will be modified to

make a bigger gel beads by using surfactant molecules having longer CH₂ chains. This is because they can form micelles of larger diameters.

3.3.1.2 Determination of physical property of newly synthesized hydrogels

The first step is rather simple. By using the conventional swelling experiment, we can determine transition temperature. This is followed by more elaborate studies. We investigate thermal behaviors of cation-loaded hydrogels, particularly absolute values of $v_{sp}(\text{gel})$, $N_s(\text{gel})$, and stoichiometry of gels by means of our pycnometry method (Tokuhiko, 1999; Tokuhiko, 2001; Tokuhiko, unpublished-1). This leads to characterization of nanoscale structure of gels (Tokuhiko, 2001). Here, the cation-loaded hydrogels (the swollen state) can be prepared by introducing hydrogels (the swollen state) into aqueous solution of lanthanide cations. We will carry out determination as usual in water at various temperatures below and above the transition temperature. After the determination, gels must be lyophilized [by freeze drying method (Tokuhiko, 1999)] in order to determine the mass of polymer networks containing lanthanide cations. The results can be compared with the reference system, i.e., un-loaded gels. By integrating all these results, we can determine the stoichiometry of cations vs functional group. The above procedure will be used in all newly synthesized hydrogels and thus, we can determine the ratio of the amounts of cations caught in gels vs. the amounts of functional group. Determination of lanthanide cations left in the original aqueous solution should buttress the above result. Either absorption or fluorescence (Dagnall, et al, 1967; Taketatsu, et al, 1972) spectroscopy will also be used for the quantitative measurement of cation content in gels and in solutions. The photometric method is convenient and accurate for the determination of concentration since many tri-valent lanthanide ions exhibit distinct colors. For example, Pr³⁺ and Tm³⁺ show green color and Pm³⁺ and Ho³⁺ exhibit orange color. Color of Eu³⁺ and Tb³⁺ is in pale pink (Sinha, 1996; Sinha, 1982).

Altogether, the above experiments constitute the characterization of newly synthesized hydrogels. However, we still do not know the nature of binding between cations and functional groups from the above experiments only. If we can pursue this problem by using other experimental methods, we could find a way to extract (catch) individual lanthanide cation instead of a group of lanthanide cations. Recovery of individual lanthanide cation is certainly one of the ultimate goals though, this particular aspect will not be pursued in this proposal.

It is important to keep in mind that the physical state of hydrogels can be understood at the nanoscale (Tokuhiko, 2001) however, it is also important to know the characteristic of the macroscopic property of gels as material. Namely, the size of gel pieces plays an important role in the actual engineering process. The efficiency of extracting various lanthanide cations will depend on the size of gel pieces because cations must penetrate into gels from the surface area. In addition, it is already known that the kinetics of volumetric transition is inversely proportional to 1.8th power to the diameter of gel pieces (Tanaka, 1986; Matsuo et al, 1988). Hence, we must find an optimum size of gel pieces by considering various engineering processes.

If these cations are radioactive elements, heat generated by decaying radio activity may affect the whole processing. It may even result in the self-contraction of gels induced by this kind of heat. Unfortunately, it is difficult to examine how this heat will affect on the volumetric contraction of gels in an ordinary laboratory environment by using aqueous solutions of radio-active lanthanide(s) cations (or real low-level liquid wastes). When radio-active lanthanide cations were caught in hydrogels, the concentration of cations in hydrogels becomes from zero to certain finite value. Higher concentration of radio-active elements per unit volume of gels will result in higher heat per unit volume of gels from decaying lanthanide cations. This implies that radio-activity per unit volume of gels will also increase. When dynamic separation of gel pieces loaded with radio-active cations were done, the filter region plus

hydrogels will experience higher dose of radiation than other regions. Thus, we need an appropriate protection against this radio-activity. Therefore, we examine how much heat must be provided to induce the volumetric contraction of gels loaded with non-radioactive cations including the transition from the swollen state of gels to the shrunken state. Thermal experiments will be carried out by using differential scanning calorimetry (DSC) at very slow scanning rate. Gels loaded with non-radio-active cations in water will be used as sample system and thus, we can obtain how much heat must be provided to the whole process. Later, heat capacity determination of better accuracy will be carried out for the same system above. These simulated experiments will form the basis for performing the same experiments by using radioactive cations in aqueous solutions (or real low-level waste) if we can have a laboratory setting with certain shield against radio-activity.

3.3.1.3 Examination of radiation effect on newly synthesized hydrogels.

An extensive study on polymerization of poly(vinyl alcohol) by γ -ray irradiation was conducted by Kokufuta' group (Wang, et al, 1997 and references therein). This is the most notable study in recent years relevant to this proposal. They have studied how to make microgels, as well as bulk gels. In order to make the latter, they found that the critical concentration and gelation dose must be about 20 g of poly(vinyl alcohol)/L and 0.3 Mrad, respectively in the *absence* of oxygen (scavenger of radicals). High-energy radiation and polymers were extensively studied and summarized in a recent review by Clough (Clough, 2001).

Although preliminary γ -ray radiation experiments on aqueous solution of poly(vinyl alcohol) carried out in our reactor facility did not show any serious destruction of polymer chains, there is a possibility of losing the state (phase) of polymer gels through destruction of polymer chains when hydrogels are exposed to radio activity. This is certainly a worrisome aspect of extracting and retaining lanthanide cations in hydrogels from aqueous solutions by the proposed dynamic filtering system. As mentioned above, this may happen particularly when the dynamic separation of hydrogels loaded with radio-active lanthanide cations is carried out. There are two factors: 1) there may be enough heat to burn polymer networks and evaporate the remaining water; and 2) radiation from radio-active lanthanide cations may destroy polymer networks.

Co-PI (A.T) and Co-PI's (T.T.) have carried out preliminary radiation experiments. We have radiated aqueous solution of poly(vinyl alcohol) and solid sample with different levels of γ -ray dose with varying times to observe how the radiation affected polymer chains in the presence of oxygen. Solid sample caused some cross-linking in the presence of oxygen (scavenger) dissolved in water; however, the cross-linking occurred only to a very small extent in aqueous solutions. At the same time, we did not observe destruction of the polymer chains within the extent of radiation of dose and time period we have used. The presence or absence of oxygen probably produced some difference in the experimental results.

According to the definition of the low-level radioactive wastes, 4.780×10^{-4} cal/(sec \cdot cm³) of heat is generated. If the volume of swollen gels containing radioactive cations is reduced to 1%, only 20 sec is needed to warm up gels by 1° C (by assuming no heat loss to others). Then, self-induced contractions of gels and even the transition may be possible. In order to simulate this situation, irradiation of hydrogels in water, as well as in aqueous solution of lanthanide cations, by γ -ray will be carried out. The destruction of polymer networks can easily be examined by using proton NMR spectra. Once all possible radio-activities are quenched, proton NMR spectra of the irradiated samples will be taken. Irradiation of γ -ray will be carried out with different amounts of dose and length of irradiation times.

3.3.2 Aerogels (co-PI, M. Bertino)

3.3.2.1 Experimental investigation of trapping metals in aerogels

The proposed synthesis technique, both with radiolysis and with chemical reducing agents, has been developed in our laboratory. We will first demonstrate the potentiality of our technique by impregnating gels with high concentrations of toxic metals (Pb, Hg). The efficiency of the technique will be measured by quantitative analysis of the washings after reduction is carried out. Preliminary results show that our technique can eliminate up to 90% of Hg metal out of a 1 M aqueous solution. As for lower concentrations of waste, we have successfully reduced 100% of the metal in solutions containing 10^{-5} mol/l of Ag, corresponding to a concentration of about 1 ppm. We will test the technique to even lower concentrations, to find the limit at which the metal concentration is too low and the clusters do not reach the critical size for stability. The technique will be extended below this threshold by adding to the gels pre-formed Ag clusters, that can act both as “electron pools”, and nucleation centers (Henglein, 1993; Henglein, 1980)

Extension of the technique to rare earth metals, which represent a relevant fraction of low- and high level radioactive waste, will be studied by first attempting to produce a colloidal suspension of metallic rare earths, and then by trying to form these particles directly in a gel. Our group recently produced Ti metal particles by irradiating a ketone solution containing Ti butoxide, and adding PMMA as a capping polymer. Since the reduction potential of electrons is of the order of -2.7 V, and the reduction potential of rare earths is of the order of -2.3 V (Henglein, 1980), it should be theoretically possible to form clusters by irradiating deaerated solutions of an organic solvent and a rare earth salt soluble in that solvent.

Characterization of the clusters would occur, as in our recent work, with tools available on campus, such as TEM, XRD, XPS, and optical spectroscopies (UV-VIS and FTIR). The work would be then extended to encapsulation of rare earth clusters inside silica, and, where the oxygen of the silica interfered with the reduction process, carbon gels, or other inorganic gels not containing oxygen.

3.3.3 Natural Convection Cell Experiments (co-PI, A. Tokuhiko)

The “dynamic filtration system” is depicted below in Figure 2 and is explained as follows. In step (1), pre-swollen gels (by water) are added to the wastewater, which may contain targeted radioactive and/or non-radioactive particles. Upon swelling in “solution” the radioactive cations from the wastewater at lower temperature diffuse into the gels; thus the swollen gels contain cations. In step (2), gels undergo volumetric contraction at a higher temperature, which may be imposed (externally, by controlling the “hot” wall temperature) or self-induced (from radioactive decay heating). At this state, the gels gradually contract and release water while retaining the targeted radioactive particles and in so doing transition to a shrunken state. In step (3), either the waste liquid is drained and/or the hydrogel encapsulating radioactive particles are separated from the liquid. Once taken out of the cell, the dehydrated hydrogels assume a dry waste form for further disposition.

Except for some limited modification of the existing natural convection cells to arrive at a prototypic DFS, the experiments are expected to be straightforward. The provisional experimental objectives corresponding to the plan (see Project Schedule and Tasks) is as follows:

- 1) Current experimental plans (regardless of this proposals outcome) will be conducted with present hydrophilic gelatin particles and selected solid particles. Preliminary range of solid particles will be investigated and measures of adsorption efficiency considered.
- 2) Upon start of the project, data analyses of Step 1 will be finished. Plans for initial experiments using hydrogel of interest with selected solid particles will start.

- 3) After initial analyses, further experiments with hydrogel of interest and solid particles will continue.
- 4) As Step 3 progresses, experiments with hydrogel of interest and select radioactive solid particles will start concurrently. The candidate solid particles include: aluminum and grades of stainless steels.

The final series of tests will demonstrate the prototypic dynamic filtering system. These test should reveal the balance of the required heat input and that self-induced transition via radioactive decay heating.

4. PROJECT SCHEDULE AND TASKS

The tasks and activities to be completed are as below. The task of gathering information (books, reports, documents and so on), sorting this information as a means of classification and establishing an archiving process will mainly be done during the summer internships by the students involved. These activities will however, be conducted throughout the year.

Calendar Year	2004									2005											2006								
Year since start								0.5													2						2		
Months since start		Start	3					6				9									12						15		
Tasks below; Calendar month to the right>>>	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5				
1 Start project																													
2 Co-PI Tadashi TOKUHIRO																													
3 Synthesis of hydrogels of poly(NIPA)																													
4 Characterization of property of NIPA hydrogels																													
5 Synthesis of hydrogels of poly(NnPA)																													
6 Characterization of property of NnPA hydrogels																													
7 Radiation examination of synthesized hydrogels																													
8 Co-PI Massimo BERTINO																													
9 Quantitative analysis of retained metal concentration																													
10 Synthesis of rare earth colloidal suspensions																													
11 Synthesis of rare earth clusters inside gels																													
12 Co-PI Akira TOKUHIRO																													
13 Initial experiments w/ hydrophilic+solid particles																													
14 Data analysis; plan exp'ts w/ hydrogel+solid pcles																													
15 Experiments w/ hdrogel+solid particles																													
16 Experiments w/ hydrogel+radioactive solid particles																													
17 Lab scale experiments of dynamic filtering system																													
18 Year 1 Report																													
19 Year 2 Report																													

References

Adrian, R.J. et al., Eds., *Proc. 9th Intl. Symp. Application of Laser Techniques to Fluid Mechanics*, Springer-Verlag, Berlin, Germany (Symp. in Lisbon, Portugal) 1996.

Amiya, T.; Tanaka, T., "Phase transitions in crosslinked gels of natural polymers", *Macromolecules*, **1987**, *20*, 1162.

Bejan, A., Convection Heat Transfer, John Wiley & Sons, Wiley Interscience, ISBN 0-471-89612-8, **1984**.

Bertino, M. F.; Hund, J. F.; Sosa, J.; Zhang, G.; Sotiriou-Leventis, C.; Leventis, N.; Tokuhira, A.; Terry, J., "High resolution patterning of silica aerogels", *J. of non-cryst. Solids*, (accepted for publication, 2003)

Bertino, M. F.; Hund, J. F.; Zhang, G.; Sotiriou-Leventis, C.; Leventis, N.; Tokuhira, A., "Formation of noble metal clusters inside mechanically strong aerogels", *J. of Sol-Gel. Technol.*, (submitted, 2003)

Bertino, M. F.; J. F. Hund, J.F.; Leventis, N., "Synthesis of mono- and bimetallic clusters inside silica aerogels with chemical reduction", (to be submitted to *J. of non-cryst. Solids*, 2003)

Buscall, R. and Goodwin, J.W., Eds., Colloidal Polymer Particles, Academic Press; (March 1995) ISBN: 0122900456

Chen, B., Mikami, F. and Nishikawa, N., "Visualization and PTV Study of Natural Convection in Particle Suspensions (Simultaneous Measurements of Velocity, Temperature and Interface between Particle-Free Fluid and Suspension)," *Nihon Kikaigakkai rombunshu*, Trans. of JSME, **1998**, *64*, B 96-103.

Clough, R. L., "High-energy radiation and polymers: A review of commercial processes and emerging applications", *Nuclear Instruments and Methods in Physics Research*, **2001**, *183*, 8.

Dagnall, R. M.; Smith, R.; West, T. S., "A specific spectrofluorimetric determination of terbium as its EDTA-sulphosalicylic acid complex". *Analyst*, **1967**, *92*, 358.

EPA-Environmental Protection Agency, <http://www.epa.gov/radiation/mixed-waste/index.html>; as of November 9, 2003.

Fricke, J., Ed, Aerogels, Proceedings in Physics, Vol 6, Springer Verlag; (March 1986) ; ASIN: 0387162569, 1986

Fricke, J., Aerogels and xerogels : growth and opportunities for the early 21st century, Technical Insights; ASIN: 1562170260; http://www.ep2.physik.uni-wuerzburg.de/ag_fricke/graphic/start_js.htm; as of November 9, 2003

Fujiwara, A.; Tokuhira, A.; Hishida, K.; Maeda, M. "Investigation of oscillatory bubble motion using dual shadow technique and its surrounding flow field by LIF-PIV", *Third International Conference on Multiphase Flow*, **1998**, CD-ROM, 351.

Fujiwara, A.; Tokuhira, A.; Hishida, K. "Application of PIV/LIF and Shadow-Image to a Bubble Rising in a Linear Shear Flow Field", *10th Intl. Symp. On Applications of Laser Tech. to Fluid Mechanics*, Lisbon, Portugal. **2000**, Archived at: http://in3.dem.ist.utl.pt/downloads/lxaser2000/pdf/38_2.pdf

Fujiwara, A.; Tokuhira, A.; Hishida, K.; Maeda, M., "Understanding bubble dynamics via PIV/LIF/IST measurement methods", *Int. J. Multiphase Flow*, **2003**, (under revision).

Hagiwara, I., Natural convection heat transfer in an enclosure with hydrophilic particles, M.S. Thesis, University of Missouri – Rolla, Nuclear Engineering, under preparation, **2003**.

Hattori, A.; Okada, M.; Kang, C., “Natural Convection of Water-Fine Particles Suspension in a Rectangular Vessel Heated and Cooled from Opposing Vertical Walls (Effect of Initial Distribution of Particle Concentration),” *Nihon Kikaigakkai rombunshu, Trans. of JSME*, **2001**, 67, 662, B, pp. 145-152

A. Henglein, A.; *Ber. Bunsenges. Phys. Chem.* **1980**, 84, 253.

Henglein, A., *Isr. Jou. of Chem.* **1993**, 33, 77-88.

Hirokawa, Y.; Tanaka, T., "Volume phase transition in a nonionic gel", *J. Chem. Phys.*, **1984**, 81, 6379.

Hirotsu, S.; Hirokawa, Y.; Tanaka, T., “Volume-phase transition of ionized *N*-isopropylacrylamide gels”, *J. Chem. Phys.*, **1984**, 81, 1392.

Hund, J. F.; Bertino, M. F.; Zhang, G.; Sotiriou-Leventis, C.; Leventis, N.; Tokuhiko, A.; Farmer, J., “Formation and Entrapment of Noble Metal Clusters in Silica Aerogel Monoliths by γ -Radiolysis”, *J. Phys. Chem. B* **2003**, 107, 465.

Hund, J. F.; Bertino, M. F.; Zhang, G.; Sotiriou-Leventis, C.; Leventis, N.; Tokuhiko, A.; Farmer, J., “Synthesis of aerogel-metal cluster composites by gamma radiolysis”, *Mater. Res. Soc. Symp. Proc.* **2003**, 740, I11.2.

Huppert, H. E., and Sparks, R. S. J., “The fluid dynamics of a basaltic magma chamber replenished by influx of hot, dense ultrabasic magma”, *Contributions to Mineralogy and Petrology*, **1980**, 75, 279.

Ito, S.; Kokufuta, E.; “LCST of aqueous copolymers of *N*-isopropylacrylamide and other *N*-substituted acrylamide”, *Polymer Preprint*, **1998**.

Ito, S.; Ogawa, K.; Suzuki, H.; Wang, B.; Yoshida, R.; Kokufuta, E., *Langmuir*, **1999**, 15, 4289.

Kang, C.; Okada, M.; Hattori, A.; Oyama, K., “Natural Convection of Water-Fine Particle Suspension in a Rectangular Vessel Heated and Cooled from Opposing Vertical Walls (Classification of the Natural Convection in the Case of Suspension with a Narrow-Sized Distribution),” *Int. J. Heat Mass Transfer*, **2001a**, 44, 2973-2982.

Kang, C.; Okada, M.; Hattori, A., “Natural Convection of Suspension with Water and Fine Particles in a Rectangular Vessel Heated and Cooled From Opposing Vertical Walls: Effects of Initial Particle Concentration Gradient,” *Experimental Heat Transfer, Fluid Mechanics, and thermodynamics*, ed. G. P. Celata, P. Di Marco, A. Goulas and A. Mariani, Edizioni ETS, Pisa, **2001b**, 1, 639-644.

Keane, R. D., Correlation Methods of PIV Analysis; in *Optical Diagnostics for Flow Processes*. L.

Lading, G. Wigley, P. Buchhave, eds., *Proc. of a Summer School on Optical Diagnostics for Flow Processes*, 26 Sept.-2 Oct. 1993, Roskilde, Denmark: Whole Field Measurements, 1994. 271.

Leventis, N.; Sotiriou-Leventis, C.; Zhang, G.; Rawashdeh, A.-M. M., *Nano Lett.* **2002**, 2, 957-60.

Loewen, E. P. and Tokuhiko, A.T., Status of Research and Development of the Pb-Alloy Cooled Fast Reactor, *Nucl. Technol.*, submitted, 2002.

- Maeda, M.; Fujiwara, A.; Tokuhira, A.; K. Hishida, K., “Investigation of motion of a relatively large bubble and the PIV visualization of surrounding flow by LIF tracer particles”, *8th Int. Symp. on Flow Visualization*, Sorrento, Italy, 1-4 September, **1998**, archived CD-ROM Proc., isbn 0-953991-0-9, National Library of Scotland, Edinburgh, Scotland, 1998
- Maekawa, M.; K. Iizuka, K.; Fujiwara, A.; Hishida, K.; Maeda, M.; Tokuhira, A., “The structure of turbulent fluid flow involving gas bubble (Measurement of the fluid flow in the vicinity of bubbles by PIV)”, *Jap. Soc. Mech. Engrs.*, **1998**, B-64, 622 (in Japanese).
- Matsuo, E. S., Tanaka, T. “Kinetics of discontinuous volume-phase transition of gels”, *J. Chem. Phys.* **1988**, 89,1695.
- Mikami, F.; Chen, B.; Nishikawa, N., “Visualization and PTV Study of Natural Convection in Particle Suspensions (Simultaneous Measurements of Velocity, Temperature and Interface between Particle-Free Fluid and Suspension),” *JSME International Journal*, Series B, **2001**, 44, 30-37.
- Numajiri, Y.; Ito, S.; Kokufuta, E.; “Thermal property of hydrogels made of N-alkylacrylamids”, *Polymer preprint*, **1998**
- Okada, M.; Matsumoto, K.; Fukazaki, M., “Influences of Initial Concentration and Supercooling Degree on the Permeability of a Porous Medium Saturated with Partially Solidified Aqueous Solution,” *Int. J. Heat Mass Transfer*, **1996**, 39, 3845-3853.
- Okada, M.; Oyama, K.; Kang, C., “Natural Convection of Water-or Aqueous Solution-Fine Particle Suspension in a Rectangular Cell,” *Proceedings of 11th IHTC*, **1998a**, 3, 525-530.
- Okada, M.; T. Suzuki, “Natural Convection of Water-Fine Particle Suspension in a Rectangular Cell,” *Int. J. Heat Mass Transfer*, **1997**, 40, 3201-3208.
- Okada, M.; Oyama, K.; Kang, C., “Natural Convection of Water-or Aqueous Solution-Fine Particle Suspension in a Rectangular Cell,” *Proceedings of 11th IHTC*, **1998b**, 3, 525-530.
- Okada, K.; Oyama, K.; Kang, C., “Natural Convection of Water-Fine Particle Suspension in a Rectangular Cell—Effects of Temperature Difference and Distribution of Particle Size—,” *Nihon Reitokuchougakkai rombunshu*, Trans. of the JSRAE, **1999**, 16, 97-104.
- Pandit, V.; T. Schuman, T.; Tokuhira, A.; Bertino, M. F.; “Synthesis of Ti nanoparticles with the radiolysis method”, (in preparation.)
- Pierre, A. C.; Pajonk, G. M., *Chem. Rev.* **2002**, 102, 4243-4265.
- Portugal, Lisbon (2003) Announcement of the 12th Int. Symp. Application of laser techniques to fluid mechanics; at <http://in3.dem.ist.utl.pt/lxaser2004/committees.asp>; as of 06/30/03
- Raffel, M.; Willert, C.; Kompenhans, J., “Particle image velocimetry: A practical guide”, 1998, Springer Verlag, Berlin, ISBN: 3540636838.
- Sano, Y.; Karino, J.; Koyama, T.; Tanaka, Y., “Structural analysis of lanthanides complexes formed with CMPO/TBP extractants by NMR”, Technical Report, JNC, **1998**, No. 3, 79.

- Schild, H. G., "Poly(*N*-isopropylacrylamide): Experiment, Theory and Application", *Prog. Polym. Sci.*, **1992**, *17*, 163 and references therein.
- Schneider, M.; Baiker, A., *Catal. Rev.-Sci. Eng.* **1995**, *37*, 515-556.
- Sinha, S. P., "Complexes of the rare earths", **1966**, *Pergamon Press*, Oxford
- Sinha, S. P., "Systematics and the properties of the lanthanides", *Nato Advanced Study Institute*, **1982**, D. Reidel Publishing Co.
- T. Suzuki, T.; Okada, M., "Natural Convection of Water-Fine Particle Suspension in a Rectangular Cell," *Nihon Kikaigakkai rombunshu, Transactions of the Japan Society of Mechanical Engineers*, **1996**, *62*, B, 241-247.
- Takeda, Y., Velocity profile measurement by ultrasound Doppler shift method, *International Journal Heat & Fluid Flow*, Vol.7, 313, 1986.
- Takeda, Y., Measurement of velocity profile of mercury flow by ultrasound Doppler shift method, *Nuclear Technology (US), ANS*, Vol.79, 20, 1987.
- Takeda, Y.; Kobashi, K.; Fischer, W.E., Observation of the transient behavior of Taylor vortex flow between rotating concentric cylinders after sudden start. *Exp. in Fluids*, *9*, 317, 1990a.
- Takeda, Y., Development of ultrasound velocity profile monitor, *Nuclear Engineering & Design*, Vol.126, 277, 1990b.
- Takeda, Y., Instantaneous Velocity Profile Measurement by Ultrasonic Doppler Method, *JSME International Journal of Fluid and Thermal Engineering, Series B*, Vol.38, No.1, 8, 1995.
- Taketatsu, T.; Yoshida, S., "Spectrophotofluorometric determination of terbium with α , α' -ethylenediiminodi(*o*-hydroxyphenylacetic acid), *Bull. Chem. Soc. Jpn.*, **1972**, *45*, 2921
- Tanaka, T. "Kinetics of phase transition in polymer gels", *Physica*, **1986**, *140A*, 261
- Tokuhiro, A., Natural convection heat transfer enhancement in mercury with gas injection and in the presence of a transverse magnetic field, *Purdue University, Nuclear Engineering, Ph.D. Thesis*, 1991.
- Tokuhiro, A.; Takeda, Y., "Measurement of flow phenomena using the ultrasonic velocity profile method in a simulated Czochralski crystal-puller", *Journal of Crystal Growth*, **1993**, *130*, 421-432.
- Tokuhiro, A.; Kimura, N., "An experimental investigation on thermal striping. Mixing phenomena of a vertical non-buoyant jet with two adjacent buoyant jets as measured by ultrasound Doppler velocimetry, *Nuclear Engineering and Design*, **1999a**, *188*, 49-73.
- Tokuhiro, A.; Maekawa, M.; Iizuka, K.; Hishida, K., "The effect of a single bubble on turbulence structure in grid turbulence by combined shadow-image and PIV technique", *Int. J. Multiphase Flow*, **1998**, *24*, 1383-1406.
- Tokuhiro, A.; Maekawa, M.; Fujiwara, A.; Hishida, K.; Maeda, M., "Measurements in the wake of two bubbles in close proximity by combined shadow-image and PIV technique", *ASME J. of Fluid Eng.*, **1999**, *121*, 191-197.

Tokuhiro, A., “Experimental investigation of a vertical planar jet by ultrasound and laser Doppler velocimetry”, *Atomic Energy Soc. Japan, J. Nucl. Sci. and Technol.*, **1999b**, 36[6].

Tokuhiro, T.; Amiya, T.; Mamada, A.; Tanaka, T., “NMR study of poly(*N*-isopropylacrylamide) gels near phase transition“, *Macromolecule*, **1991**, 24, 2936.

Tokuhiro, T., Ito, S.; Kokufuta, E., “Reversed thermal behaviors of poly[*N*-(1,3-dioxolan-2-ylmethyl)-*N*-methyl-acrylamide] and its cross-linked analogue in liquids: water vs alcohols”, *Macromolecules*, **1998**, 31, 8549.

Tokuhiro, T., “Temperature dependence of density of polymer gels: 1. A pycnometry method applied to poly(*N*-isopropylacrylamide) – water system”, *J. Phys. Chem., B*, **1999**, 103, 7097.

Tokuhiro, T., “Temperature dependence of density of polymer gels: 2. Poly[*N*-(1,3-dioxolan-2-ylmethyl)-*N*-methyl-acrylamide] Networks – water or alcohol system”, *J. Phys. Chem., B*, **2001**, 153, 11455-11960.

Tokuhiro, T. (unpublished-1), “Temperature dependence of density of polymer gels: 3. Effects of ionizable group in copoly(*N*-isopropylacrylamide/acrylic acid or sodium acrylate) - water systems” (to be submitted to *J. Phys. Chem. B*.)

Tokuhiro, T., (unpublished-2), “Dynamics of solvent (water) molecules in the volumetric contraction-expansion of polymer gels. 1. Poly(*N*-isopropylacrylamide) networks – water system”(to be submitted *J. Chem. Phys.*).

Tokuhiro, T., (unpublished-3), “DSC study of hydrogels of poly(NIPA) with varying water content”.

Wang, B.; Mukataka, S.; Kodama, M.; Kokufuta, E., “Viscometric and light scattering studies on microgel formation by γ -ray irradiation to aqueous oxygen-free solution of poly(vinyl alcohol)”, *Macromolecules*, **1997**, 13, 6108.

APPENDIX B --- Year 1 Report

ANNUAL TECHNICAL PROGRESS REPORT NEER Grant: DE-PS07-03ID14540

Project Title: Radiolytically-induced novel materials and their application to waste processing

Covering Period: June 1, 2004 to June 30, 2005

Report Date: July 1, 2005

Recipient: University of Missouri – Rolla, Rolla, MO 65409-0170

Award Number: DE-PS07-03ID14540

Co-Investigators: Massimo Bertino, University of Missouri – Rolla (massimo@umr.edu), and Tadashi Tokuhito, University of Missouri – Rolla (tadashi@umr.edu)

Proposal Objectives:

The DOE NEER project underway is an experimental study on the potential application of two material processes based on radiolytic reactions using the UMR Reactor facility as follows: 1) silica-polymer based aerogel composites that encapsulate cluster of specific metals and 2) polymer gels made of thermo-sensitive polymer networks for encapsulating LLW particulates. 3) Finally, the functional design of a prototypic natural convection cell to process liquid waste streams will be tested.

1. Introduction

The proposed project concerns experimental studies on the potential application of two material processes based on radiolytic reactions using the UMR Reactor facility as follows: 1) silica-polymer based aerogel composites that encapsulate cluster of specific metals and 2) polymer gels made of thermo-sensitive polymer networks for encapsulating LLW particulates. The former start as aqueous/liquid solutions of based catalyzed silica hydrogels and metal ions, such as silver. The metal ions are reduced radiolytically and migrate through the solution to form clusters. Upon post-irradiation processing, aerogel monoliths, extremely lightweight but mechanically strong, that encapsulate the metals are produced. The latter gels exhibit thermally induced volumetric contraction at 20°-50° C by expelling water from the gels' physical state. Further, some functional groups that capture di- or tri-valent cations from aqueous solutions can be incorporated into the polymer networks on synthesis, including by radiolytic means. These polymer gels retain cations after volumetric contraction and have the ability to physically trap solid particulates in liquid waste streams. The study will see if the radioactive decay heat of isotopic particulates can self-induced the concentration of radioactive cations. Finally, 3) the functional design of a prototypic natural convection cell to process liquid waste streams will be tested.

The research progress made to date of each co-PI is as follows. Although there were initial delays in finding the appropriate student to work on each aspect of the project, the graduate students are as follows:

- 1) Ms. Sita Akella is a M.S. student in Chemical Engineering (ChE). She is being co-advised by co-PI A. Tokuhito, Dr. Kimberly Henthorn (UMR-ChE) and co-PI T. Tokuhito. She is working primarily with co-PI T. Tokuhito on developing a methodology to produce thermally-sensitive polymer gels and to characterize their macro/micro properties/structure by photometry, atomic absorption spectroscopy, proton Nuclear Magnetic Resonance (NMR) and magnetic susceptibility.
- 2) Ms. Lisa Wulff is a M.S. student in Environmental Engineering (EnvE). She is being co-advised by co-PI A. Tokuhito and Dr. Mark Fitch (UMR-EnvE). She is working on developing a prototypic natural convection cell and using this cell to characterize the uptake of metallic solid particulates and metallic ions as amenable by silica and polymer gels.

- 3) Mr. Brian Heckman is a M.S. student in Physics. He is being co-advised by co-PI M. Bertino and A. Tokuhito. He has recently started and will extend the work reported here. He will be investigating the applicability of silica gels to known range of fission products and species originating from spent fuel processing streams.

The proposal also allocated summer support for up to two undergraduates per summer in order to provide research opportunity related to the project. Due to a later start in the summer of 2004, three students have joined our effort in summer 2005, as follows:

- 1) Mr. Jaime Arrocha is learning and assisting co-PI T. Tokuhito with the NMR portion of the project. Specifically, he is putting together the instrument to measure magnetic susceptibility.
- 2) Ms. Emma Schmitze is preparing PVA-based gels to be gamma irradiated and subsequently tested using proton NMR.
- 3) Mr. David Bash is assisting co-PI A. Tokuhito and Ms. Lisa Wulff in operation of the prototypic natural convection cells.

2. Silica gels to capture metallic constituents (M. Bertino)

In the research period we synthesized poly[*N*-isopropylacrylamide(NIPA)], copoly[NIPA(75 mol %)/sodium acrylate (NaAc)(25 mol %)], carboxymethylcellulose and silica gels following conventional recipes. Protocols were developed and equipment (mostly glassware) was purchased for synthesizing comparatively large gel quantities, between about 200 and 1000 mL per batch.

The gels were the main components of a novel approach for waste disposal. In our procedure, a gel is prepared according to conventional protocols. The gel is then bathed several times in distilled water to wash out solvents and residues from the preparation (Figure 1a). The gels are then bathed in a solution containing a water-soluble metal salt, like Nickel sulfate (Figure 1b). Ni ions diffuse inside the gels, and equilibrium is reached within a few hours after beginning of the bathing. At this point, a highly concentrated aqueous solution of Na₂S is poured inside a hole drilled on top of the gel before bathing (Figure 1c). S²⁻ ions react with Ni ions to form black Ni sulfide nanoparticles. Formation of Ni sulfide decreases the Ni ion concentration inside the gel. As a consequence, additional Ni ions diffuse from the solution inside the gel (Figure 1d). Steps c and d can be repeated several times, and the ion concentration in the initial solution can be considerably decreased, as indicated by the change in color shown in Figure 2. Quantitative analysis of the ion concentration is under way. Comparable results were obtained with carboxymethylcellulose, silica, copoly[NIPA(75 mol %)/sodium acrylate (NaAc)(25 mol %)] gels. The chemical identity of the nanoparticles is confirmed by XRD, shown in Figure 3. The end product black Ni-sulfide is depicted in Figure 4. Nickel is here presented as an representative metal.

Our process has several promising features, and may be considered in a number of applications.

- 1) Virtually all the Ni ions are converted to sulfides inside the gel. No black precipitates were observed in the bathing solution, indicating that sulfides did not leach outside the gels. Atomic absorption and neutron activation measurements are planned to determine Ni concentration in the solution before and after treatment.
- 2) The process does not depend strongly on gel type. We have successfully employed carboxymethylcellulose, copoly[NIPA(75 mol %)/sodium acrylate (NaAc)(25 mol %)] and silica gels. The main difference consisted in the velocity of diffusion. Equilibrium was reached fastest for silica gels (3-6 hours), and slowest for copoly[NIPA(75 mol %)/sodium acrylate (NaAc)(25 mol %)]gels (several days).
- 3) The capacity of the gels is high, and gels can be used multiple times to absorb ions from a solution. To date, we have employed gels twice to absorb highly concentrated Ni solutions (6 g/l and higher). We typically employed 100 mL of wet gel (corresponding to 5 g of dry gel) to absorb ions from a 200 mL solution with a Ni ion concentration of 6 g/l.
- 4) Our protocol works for both organic and silica gels. This allows a great flexibility. For example, one could employ organic gels in the case of a valuable metal (Ni, but also Au, or Ag). The gels could be easily pyrolyzed at low temperatures, and the ore recovered. In case of radioactive materials, one would use a silica gel, which could then be transformed into a glass by moderate to high heating (800-1000°C).

We are currently finishing characterization of the materials, and working to extend the quantities amenable to our protocol, both in terms of gel volume and solution volume.

In the next year, we plan to:

- 1) Extend our protocol from the model system represented by Ni sulfate to materials more relevant for the nuclear waste disposal problem. In particular, we plan to apply our protocol to the case of Nd ions, representative of the class of lanthanides. Like in the case of Ni ions, a Na_2S solution will be added on top of the gels to form the nearly insoluble NdS. Nd concentrations in the parent and exhausted solution will be monitored with neutron activation. Another material that we plan to tackle is Cs. In this case, Cs ions will be precipitated by adding perchloric acid, or phosphoric acid, to form the poorly soluble Cs perchlorate. Sr will be immobilized by addition of a carbonate, or by bubbling CO_2 through the solution.
- 2) Improve the processing rate of our process. In this case, we will prepare a column of comparatively small (a few mm in diameter) gel particles, obtained by grinding a large gel. The gel particles will be bathed in the precipitating agent, and packed in a column. The metal ion solution will be then added, dropwise, from the top. Because of the small size of the gel particles, diffusion inside and through the particles is expected to be considerably faster.

Currently involved students: Brian Heckman, M.S. candidate. Due to the (notorious) shortage of suitable students, no students were found over a large part of the first phase of the project. A suitable student (Heckman) was identified and supported in the spring of 2005. A large part of the work described in this report has been carried out by Dr. Bertino personally. Another student, Samuel Petersen from Rolla High School is currently working on the program (supported by a University outreach program) and will enroll as a Physics major in the Fall. He is learning and conducting neutron activation analysis experiments during the summer of 2005.

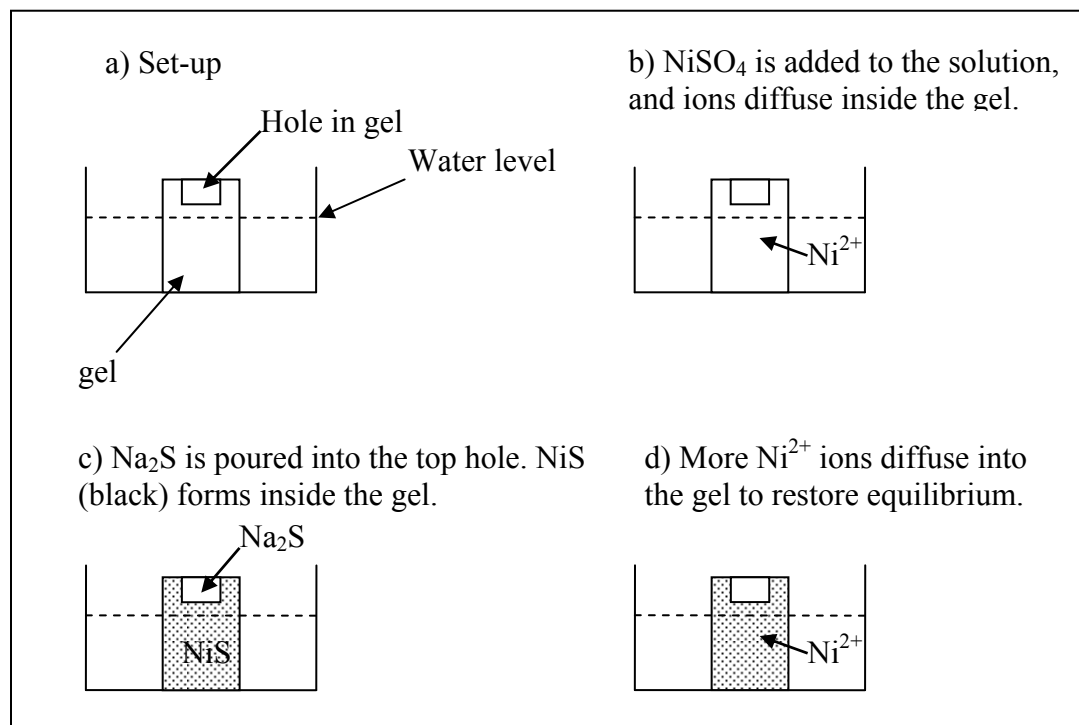


Figure 1. Schematic representation of the bathing/ NiS formation procedure.

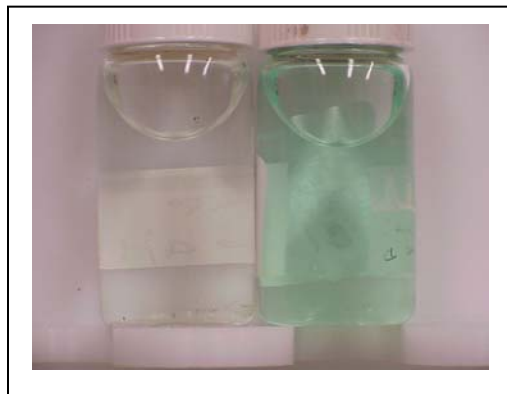


Figure 2. Color of the bathing solution before (right) and after (left) treatment. Notice the change in color that indicates concentration of Ni^{2+} ions.

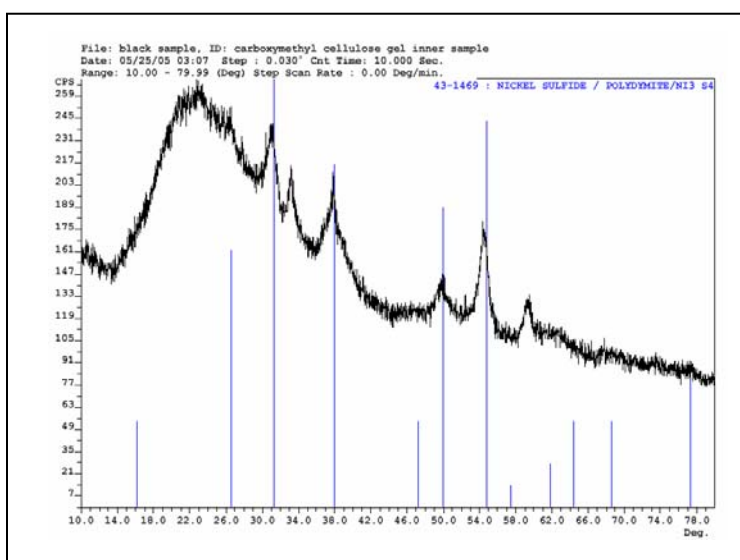


Figure 3. X-Ray diffraction of a carboxymethylcellulose/sulfide composite. The blue lines correspond to peaks arising from Ni_3S_4 . The remaining peaks remain to be identified

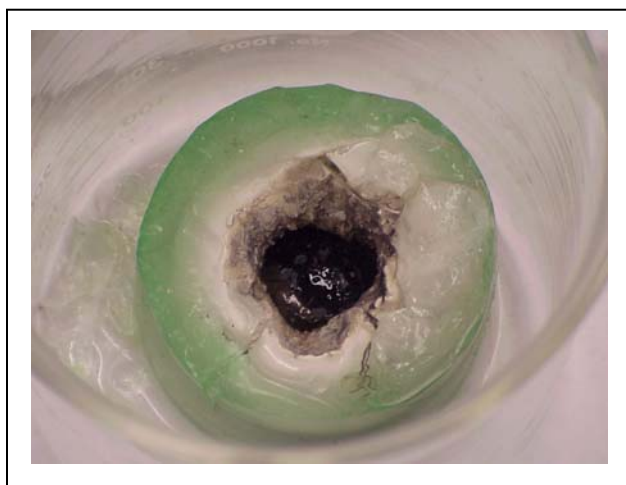


Figure 4. Top down view of the end product gel with “black” nickel-sulfide in the center as described.

3. Developing thermally-sensitive polymer gels (T. Tokuhira)

Since the intended application is to process mixed or metallic particle/cation in a thermally-driven natural convection system within a lower temperature range (10°-40°C), we (T. Tokuhira and student, S. Akella) have focused our attention on hydrogels made of 1) thermally-sensitive polymer networks containing 2) some functional groups. Previous studies¹⁻³ showed that contraction in the volume of thermally-sensitive polymer hydrogels arises from the loss of water to its exterior, as induced by increasing temperature. The primary component of thermally-sensitive polymer networks is poly(*N*-isopropylacrylamide) [poly(NIPA)] with *N*, *N'*-methylenebisacrylamide (BIS) as a cross-linking agent. The secondary polymer component contains some functional group and thus, they form copolymer networks with NIPA. The secondary component may possibly consist of two different functional groups. One of the major effects on the physical properties of poly(NIPA) by the secondary component is exhibited as changes in the volumetric phase transition temperature (Tr.T) and the volume of gels. The role of functional groups in the intended application is the ability to “capture and retain” metallic cations in the polymer networks. Further, depending on the processing method, polymer “clusters” approaching a nominal size of one to several 100 μm may physically encapsulate particulates within a comparable to smaller range.

It has been found that when sodium acrylates (*x* mM) are incorporated into the poly(NIPA) networks, the carboxylic group “captures and retains” some transition metallic cations that are originally present in water. Metallic cations examined so far are salts made of mostly the second and third row transition metals such iron, cobalt, nickel, copper, and chromium plus a rare-earth element, terbium^{4,5}. It is a fortunate coincidence that mixed waste, from fission reactors and non-nuclear industrial processes, includes some of these metallic isotopes. However, we do not at this time know what kind of functional groups is most suitable for the above treatment.

By choosing functional groups that are known to serve as good ligands for metallic cations, we have successfully synthesized so far the following copoly [NIPA(700 mM – *x*)/Y(*x*)] networks as tabulated in Appendix 1. In these tables, Y represents a secondary polymeric residue containing the specific functional group in units of mM. All gels were synthesized by leaving pre-gel solutions overnight at 4°C. Additionally, we are now in the process of synthesizing with CH₂=CH(CH₂-PO₃). We have briefly examined the physical property of hydrogels produced as given in Appendix 1. Table 1 summarizes the preliminary results for the volumetric phase transition temperatures for the hydrogels of above copolymer networks. The replacement of NIPA by *N*-*t*-butylacrylamide (NtBA) has lowered the transition temperature⁶. This special character was utilized to lower the transition temperature of copolymer of NIPA and two secondary polymer components (sodium acrylate and NtBA).

3.1 Determination of the content of metallic cations caught in gel pieces

We are in a process of determining the ratio of the number of a specific functional group versus that of metallic cation caught in gel pieces. We are now evaluating the following:

- a) effect of the conformation of polymer networks,
- b) effect of temperature, and
- c) effect of concentration of metallic salts in water.

Further, the combined effects of both a) and b) can be examined by choosing temperature a few degrees below and above Tr. T. In this type of experiment, we should be kept in mind that Tr. T's varies from one chemical composition of copolymer to another. The analytical methods to be employed for determination of the amount of cations caught in gels are:

- 1) photometric determinations of aqueous solutions of metallic cations (in the visible region) before and after adsorption (indirect determination); and
- 2) atomic absorption of metallic cations caught in gel pieces.

From the latter study, we will be able to find the stoichiometry of metallic cation and polymer networks. This can provide insights into the nature of chemical and/or physical binding between the metallic cation and possible ligand molecules including specific functional group. Further investigation in nature of binding will be carried out by: 1) the magnetic susceptibility determined by Gouy balance and also by 2) proton NMR chemical shift induced by the paramagnetic effect of the metallic cation. An customized Gouy balance is under development and uses a 1.4 Tesla permanent magnet (previously used for proton CW NMR spectrometer). Our 400 MHz high-resolution FT-NMR spectrometer will be used for the proton NMR experiment noted above. All transition metals are capable of forming various types of hybrid orbitals made of 3*s*, 3*p* and 3*d* (or higher) atomic orbitals. Thus, they are able to form coordination-type chemical bonds with possible electron-donor ligand groups. In the case of hydrogels as previously

described, these coordination-type chemical bonds may be formed with specific (electron donor) functional groups and water molecules retained in the gels.

Table 1. Volumetric phase transition temperature of hydrogels made of various Copoly[NIPA(700 mM – x)/Y(x mM)].

Minor polymeric residue (Y)	Composition (x mM)	Transition temperature [°C]
Two-component copolymer		
–CH ₂ –CH(COONa)–	32	39
–CH ₂ –CH(COONa)–	175	55
–CH ₂ –CH(CH ₂ –C≡N)–	32	
–CH ₂ –CH(CH ₂ –C≡N)–	175	50
Three-component copolymer		
Y1: –CH ₂ –CH(COONa)–	175	45
Y2: –CH ₂ –CH[C=ONH–C(CH ₃) ₃]–	52.5	

4. Prototypic natural convection cell for solid-liquid waste processing

We have refined the natural convection cell used by Hagiwara⁶ in order to prepare for experiments using silica and/or polymer gel solutions. Due to the effort needed to produce these solutions, at the moment we anticipate using up to 10%vol in the prototype convection cell. Hagiwara who carried out the preliminary work studied the local heat transfer for natural convection with a nominal hydrophilic gelatin size 134µm and 0.026wt% loading. Gelatin is a structural protein also known as collagen (essentially a triple helix of polypeptide amino acid chains) and in consumable form, derived from animal collagen. Hagiwara showed that due to sedimentation of particles the local heat transfer degrades toward the conduction mode at the bottom of the cell; however, the heat transfer is slightly enhanced due to the buoyant particles in the upper portion of the cell. The operational ΔT ($=T_{\text{hot}} - T_{\text{cold}}$) is in workable range with respect to Table 1. A schematic of the convection cell is given in Figure 5, followed by a photo in Figure 6. Figure 7 shows a representative heat transfer result for gelatin size 134µm and 0.026wt% loading. The present student, L. Wulff, has verified the single phase convection results of Hagiwara.

To date, Wulff has worked in closely with S. Akella, to collaboratively learn how to produce the polymer gels as described above. With the methodology mostly developed, Wulff has recently learned how to operate the natural convection cell and to carry out the data acquisition process for heat transfer characterization. Thus over the next six months with an additional six months to conclude the research, the following major tasks will be undertaken with respect to developing a prototypic natural convection cell to process the targeted metallic ions and metal particulates:

- 1) With the delivery of 200 grams of the Polyscience poly[styrene(92)/divinylbenzene(8, crosslinker)] particles (200-400 mesh; corresponding to 74-37mm), conduct some initial experiments on metallic ion and metal particulate “uptake/loading” under planned and controlled conditions. Coordinate with T. Tokuhira.
- 2) Conduct some initial experiments on metallic ion uptake/loading under planned and controlled conditions in collaboration with M. Bertino.
- 3) Concurrently develop a methodology to characterize the extent of uptake/loading of the targeted species for both polymer and silica gels. With respect to the physical encapsulation of metal particulates, a phenomenological model should be proposed.
- 4) Begin planning for limited irradiated testing of polymer gels in collaboration with T. Tokuhira in order to assess the influence of cross-linking on metallic ion and metal particulate “uptake/loading”.

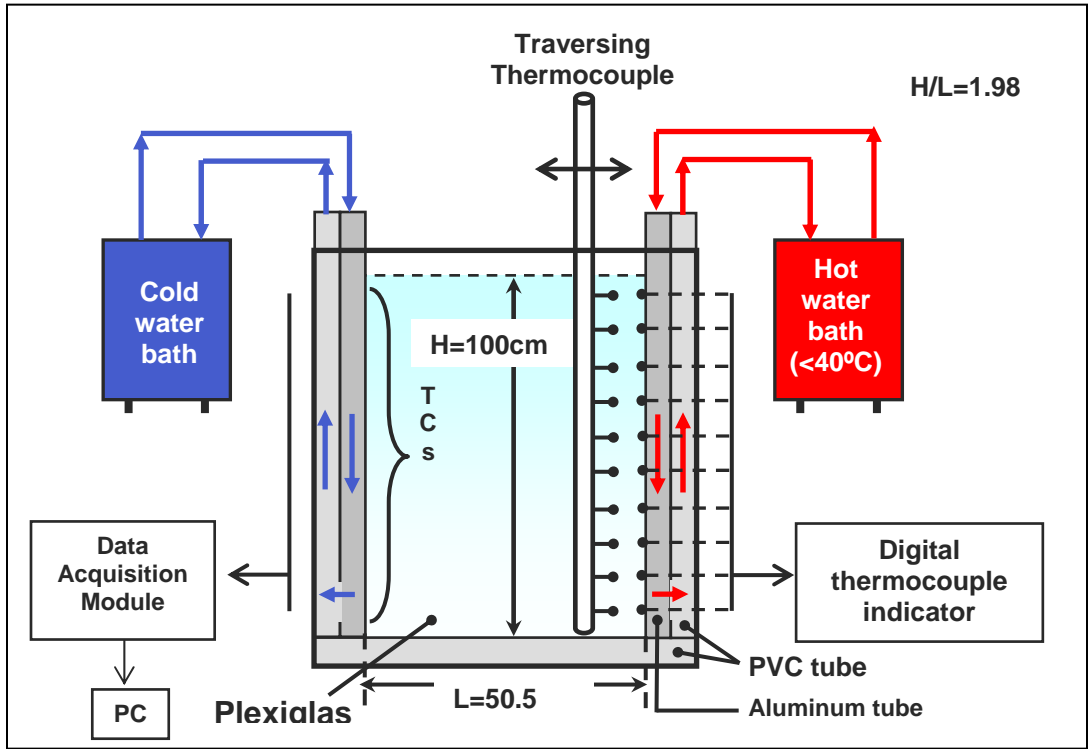


Figure 5. Schematic of the prototype natural convection cell (TCs - thermocouples).

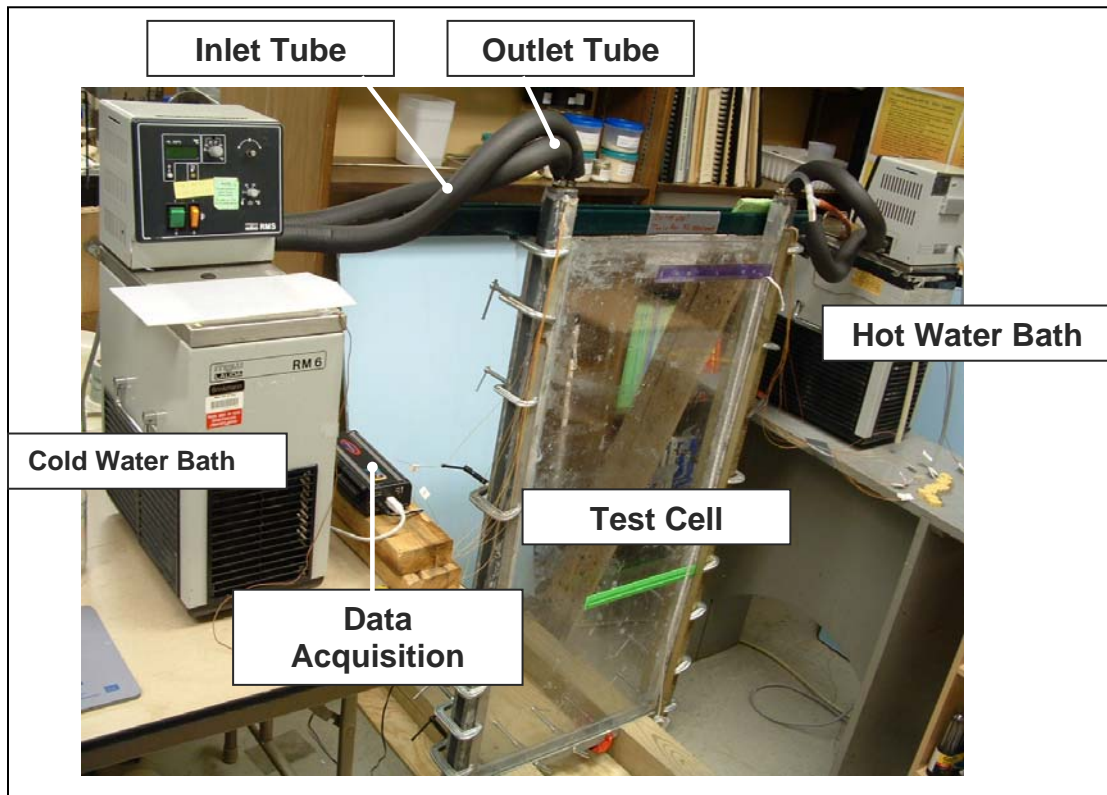
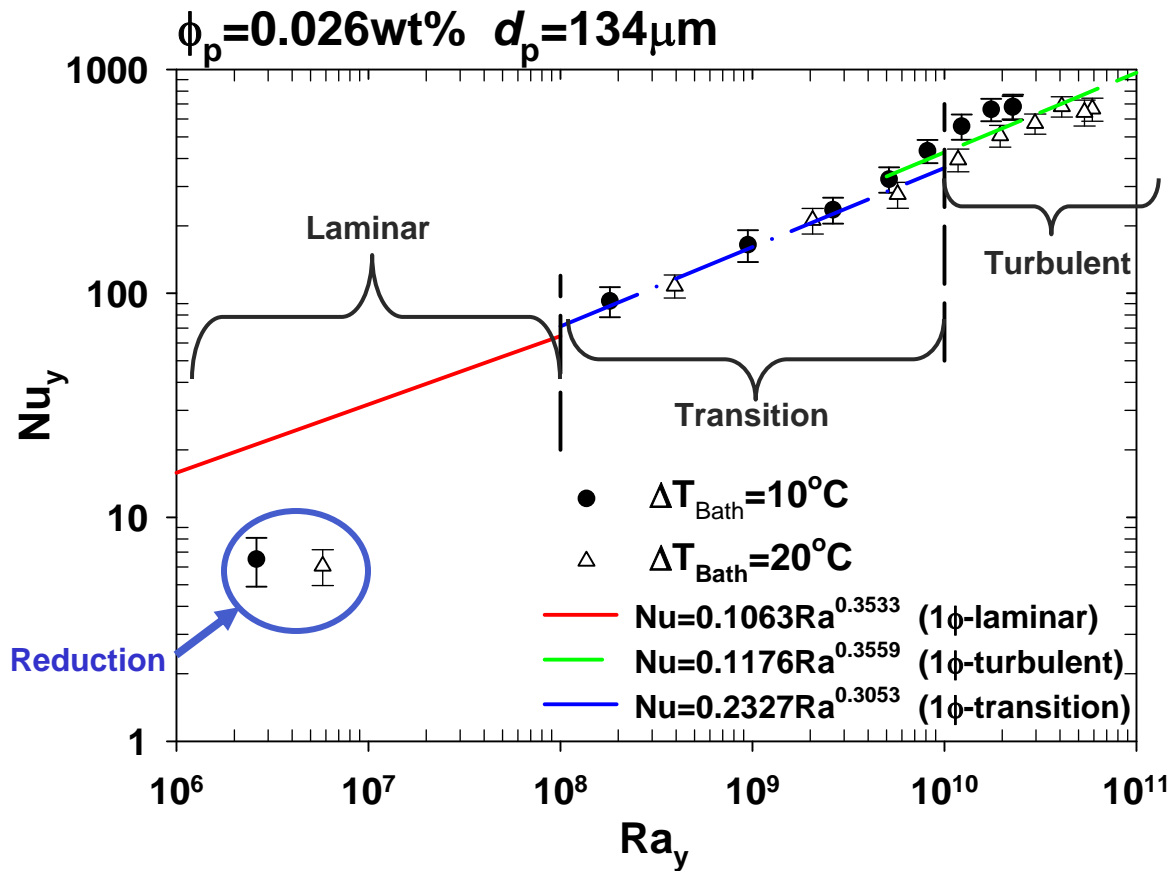


Figure 6. Photo of one of the prototype natural convection cells.



Sediment layer of gelatin particles was formed at the bottom of the cell.

Figure 7. Local heat transfer correlation for single-phase (1 ϕ) and with gelatin particles of weight % and nominal particle diameter as given, with 10° and 20°C temperature differences.

REFERENCES

- 1) T. AMIYA, Y. HIROKAWA et al. *J. Chem. Phys.* **86**, 2375 (1986).
- 2) Y. HIROKAWA, T. TANAKA, *J. Chem. Phys.*, **81**, 6379 (1984).
- 3) T. TOKUHIRO, submitted to *J. Phys. Chem.B*, (2005).
- 4) J. F. HUND, M.F. BERTINO et al., *J. Phys. Chem. B*, **107**, 465 (2003).
- 5) J. F. HUND, M.F. BERTINO et al., *Mater. Res. Soc. Symp. Proc*, **740**, 1112 (2003).
- 6) T. TOKUHIRO, *private communication to A. Tokuhiro*, (2005).
- 7) I. HAGIWARA, M.S. Thesis, Nuclear Engineering, University of Missouri – Rolla, Rolla, MO (USA) (2004)
- 8) A. TOKUHIRO and I. HAGIWARA, *JSME Int. J., Ser. B*, to be submitted (2005).

Appendix 1 Synthesis of polymer gels

1.1 General Procedure

The primary monomer (*N*-isopropylacrylamide (NIPA)) and one of the secondary monomers [allyl-cyanide (AC), sodium acrylate (NaAc), or allyl alcohol (AA)] (the total monomer concentration was kept at 700 mM), appropriate amounts of crosslinker (*N,N'*-methylene-bis-acrylamide (BIS)) and chain carrier (*N, N, N', N'*-tetramethyl-ethylenediamine (TEMED)) were dissolved in water. Nitrogen gas was then bubbled through the solution for approximately 20 minutes in order to remove oxygen. Immediately after adding ammonium per-sulfate (APS) (initiator for radical polymerization), the mixture was kept in the refrigerator (4° C) for gradual formation of homogeneous gels overnight. The amount of BIS was varied in the following synthesis according to the softness/hardness of the synthesized gel.

1.2. Single-component gel (Pure NIPA)

In the synthesis of 700 mM pure NIPA polymer gel, the raw materials required are shown in Table 1.1.

Table1.1 Pure NIPA

Sample #	NIPA	BIS	TEMED	APS
1	1.9857 g	0.0331 g	0.1 mL	2 drops
2	1.9857 g	0.0331 g	0.5 mL	2 drops
3	1.9857 g	0.0331 g	1 mL	2 drops
4	1.9857 g	0.0662 g	3 mL	2 drops

1.3. Two-component gel systems

1.3.1. Copolymer of NIPA and NaAc

Different combinations of NIPA and NaAc were made as tabulated in the Table 1.2.

Table 1.2 Copolymer of NIPA and NaAc

Sample No.	Sample Short Description	NIPA	NaAc	BIS	TEMED	APS
1	32 mM NaAc & 668 mM NIPA	1.89 g	0.075 g	0.0331 g	0.3 mL	2 drops
2	32 mM NaAc & 668 mM NIPA	1.89 g	0.075 g	0.0331 g	0.5 mL	2 drops

3	32 mM NaAc & 668 mM NIPA	1.89 g	0.075 g	0.0662 g	0.5 mL	2 drops
4	32 mM NaAc & 668 mM NIPA	1.89 g	0.075 g	0.0662 g	0.8 ml	2 drops
5	32 mM NaAc & 668 mM NIPA	1.89 g	0.075 g	0.0662 g	5 mL	2 drops
6	175 mM NaAc & 525 mM NIPA	1.4852 g	0.4114 g	0.0331g	0.5 mL	2 drops
7	175 mM NaAc & 525 mM NIPA	1.4852 g	0.4114 g	0.0662 g	1 mL	2 drops
8	175 mM NaAc & 525 mM NIPA	1.4852 g	0.4114 g	0.0662 g	3 mL	2 drops
9	175 mM NaAc & 525 mM NIPA	1.4852 g	0.4114 g	0.0662 g	5 mL	2 drops

1.3.2. Copolymer of NIPA and AC

Varying compositions of NIPA and AC were made as listed in the Table 1.3.

Table 1.3 Copolymer of NIPA and NaAc

Trials	NIPA	AC	BIS	TEMED	APS
1) 32 mM NaAc & 668 mM NIPA	1.89 g	0.0563 g	0.0331 g	0.3 mL	2 drops
2) 32 mM NaAc & 668 mM NIPA	1.89 g	0.0563 g	0.0331 g	0.5 mL	2 drops
3) 32 mM NaAc & 668 mM NIPA	1.89 g	0.0563 g	0.0662 g	0.8 mL	2 drops
4) 32 mM NaAc & 668 mM NIPA	1.89 g	0.0563 g	0.0662 g	5 mL	2 drops
5) 32 mM NaAc & 668 mM NIPA (45 ml water)	3.401 g	0.096 g	0.1196 g	9 mL	4 drops
6) 175 mM NaAc & 525 mM NIPA	1.4854 g	0.2934g	0.0331g	0.5 mL	2 drops
7) 175 mM NaAc & 525 mM NIPA	1.4852 g	0.2934g	0.0662 g	1 mL	2 drops
8) 175 mM NaAc & 525 mM NIPA	1.4852 g	0.2934g	0.0662 g	3 mL	2 drops
9) 175 mM NaAc & 525 mM NIPA	1.4852 g	0.2934g	0.0662 g	5 mL	2 drops

1.3.3. Copolymer of NIPA and AA

Varying compositions of NIPA and allyl alcohol were made as listed in the Table 1.4.

Table 1.4 Copolymer of NIPA & AA- Experimental data

Trials	NIPA	AA	BIS	TEMED	APS
1) 175 mM AA & 525 mM NIPA	1.4853 g	0.2541 g	0.0662 g	5 mL	2 drops
2) 175 mM AA & 525mM NIPA	1.4853 g	0.2541 g	0.0993 g	5 mL	2 drops
3) 350mM AA& 350mM NIPA	0.9902 g	0.5048 g	0.0662 g	5 mL	2 drops
4) 700 mM AA	-	1.015 g	0.0662 g	5 mL	2 drops

1.4. Three-component gel systemS

The three component gel systemS consist of NIPA, NaAc and NTBA. The ratio of NIPA and NaAc is kept constant at 3:1 and the NIPA was replaced by NTBA in various proportions as shown in the Table 1.5

Table 1.5 Copolymer of NIPA, NaAc & NTBA - Experimental data

Trials	NIPA	NaAc	NTBA	BIS	TEMED	APS
1) 10% NTBA = 472.5 mM NIPA +52.5 mM NTBA + 175 mM NaAc	1.4852 g	0.4114g	0.1667 g	0.0662 g	5 mL	2 drops
2) 20% NTBA = 420 mM NIPA + 105 mM NTBA + 175 mM NaAc	1.188 g	0.4114g	0.333 g	0.0662 g	5 mL	2 drops
3) 25% NTBA = 393.75 mM NIPA +131.25 mM NTBA + 175 mM NaAc	1.114 g	0.4114g	0.4166 g	0.0662 g	5 mL	2 drops
3) 30% NTBA = 367.5 mM NIPA +157.5 mM NTBA + 175 mM NaAc	1.0396 g	0.4114g	0.5 g	0.0662 g	5 mL	2 drops