

The Impact of High Level Gamma Radiation on Immobilized Waste Forms in Polymeric Matrices

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A new polymer-based composite binder was developed for the containment/immobilization of radioactive waste forms. This material was subjected to a variety of physicochemical tests to determine its suitability for this purpose. It appears that this composite material possesses superior qualities in terms of resisting radiation damage, retaining the radio isotopes after radiation exposure, and resisting biodegradation. Further, a combination of chemical fixation/immobilization technology with the radiation-resistant binder was studied. Our evaluation procedures, the results, and its potential applications based on our conclusions are presented in this article.

INTRODUCTION

The tremendous growth in the nuclear energy industry demands the need for safe, cost-effective immobilization of wastes generated. It would be an added plus, should we develop an immobilization process, if the stored monoliths can perhaps be dissolved in a solvent and the radio nuclides be recovered for novel applications in the future.

Initially, physical characteristics such as unconfined compressive strength (UCS), permeability, diffusion coefficient, flexural strength, and weathering properties have been considered to be the deciding factors in the successful immobilization of hazardous wastes. However, later works have shown that the governing properties of an effective immobilization process include the solubility product constant and the partition coefficient of the final form of the waste.

The chemical fixation/immobilization process for containing hazardous waste has been accepted and used as a viable alternative to other remediation techniques worldwide. This is due to the simplicity and cost-effectiveness of this technology.

When the contaminants present at a site are heavy metal ions such as lead, mercury, etc., simple cement/pozzolone based binders will be sufficient for the immobilization. On the other hand, when organics and radioactive species constitute the waste, the present day immobilization technologies become inadequate. The structural damage to the matrix by radioactive isotopes and subsequent poor leaching characteristics of

cement based binders have deterred the use of cement as a binder. For the same reason, the in-situ vitrification process (ISV) also appears to be a poor candidate.

On the basis of the discussion above, we strived to develop a process using both chemical fixation and a compatible binder system that would (1) effectively immobilize (chemically and mechanically) radioactive waste, (2) resist structural damage from heavy doses of radiation (gamma), (3) show excellent leaching characteristics after radiation, (4) retain good mechanical properties after radiation, and (5) not undergo biodegradation. The development, evaluation procedures, and the results of our investigations are presented in this article.

EXPERIMENTAL

A ten-kilogram quantity of clean Ottawa sand was spiked with a solution containing arsenic, cadmium, cobalt, chromium, copper, nickel, lead, and zinc. An appropriate quantity of the solution was added to generate a matrix containing 1000 ppm (mg/kg) levels of these priority pollutants. After drying, several samples were taken from the lot and analyzed for those elements. Appropriate reagents (in solution) were added to effect chemical fixation of the spiking species. A number of monoliths were made containing 16.5 percent (by weight) of the composite binder (supplied by BondTech International Corporation, Hudson, Wisconsin) and 83.5 percent (by weight) of the spiked Ottawa sand. The components were thoroughly mixed in a Hobart-type mixer for homogeneity. The samples were allowed to cure for 24 hours. One set of samples was retained for various pre-irradiation analyses. The rest of the samples were sent for radiation studies at Pacific Northwest Laboratories (PNL), Richland, Washington. At PNL, the samples were exposed to gamma radiation from several ^{60}Co sources. The samples were exposed to a total of 1.1×10^8 R (roentgen). After this exposure, both nonirradiated and irradiated samples were subjected to Fourier Transform Infra-Red (FTIR) analyses and American Nuclear Society Leach Test (ANS 16.1) at RMC Environmental Laboratory, West Plains, Missouri. Biodegradation studies were conducted at the Analytical Bio-Chemistry (ABC) Labs, Columbia, Missouri. Energy absorption studies, calibration uncertainty calculations, and data evaluation were done at the Argonne National Laboratories (ANL), Chicago, Illinois. Further 10 CFR 61 studies (Federal compliance requirements for stabilized radioactive waste forms) were conducted at RMC Environmental Laboratory. The FTIR work was done using a Perkin-Elmer 1600 FTIR Spectrometer. The metal ions were analyzed using a Varian AA-1275/GTA95 Spectrometer. Other mechanical property evaluations were carried out using the American Society for Testing and Materials (ASTM) procedures.

The components were thoroughly mixed in a Hobart-type mixer for homogeneity.

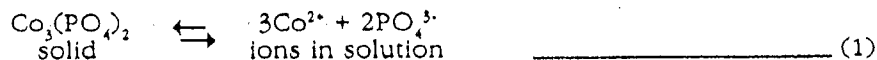
RESULTS AND DISCUSSION

The results of ANS 16.1 are presented in **Exhibits 1 to 8**. The bar graphs of the data from Exhibits 1 to 8 are presented in **Exhibits 9 to 14**. The incremental leach versus time are shown in **Exhibits 15 to 21**. The infrared

spectra are presented in **Exhibits 22** and **23**. UCS data are shown in **Exhibit 24**. Biodegradation data, thermal cycling data, combustibility, corrosivity, and weathering properties are shown in **Exhibit 25**.

The ANS 16.1 data indicate that two major requirements of this immobilization technology, namely, chemical fixation followed by placing the immobilized species in a radiation resistant composite matrix, have been met satisfactorily.

Considering the chemical fixation, the leach value of any species in question primarily depends upon a constant known as the solubility product constant (Ksp). When a stabilized monolith comes in contact with a groundwater system, the stabilized species attain an equilibrium with the water surrounding the monoliths. Let us consider the case of cobalt, where the Co^{2+} ion has been converted into $Co_3(PO_4)_2$ by the addition of appropriate reagents. When $Co_3(PO_4)_2$ ionizes, we get the following equilibrium:



at equilibrium

$$\frac{[Co^{2+}]^3 [PO_4^{3-}]^2}{\underset{\text{solid}}{[Co_3(PO_4)_2]}} = (\text{constant}) K \text{ (2)}$$

Since the concentration of a solid is considered as unity, we now get a new constant Ksp known as solubility product constant:

$$Ksp = [Co^{2+}]^3 [PO_4^{3-}]^2 \text{ (3)}$$

The value of Ksp has been experimentally determined to be:

$$2.0 \times 10^{-35} \text{ for } Co_3(PO_4)_2$$

$$\text{(i.e.) } [Co^{2+}]^3 [PO_4^{3-}]^2 = 2.0 \times 10^{-35}$$

During our immobilization, we had kept the concentration of PO_4^{3-} at 0.1 mole/l. Substituting this value in equation (3) we get:

$$[Co^{2+}] = \sqrt[3]{\frac{2.0 \times 10^{-35}}{(0.1)^2}} = 1.26 \times 10^{-11} \text{ moles/kg.}$$

Since the atomic weight of cobalt is 58, the amount of Co in one liter will be

$$\begin{aligned} & 1.26 \times 10^{-11} \times 58 \text{ g/kg.} \\ & = 7.3 \times 10^{-10} \text{ g/kg.} \\ & = 73.0 \text{ parts per trillion (ppt)} \end{aligned}$$

Exhibit 1. ANS 16.1 Incremental Leach Data Total Irradiation 1.1E08R Initial Contaminant Levels 1000 PPM

Hours	Sample 1		Sample 2		Sample 3	
	As Irr.	As Non-irr.	As Irr.	As Non-irr.	As Irr.	As Non-irr.
	PPM	PPM	PPM	PPM	PPM	PPM
2	BDL		BDL		BDL	
7	BDL		BDL		BDL	
24	BDL	BDL	BDL	BDL	BDL	BDL
48	BDL	BDL	BDL	BDL	BDL	BDL
72	BDL	BDL	BDL	BDL	BDL	BDL
120	BDL	BDL	BDL	BDL	BDL	BDL
168	BDL	BDL	BDL	BDL	BDL	BDL

BDL—Below Detection Level

Exhibit 2. ANS 16.1 Incremental Leach Data Total Irradiation 1.1E08R Initial Contaminant Levels 1000 PPM

Hours	Sample 1		Sample 2		Sample 3		Average	
	Cd Irr.	Cd Non-irr.	Cd Irr.	Cd Non-irr.	Cd Irr.	Cd Non-irr.	Cd Irr.	Cd Non-irr.
	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
2	0.37		0.35		0.19		0.303	
7	0.6		0.41		0.24		0.417	
24	0.46	2.2	0.64	3.24	0.44	2.1	0.513	2.513
48	0.35	0.46	0.5	0.69	0.3	0.37	0.383	0.507
72	0.41	0.25	0.24	0.37	0.27	0.27	0.307	0.297
120	0.28	0.42	0.49	0.65	0.31	0.51	0.360	0.527
168	0.2	0.31	0.35	0.3	0.2	0.24	0.250	0.283

THE IMPACT OF HIGH LEVEL GAMMA RADIATION ON IMMOBILIZED WASTE FORMS IN POLYMERIC MATRICES

Exhibit 3. ANS 16.1 Incremental Leach Data Total Irradiation 1.1E08R Initial Contaminant Levels 1000 PPM

Hours	Sample 1		Sample 2		Sample 3		Average	
	Co Irr.	Co Non-irr.	Co Irr.	Co Non-irr.	Co Irr.	Co Non-irr.	Co Irr.	Co Non-irr.
	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
2	0.68		0.63		0.36		0.557	
7	1.3		1		0.64		0.980	
24	1.28	5.06	1.52	7.9	1	4.5	1.267	5.820
48	0.85	0.98	1.31	1.2	0.72	0.82	0.960	1.000
72	0.65	0.4	1	0.59	0.62	0.52	0.757	0.503
120	0.73	0.8	1.2	1.12	0.87	0.92	0.933	0.947
168	0.58	0.46	0.88	0.48	1.34	0.32	0.933	0.420

Exhibit 4. ANS 16.1 Incremental Leach Data Total Irradiation 1.1E08R Initial Contaminant Levels 1000 PPM

Hours	Sample 1		Sample 2		Sample 3	
	Cr Irr.	Cr Non-irr.	Cr Irr.	Cr Non-irr.	Cr Irr.	Cr Non-irr.
	PPM	PPM	PPM	PPM	PPM	PPM
2	BDL		BDL		BDL	
7	BDL		BDL		BDL	
24	BDL	BDL	BDL	BDL	BDL	BDL
48	BDL	BDL	BDL	BDL	BDL	BDL
72	BDL	BDL	BDL	BDL	BDL	BDL
120	BDL	BDL	BDL	BDL	BDL	BDL
168	BDL	BDL	BDL	BDL	BDL	BDL

BDL—Below Detection Level

Exhibit 5. ANS 16.1 Incremental Leach Data Total Irradiation 1.1E08R Initial Contaminant Levels 1000 PPM

Hours	Sample 1		Sample 2		Sample 3		Average	
	Cu Irr.	Cu Non-irr.	Cu Irr.	Cu Non-irr.	Cu Irr.	Cu Non-irr.	Cu Irr.	Cu Non-irr.
	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
2	0.11		0.04		0.03		0.060	
7	0.07		0.02		0.02		0.037	
24	0.06	0.08	0.04	0.13	0.001	0.1	0.034	0.103
48	0.12	0.08	0.07	0.09	0.07	0.11	0.087	0.093
72	0.07	0.07	0.09	0.09	0.07	0.07	0.077	0.077
120	0.07	0.14	0.11	0.15	0.08	0.14	0.087	0.143
168	0.08	0.08	0.1	0.07	0.06	0.08	0.080	0.077

Exhibit 6. ANS 16.1 Incremental Leach Data Total Irradiation 1.1E08R Initial Contaminant Levels 1000 PPM

Hours	Sample 1		Sample 2		Sample 3		Average	
	Ni Irr.	Ni Non-irr.	Ni Irr.	Ni Non-irr.	Ni Irr.	Ni Non-irr.	Ni Irr.	Ni Non-irr.
	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
2	1.06		1.07		0.6		0.910	
7	2.21		1.43		0.81		1.483	
24	1.9	5.96	2.66	12.2	1.62	6.2	2.060	8.120
48	1.2	1.3	1.93	1.7	1.2	1.1	1.443	1.367
72	0.87	0.6	1.52	0.93	0.93	0.75	1.107	0.760
120	0.96	1.1	1.77	1.8	1.21	1.34	1.313	1.413
168	0.74	0.8	1.32	0.87	1	0.61	1.020	0.760

THE IMPACT OF HIGH LEVEL GAMMA RADIATION ON IMMOBILIZED WASTE FORMS IN POLYMERIC MATRICES

Exhibit 7. ANS 16.1 Incremental Leach Data Total Irradiation 1.1E08R Initial Contaminant Levels 1000 PPM

Hours	Sample 1		Sample 2		Sample 3	
	Pb Irr.	Pb Non-irr.	Pb Irr.	Pb Non-irr.	Pb Irr.	Pb Non-irr.
	PPM	PPM	PPM	PPM	PPM	PPM
2	BDL		BDL		BDL	
7	BDL		BDL		BDL	
24	BDL	BDL	BDL	BDL	BDL	BDL
48	BDL	BDL	BDL	BDL	BDL	BDL
72	BDL	BDL	BDL	BDL	BDL	BDL
120	BDL	BDL	BDL	BDL	BDL	BDL
168	BDL	BDL	BDL	BDL	BDL	BDL

BDL—Below Detection Level

Exhibit 8. ANS 16.1 Incremental Leach Data Total Irradiation 1.1E08R Initial Contaminant Levels 1000 PPM

Hours	Sample 1		Sample 2		Sample 3		Average	
	Zn Irr.	Zn Non-irr.	Zn Irr.	Zn Non-irr.	Zn Irr.	Zn Non-irr.	Zn Irr.	Zn Non-irr.
	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
2	0.13		0.16		0.15		0.147	
7	0.19		0.12		0.08		0.130	
24	0.16	0.35	0.19	0.62	0.13	0.31	0.160	0.427
48	0.22	0.17	0.22	0.2	0.12	0.16	0.187	0.177
72	0.11	0.12	0.19	0.15	0.09	0.13	0.130	0.133
120	0.17	0.2	0.27	0.32	0.14	0.26	0.193	0.260
168	0.15	0.14	0.15	0.1	0.1	0.1	0.133	0.113

Exhibit 9. ANS 16.1 Leach Data—Sample 1

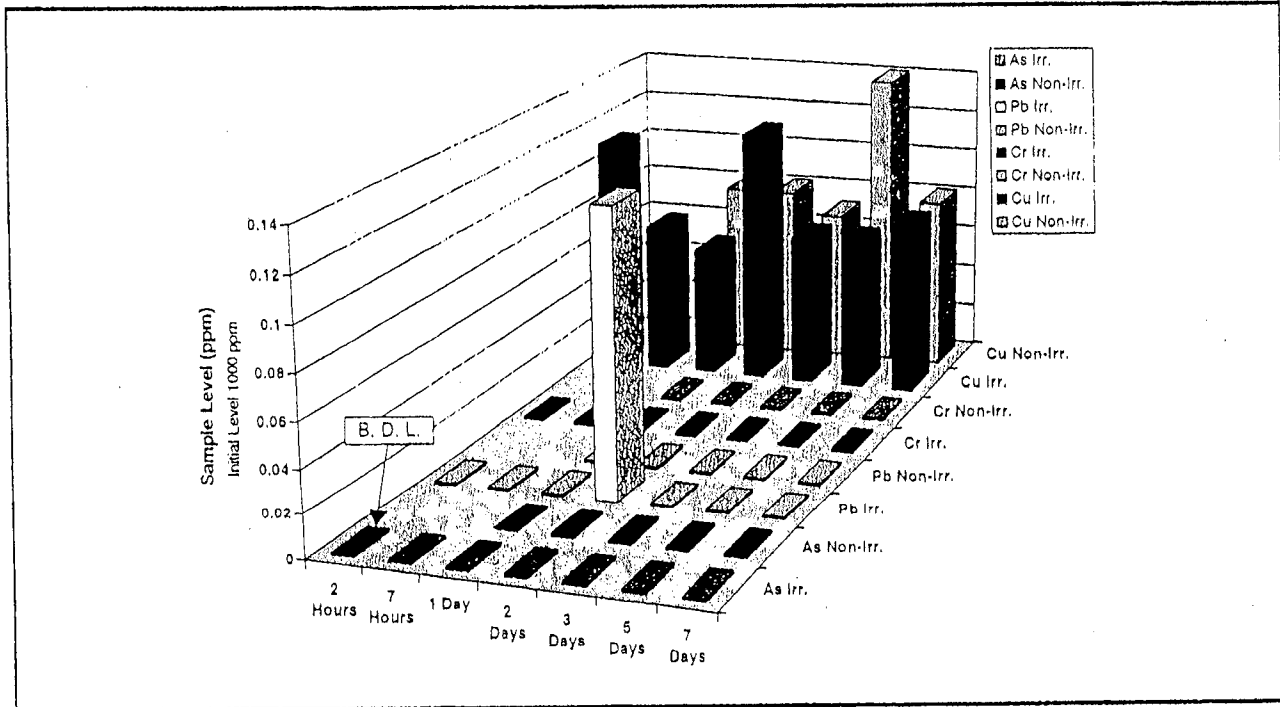


Exhibit 10. ANS 16.1 Leach Data—Sample 1

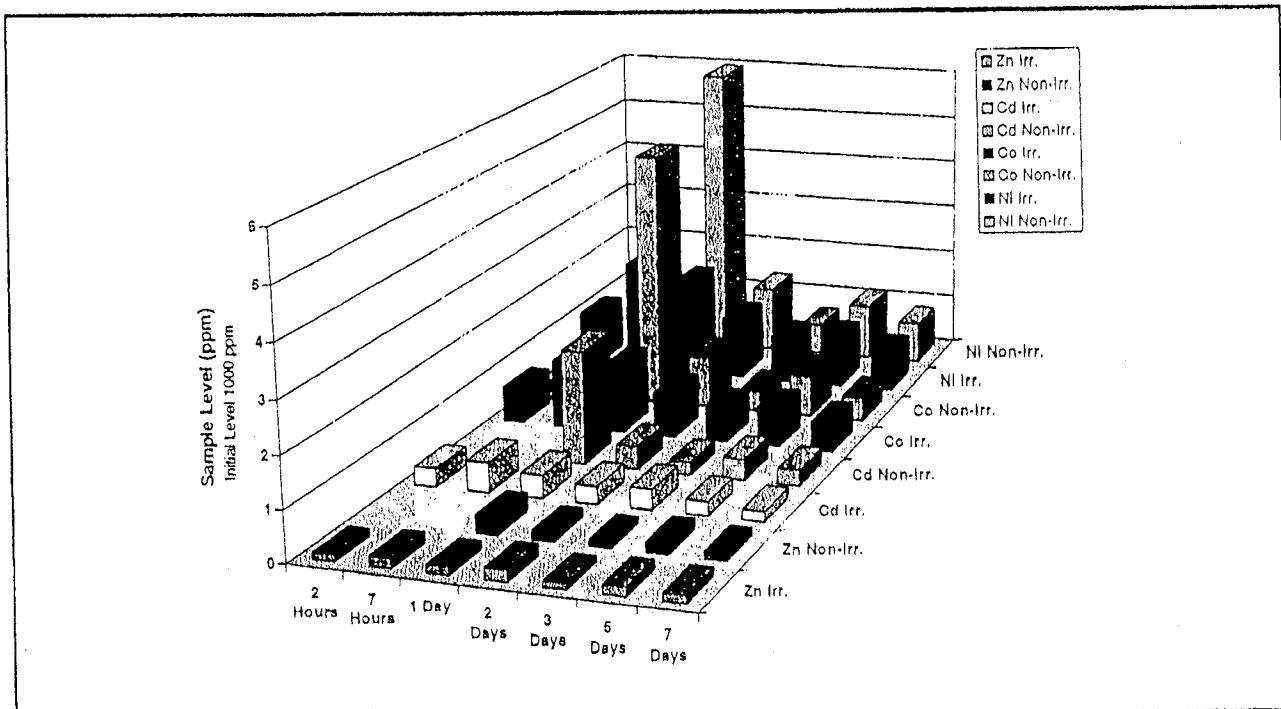


Exhibit 11. ANS 16.1 Leach Data—Sample 2

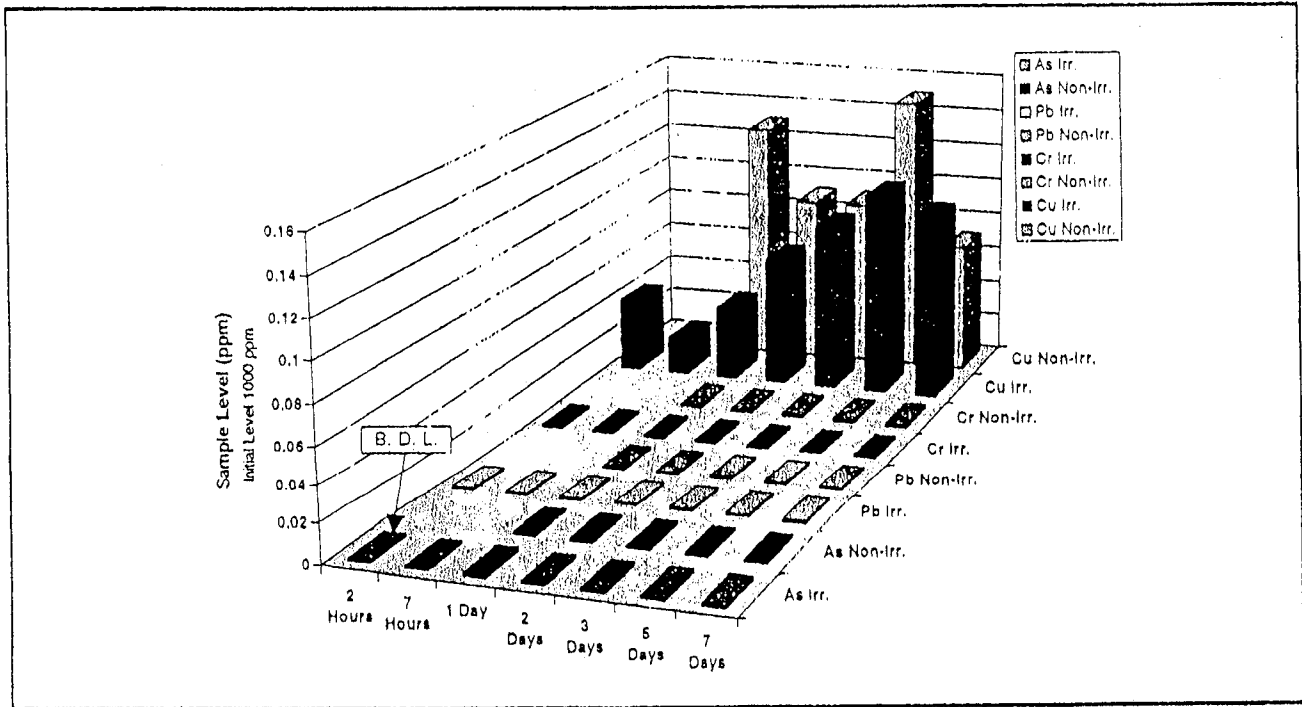


Exhibit 12. ANS 16.1 Leach Data—Sample 2

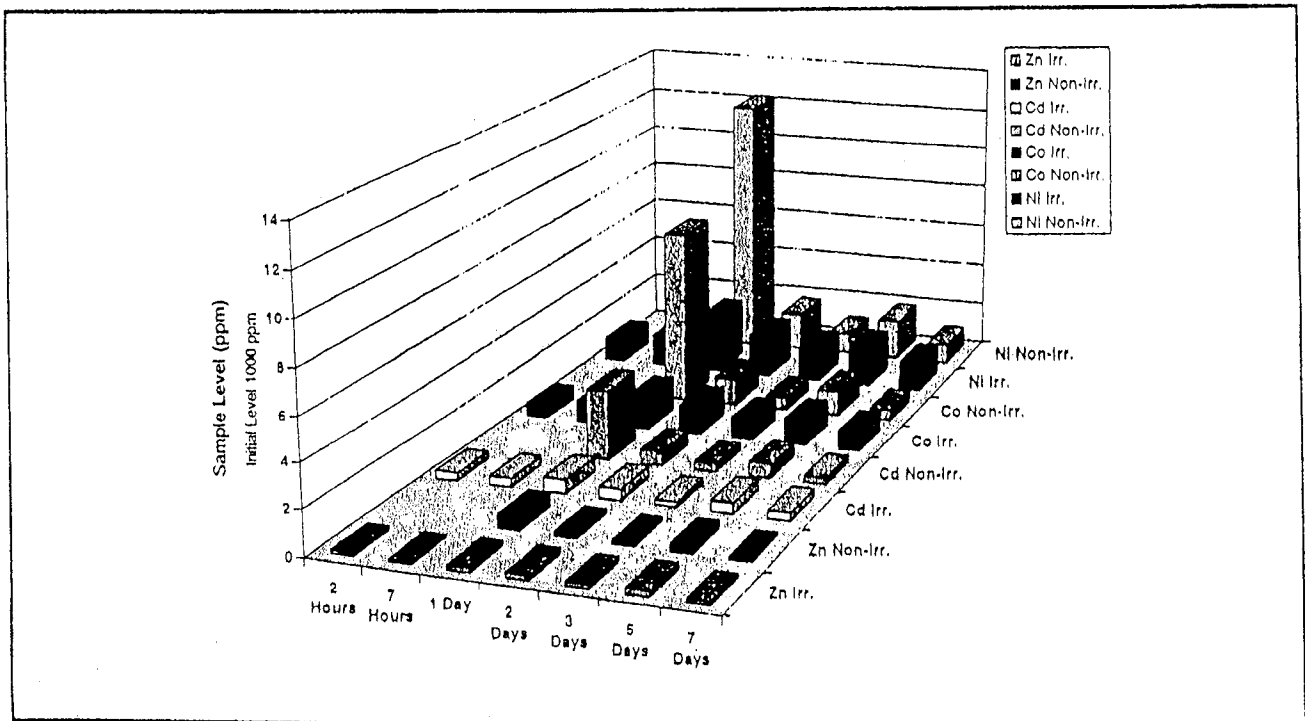


Exhibit 13. ANS 16.1 Leach Data—Sample 3

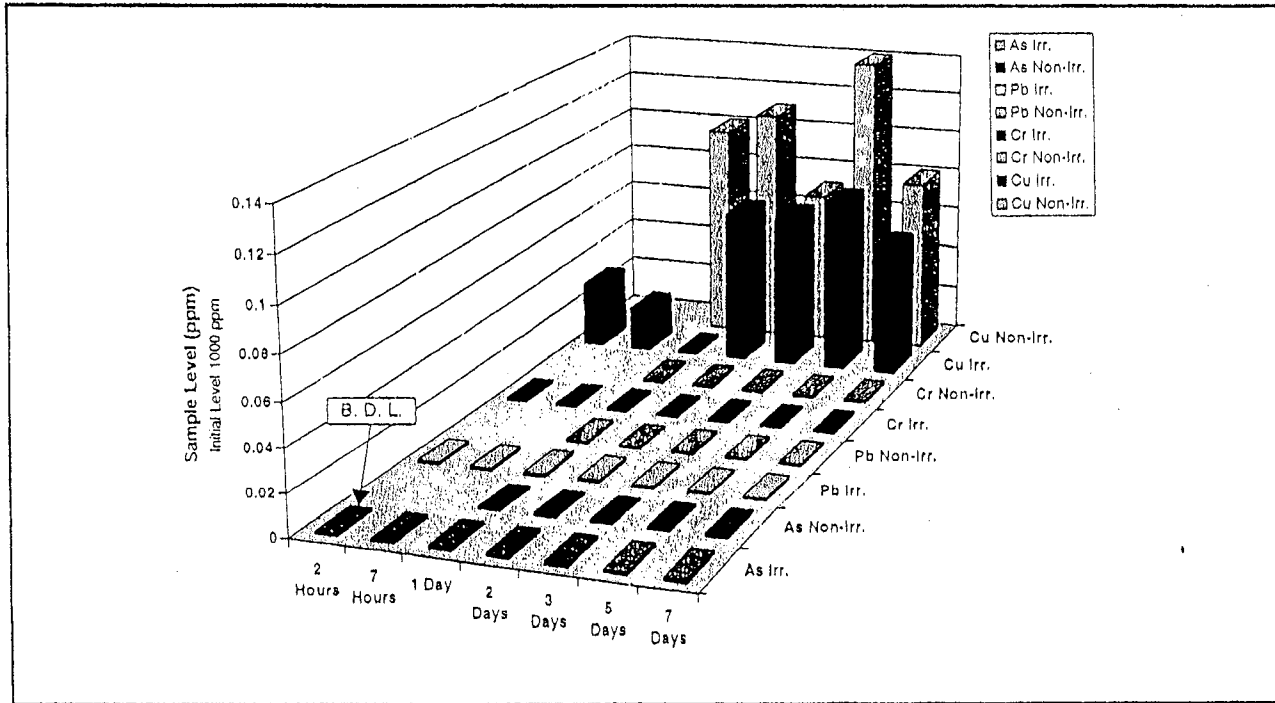


Exhibit 14. ANS 16.1 Leach Data—Sample 3

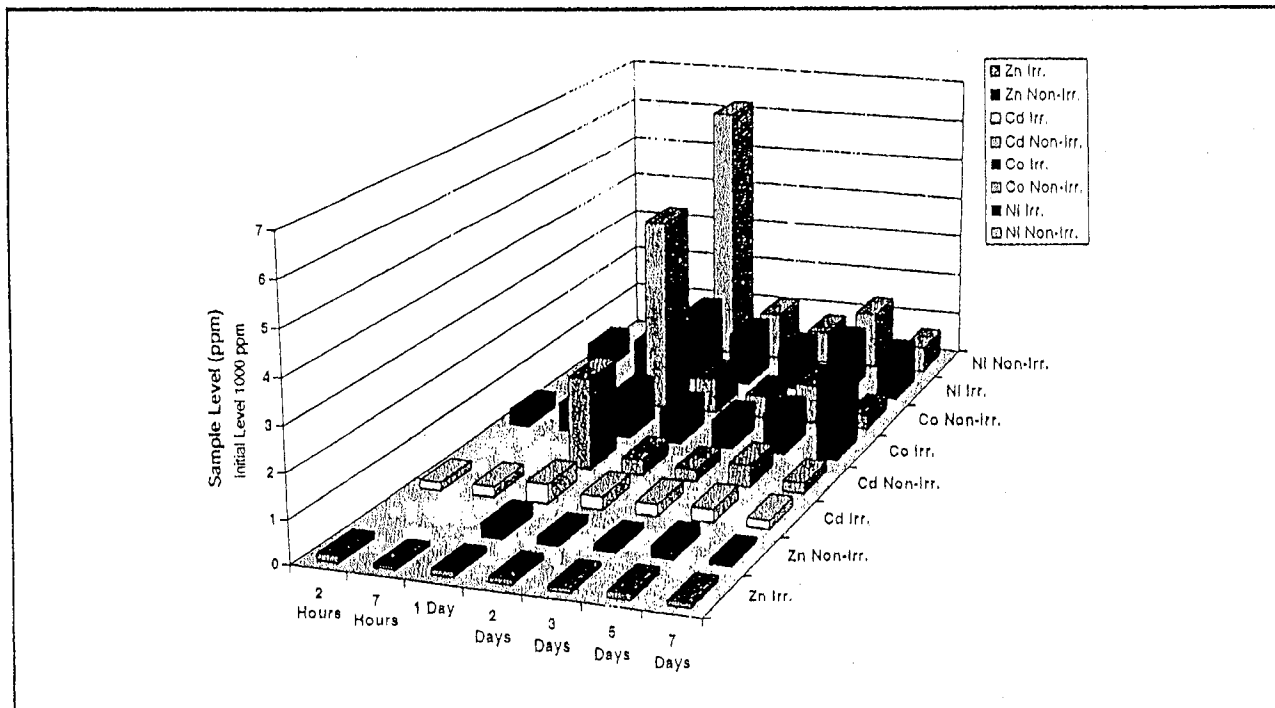


Exhibit 15. ANS 16.1 Average Leach Data 1.1×10^8 R Exposure

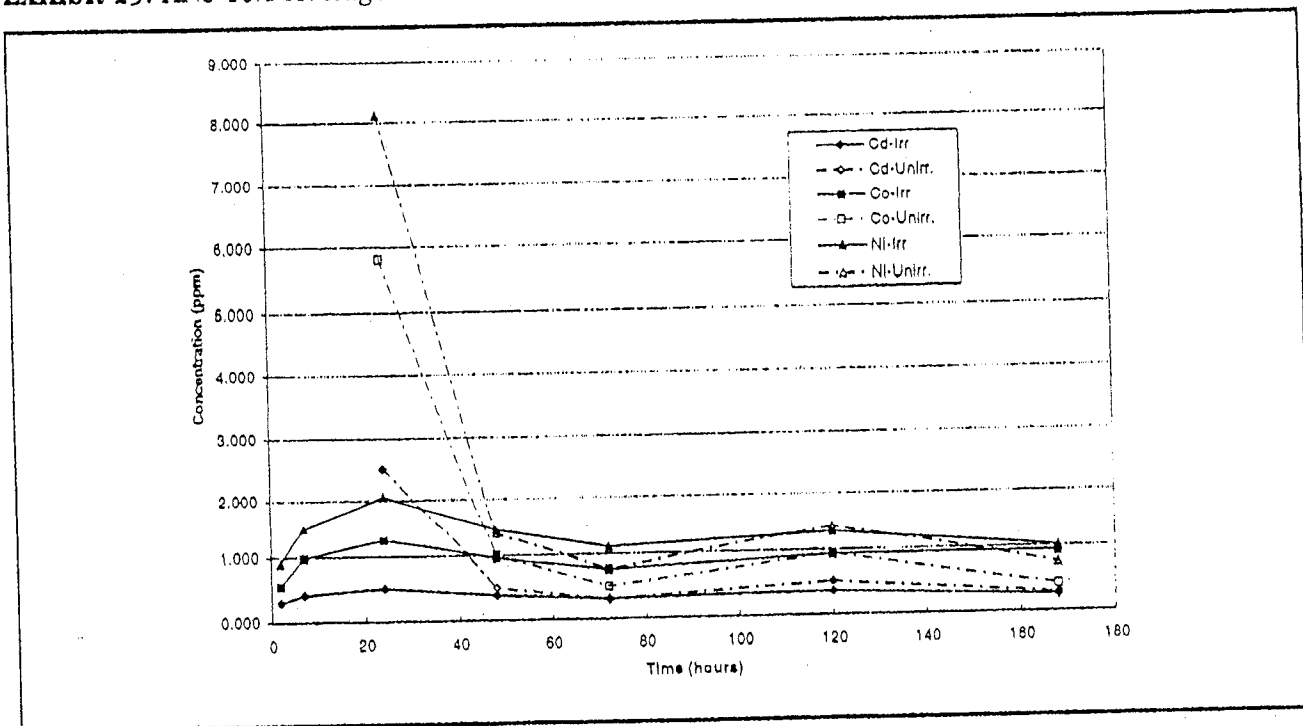


Exhibit 16. ANS 16.1 Average Leach Data 1.1×10^8 R Exposure

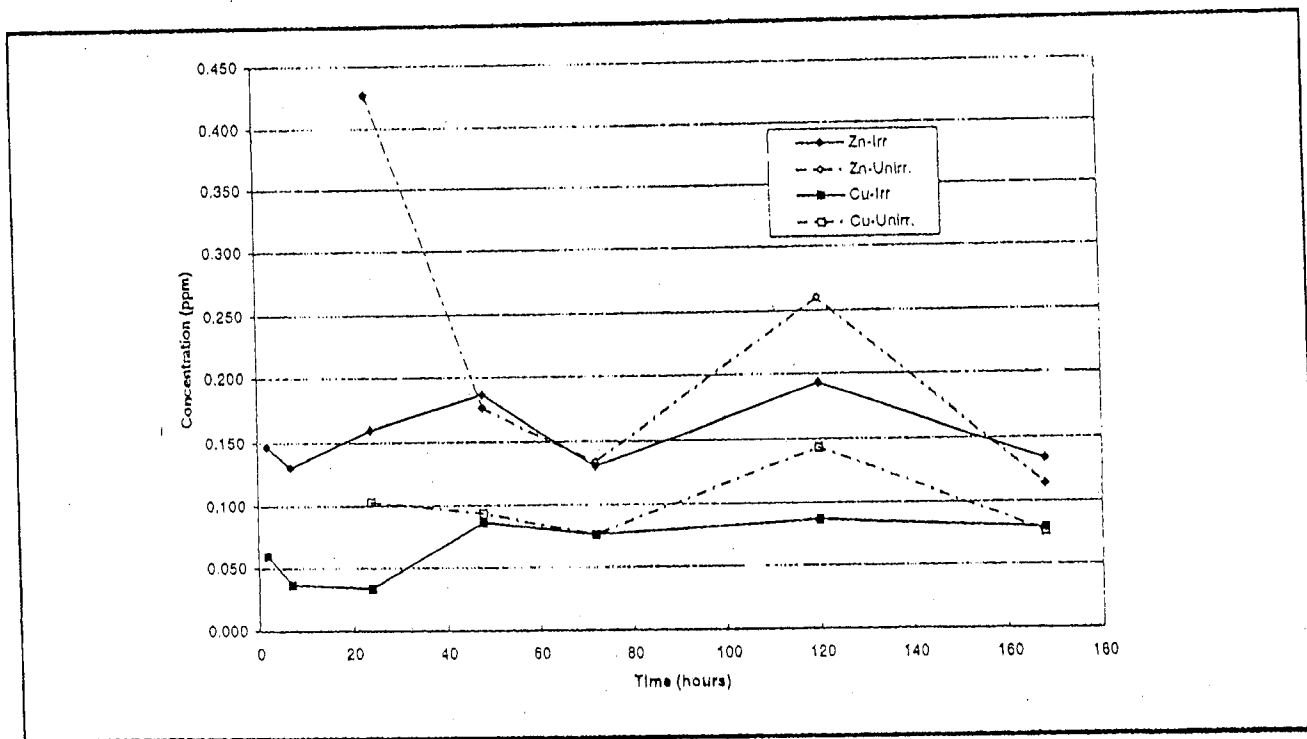


Exhibit 17. ANS 16.1 Leach Data—Cadmium 1.1×10^8 R Exposure

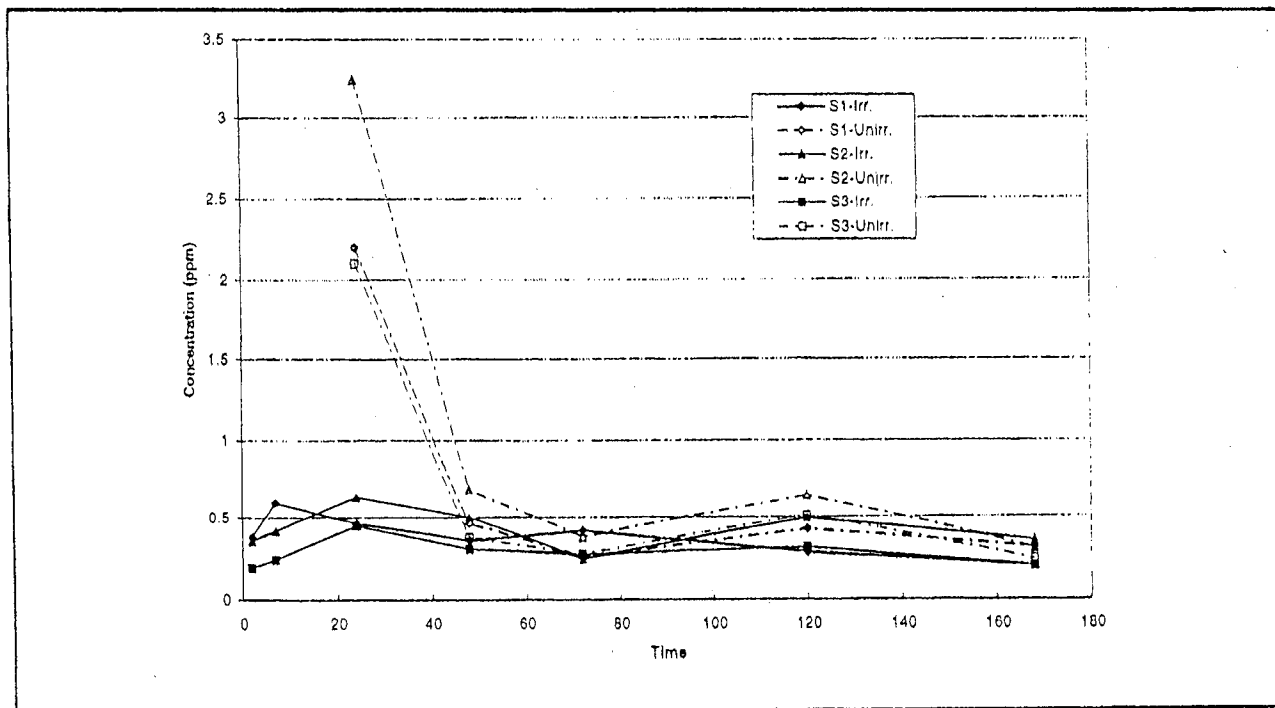


Exhibit 18. ANS 16.1 Leach Data—Cobalt 1.1×10^8 R Exposure

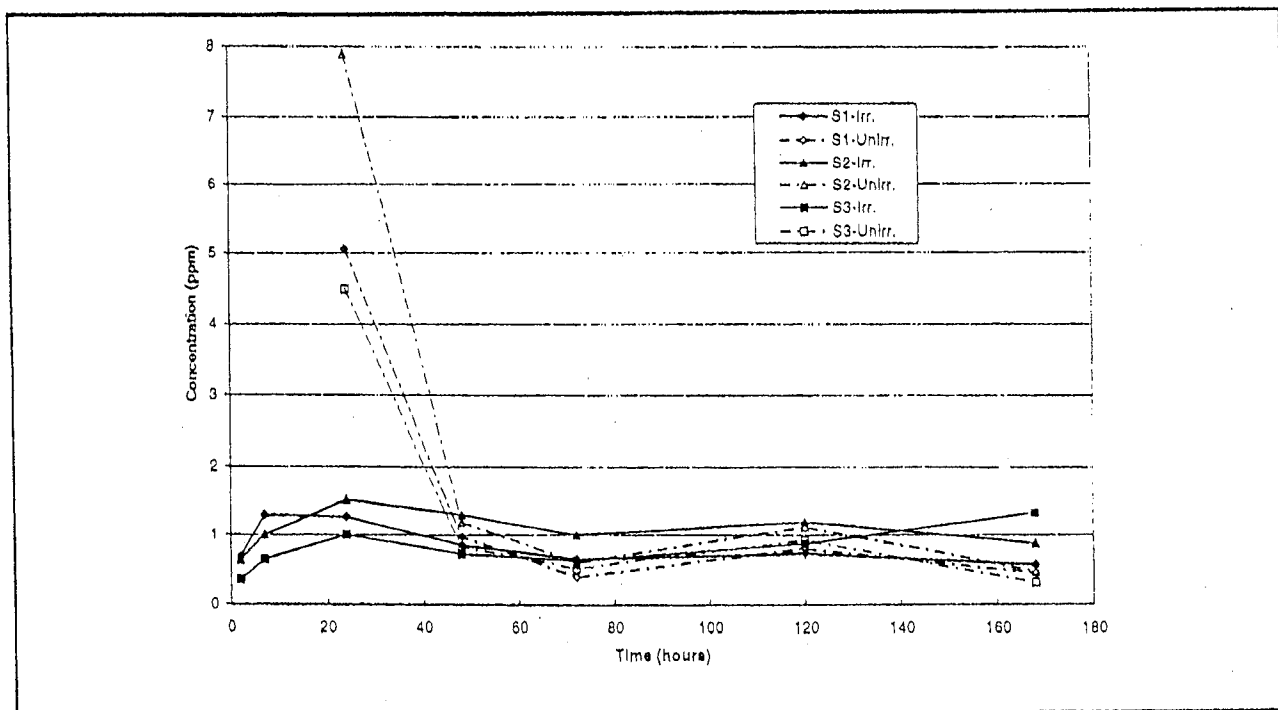


Exhibit 19. ANS 16.1 Leach Data—Copper 1.1×10^8 R Exposure

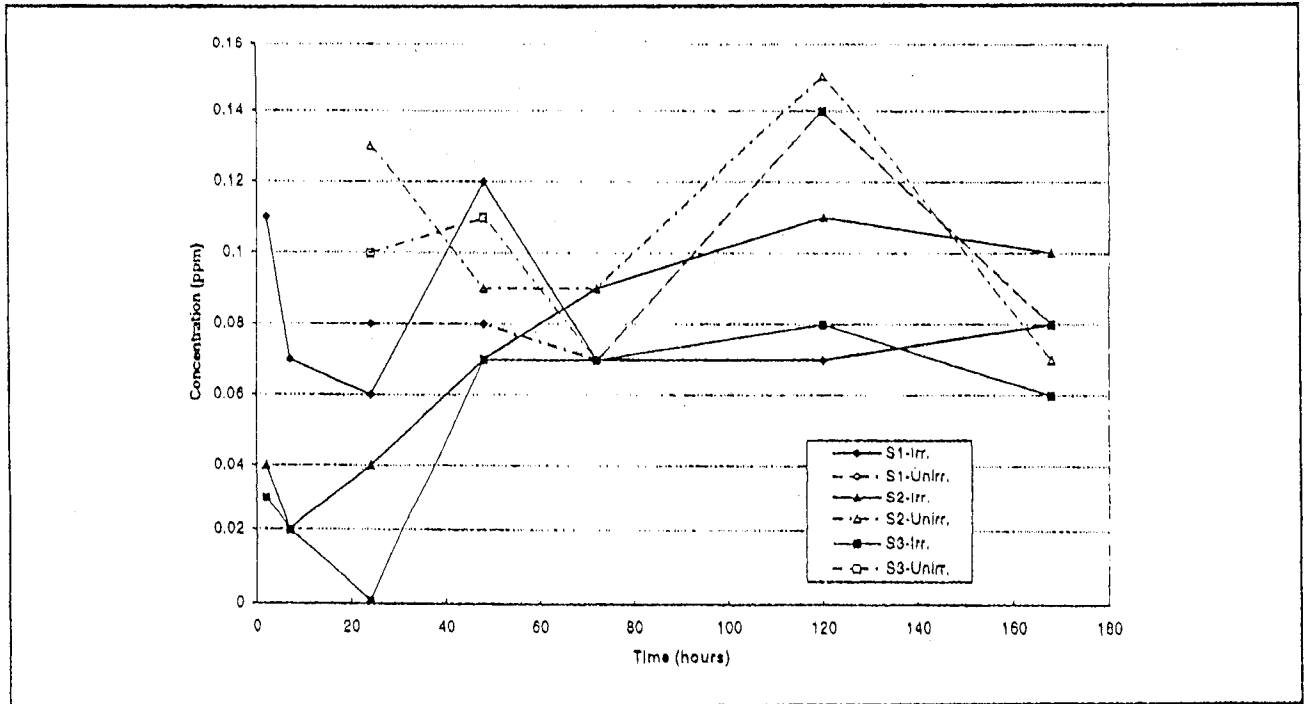


Exhibit 20. ANS 16.1 Leach Data—Nickel 1.1×10^8 R Exposure

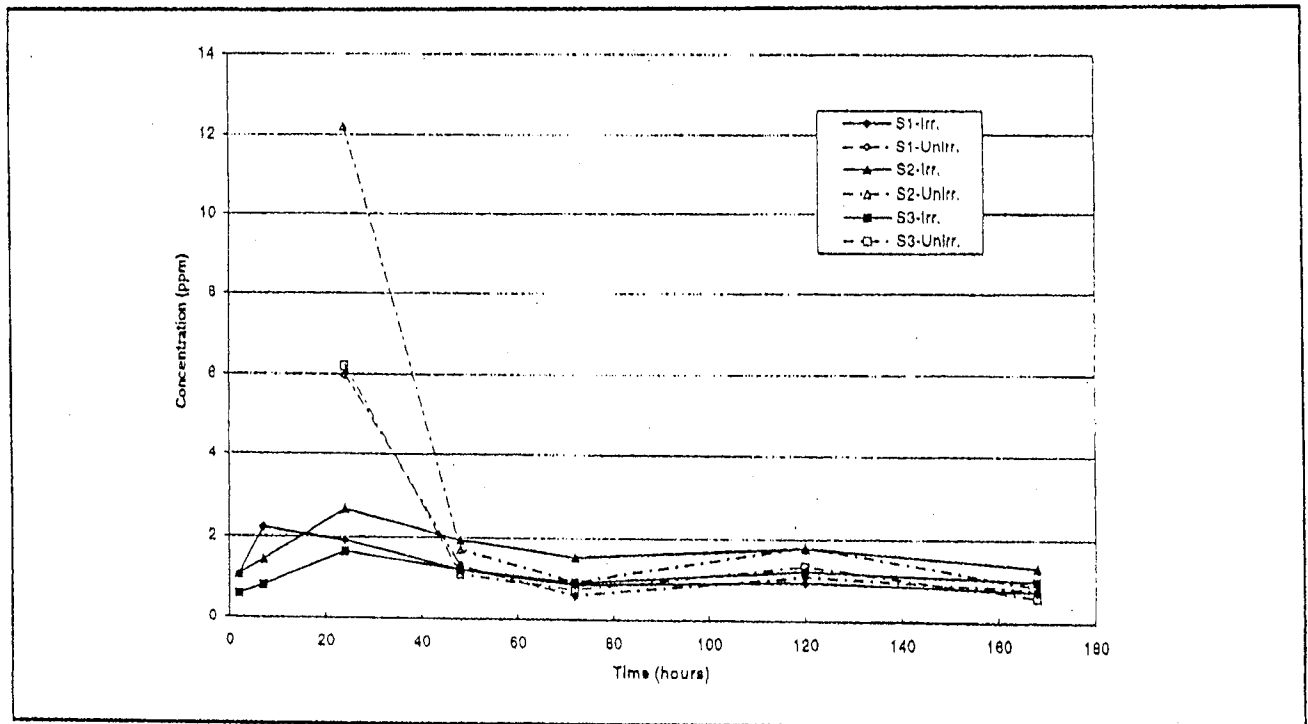


Exhibit 21. ANS 16.1 Leach Data—Zinc 1.1×10^8 R Exposure

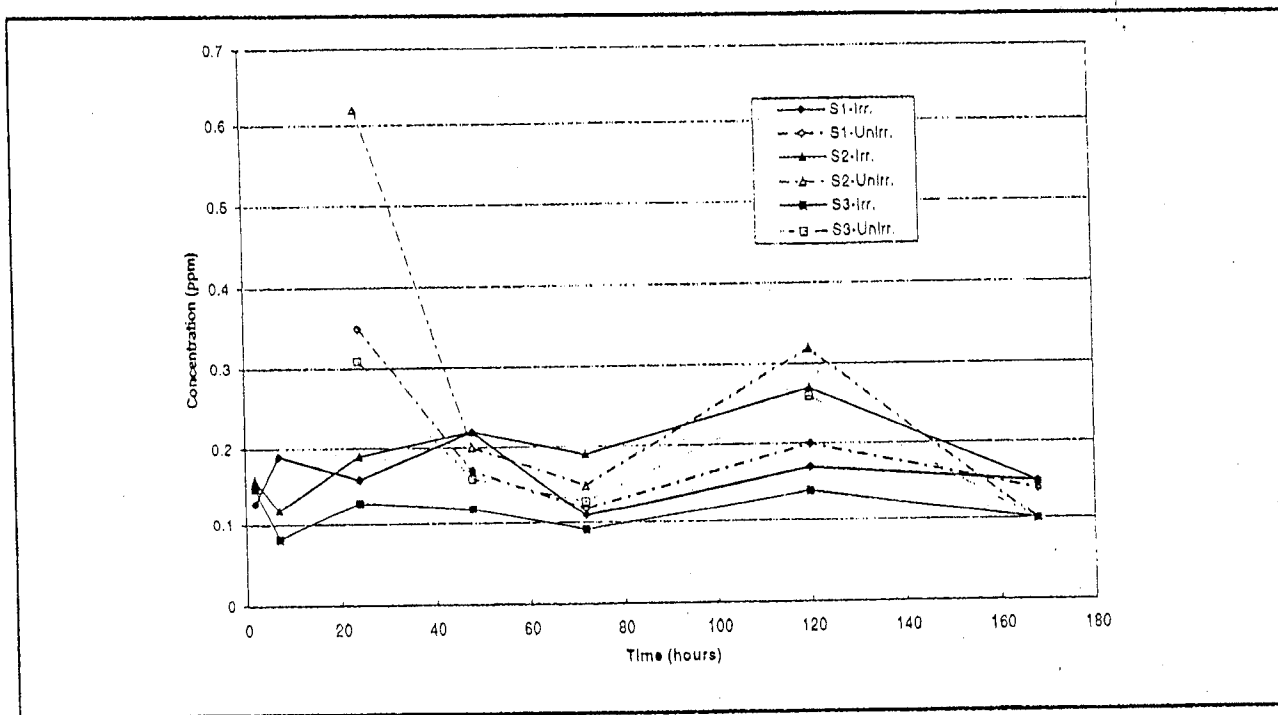


Exhibit 22. Infrared Spectra of Nonirradiated and Irradiated Monoliths (10 million roentgens)

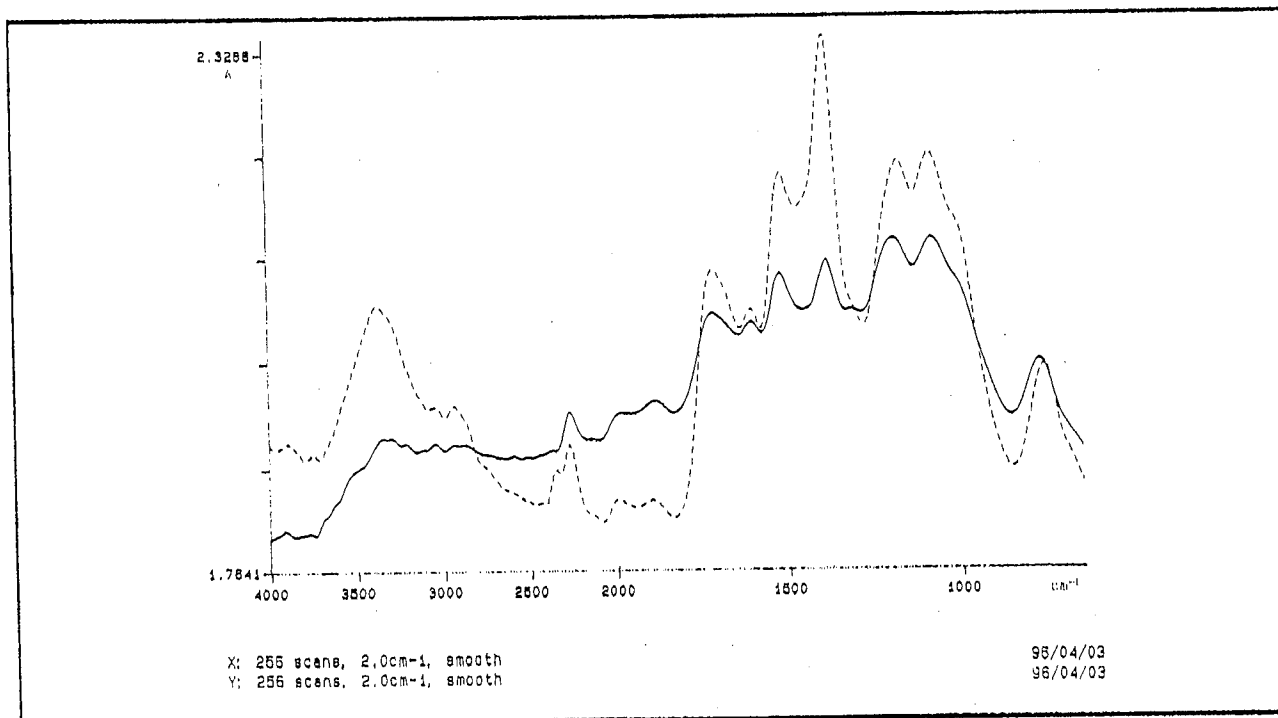
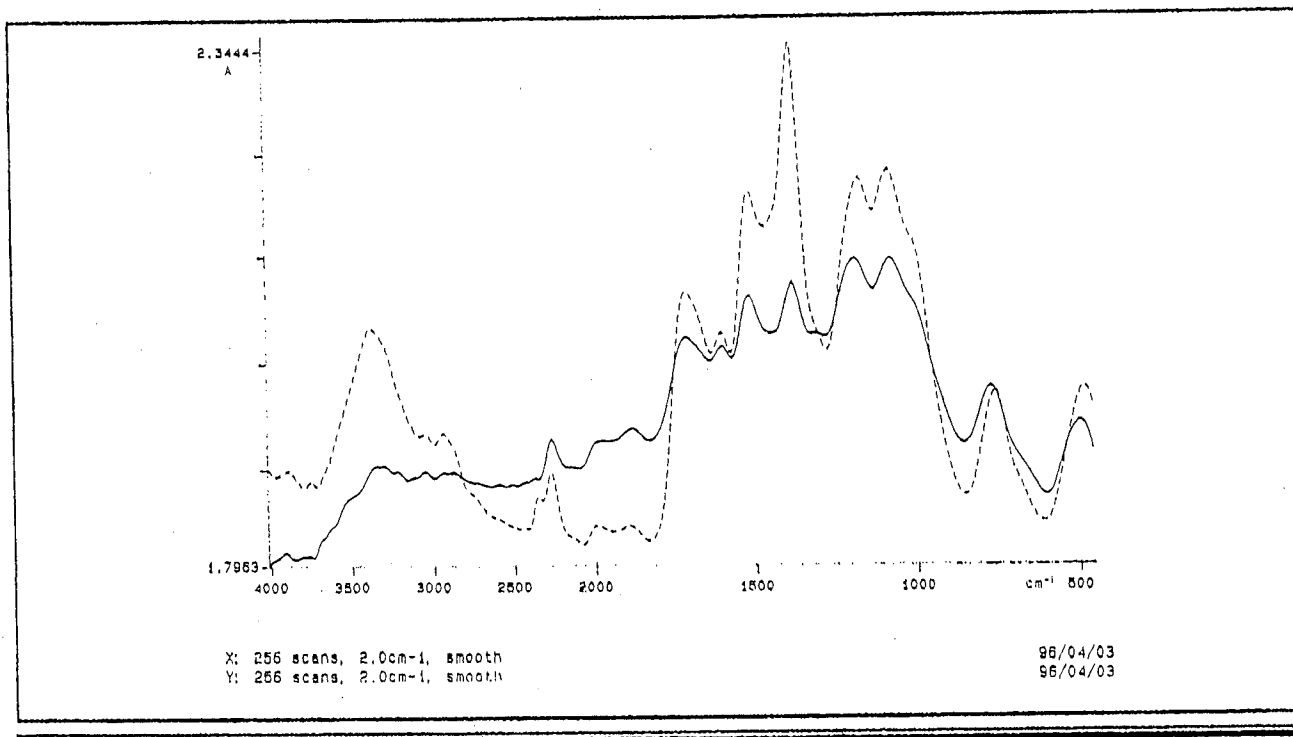


Exhibit 23. Infrared Spectra of Nonirradiated and Irradiated Monoliths (110 million roentgens)

To bring about this effect, trisodium phosphate solution was added (stoichiometrically) to the spiked sand. The actual ANS 16.1 data for Co reaffirms and validates the concepts discussed above.

The post-irradiation leach data reveal that even after heavy doses (1.1×10^8 roentgens), the composite matrix did not undergo any significant deterioration. In some cases (e.g. Cu^{2+}) the leach numbers for irradiated samples actually showed an improvement. This could be due to rearrangements in the matrix after irradiation leading to tighter bonding between the ions and the binder.

The infrared data for the nonirradiated and irradiated monoliths (Exhibits 22 and 23) indicate that the gamma radiation has not brought about any significant chemical/structural damage to the monolithic matrix. Also, the presence of transition elements did not seem to have caused any catalytic degradation of the matrix during the irradiation.

The UCS data (**Exhibit 24**) suggest that the gamma irradiation has not damaged the mechanical properties of the matrix. The values (~ 5000 psi) obtained during our investigations are much higher than the regulatory requirement of 50 psi.

The biodegradation studies constitute a vital part of this investigation. Should a given matrix be vulnerable to biodegradation, the resulting release of radio isotopes would bring about catastrophic consequences. The ASTM method G22-76 determined that *pseudomonas aeruginosa* (test organism), could not survive on the monolithic surfaces. All three samples

Exhibit 24. Unconfirmed Compressive Strength

Sample ID	Psi	Average Psi
Nonirradiated		
#1	4760	5110
#2	5340	
#3	5210	
Irradiated		
#1	4990	5066
#2	5180	
#3	5030	

Exhibit 25. Biodegradation Data
10 CFR 61 Compliance Data

Property	Result
Flammability combustion characteristics	After the addition of flame retardant (6% by weight) no sustained combustion at 900°C
Corrosivity	No corrosion in HCl atmosphere
Weathering	No observable changes
Thermal Cycling between -40°C and 60°C	No creep shrinkage
Biodegradation	No change
UCS after biodegradation	Does not allow the growth of bacteria or microorganism on surface

destroyed the microorganism within the test period of 21 days. This can be explained in terms of the phenolic-OH functional groups present in the matrix. These compounds are known to have disinfectant characteristics. The UCS tests after biodegradation evaluations revealed no significant change in their values.

The thermal cycling between -40°C and 60°C of nonirradiated and irradiated samples did not exhibit either creep or shrinkage. This would indicate a very small value for the coefficient of cubical expansion for the matrix.

The samples were also tested for corrosion in an acidic atmosphere and did not undergo any perceptible changes, indicating the passive nature of the matrix.

The samples were evaluated for fire resistance/flashpoint.

The samples were evaluated for fire resistance/flashpoint. In the absence of additives, the vapors of the matrix when subjected to flame were combustible. However, addition of commercially available flame retardants (~6.0% by weight) prevented the ignition/combustion of the matrix as well as the vapors.

The design of our matrix, the protocols, and the results obtained from the evaluation suggest that our composite matrix does not undergo chemical/structural damage even after exposure to gamma radiations at the level of 1.1×10^8 roentgens. It can also be said that by employing fundamental concepts of chemical equilibria one can chemically immobilize elements (radioactive/non-radioactive) successfully. Our binder has also been found to be nonbiodegradable. The other physicochemical properties (combustibility, corrosivity, UCS, etc.) conform to the regulatory (10 CFR 61) requirements for immobilization technologies.

These unusual, but desirable, qualities of this binder present us with some interesting possibilities, such as innovative waste management technologies designed for resource recovery. High level wastes such as tank farm wastes can be immobilized chemically and stored inside the composite on a short-term as well as a long-term basis. Further, when suitable applications for the stored isotopes are developed in the future, the matrix can be dissolved in an organic solvent and the desired isotope can be isolated. It has also been observed that this composite bonds well to metallic and nonmetallic surfaces. Contaminated areas (metallic and building surfaces in reactors) can be contained by spraying the affected areas with this composite. In such cases, where free leachable metal ions are not present, there is no need for chemical fixation prior to the application of composite on the surface. Yet another application would be in the sealing of highly radioactive sarcophagi of decommissioned reactors at various sites.

CONCLUSIONS

We have developed a composite binder for the containment and immobilization of radio nuclides. This composite exhibits high resistance toward (1) radiation damage, (2) corrosion, (3) combustion, (4) biodegradation, and (5) weathering. It appears that this could be a potential solution for sealing off decommissioned reactors and also to immobilize radio isotopes in soil, tank wastes and other waste forms. The uniqueness of this technology lies in the fact that these isotopes can be retrieved when desired by the use of organic solvents if and when new applications for the isotopes are developed.

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