

LOW-LEVEL RADIOACTIVE WASTE VITRIFICATION: EFFECT OF Cs PARTITIONING

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ABSTRACT

The traditional Low-level Radioactive Waste (LLW) immobilization options are cementation or bituminization. Either of these options could be followed by shallow land burial (SLB) or above ground disposal. These rather simple LLW procedures appeared to be readily available, to meet regulatory requirements, and to satisfy cost constraints. The authorization of State Compacts, the forced closure of half of the six SLB disposal facilities of the nation, and the escalation of transportation/disposal fees diminish the viability of these options. The synergetic combination of these factors led to a reassessment of traditional methods and to an investigation of other techniques. This paper analyzes the traditional LLW immobilization options, reviews the impact of the LLW stream composition on Low-Level Waste Vitrification (LLWV), then proposes and briefly discusses several techniques to control the volatile radionuclides in a Process Improved LLWV system (PILLWV).

LLW IMMOBILIZATION OPTIONS ANALYSIS

The traditional LLW immobilization techniques have been reported to present serious technical and economic disadvantages.<sup>1</sup> Cementation<sup>2</sup> and bituminization<sup>3</sup> have well documented cesium leachability problems. Cesium leaching in cement is so significant that special treatment schemes are used in defense waste treatment.<sup>4</sup> Reference 3 explicitly states that bituminization is ill-advised for immobilization of cesium. Cementation suffers from two separate disadvantages in that it increases the waste volume and has a low waste loading.<sup>2</sup> Vitrification, on the other hand, produces smaller waste volumes<sup>1</sup> which is more appealing for SLB and/or above ground disposal, and it has better leaching resistance.<sup>2</sup> Finally, disposal fees at the three operating SLB sites have escalated by up to 300% since 1983.<sup>5,6</sup> These technical and economic problems establish the requirement for an alternative to the traditional LLW immobilization options.

Reference 1 describes in detail a proposed LLWV process which is summarized in Fig. 1. Additionally, Ref. 1 establishes the technical superiority of the LLWV waste form, and shows that the process is cost competitive with traditional LLW immobilization options. This paper proposes and evaluates improvements to this process.

LLW STREAM COMPOSITION IMPACT ON LLWV

The major problem-causing radionuclide for the LLWV process is cesium. It poses significant health hazards<sup>7</sup> and is a predominant radionuclide in LLW streams.<sup>8,9</sup> An analysis (Table I) of the Safety Assessment contained in Ref. 1 shows that cesium is the major contributor to the source term for LLWV Design Basis Accidents.

TABLE I

Source Term Analysis

Design Basis Accident	% Cs in Source Term
Glass Leakage	100
Thermal Shock Wave	100
Inoperative Scrubber	50
Venturi Leak	50
Full Container Drop	100
Cell Cover Dropped	50
Melter Pressurization	50
Plenum Leakage	50
Regeneration Solution Spill	50

Cesium, also is reported to be absorbed in the walls of the glass melter and in the components of the off-gas system at vitrification test facilities.<sup>10</sup> The absorption of cesium produces an unacceptable system mass balance.<sup>10</sup> Furthermore, the cesium can be randomly desorbed.<sup>10</sup> The absorption and random desorption of cesium would seriously hinder the licensing process of a commercial LLWV facility. Control of the cesium at LLWV installations appears to be warranted.

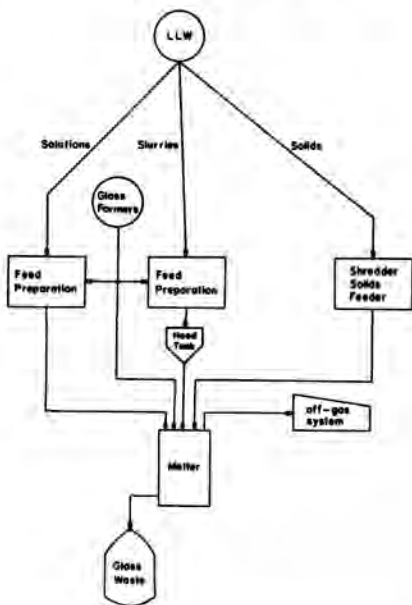


Fig. 1. Proposed LLWV Process1

## PROCESS IMPROVED LLWV

The PILLWV process controls the volatility of cesium by removing the radionuclide from the initial LLW stream, then fixing it within the partitioned waste stream. The partitioning and fixing are done prior to the feed preparation step of Fig. 1. Numerous processes that selectively separate or fix cesium are reported in the literature and are in various stages of development both in the U.S. and elsewhere. These processes include ion exchange,<sup>11,12</sup> chemical precipitation,<sup>13</sup> and electro dialysis.<sup>14</sup> Each process in turn will be briefly reviewed.

### ION EXCHANGE

Ion exchange is a well developed industrial application and is currently used in the management of High-Level Wastes (HLW) at Defense Waste Processing Facilities.<sup>4,11,12</sup> Adaptation of the ion exchange process to wastes other than HLW is novel in this country, but it has received moderate study in Sweden,<sup>15</sup> Japan,<sup>16</sup> and the USSR.<sup>17,18</sup> These processes were developed to reduce the volume of the waste prior to immobilization by traditional techniques (vitrification for HLW, and cementation or bituminization for non-HLW). In Fig. 2 the conceptual design of the ion exchange process improvement to LLWV is shown.

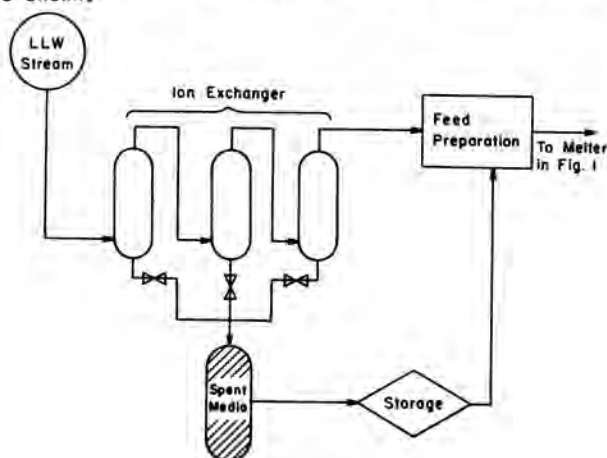


Fig. 2. LLW Ion Exchange System

A continuous ion exchange system is recommended due to its demonstrated efficiency and economy for nuclear<sup>18</sup> and non-nuclear<sup>19</sup> applications. The technical criteria used to determine the ion exchange media include high cesium selectivity, high radiation resistivity, and good thermal stability. The selection of the ion exchange medium should be tailored to a particular LLW stream, however several effective candidates are given in Table II.

TABLE II

### Ion Exchange Media Candidates

Medium	Waste Form	DF <sup>+</sup>
Duolite CS-100 <sup>++20,21</sup>	HLW	10000
Titanates <sup>16</sup>	HLW	10000
Duolite ARC-359 <sup>++4</sup>	HLW	10000
Γ-Zirconium Phosphate <sup>21,22</sup>	TMI Accident	10000

<sup>+</sup>Decontamination Factor

<sup>++</sup>Duolite CS-100 and Duolite ARC-359 are manufactured by Diamond Shamrock Corporation

All of the candidate media have high cesium selectivity and radiation resistivity. In addition, these ion exchange media retain cesium during heat treatment. The first three media of TABLE II have been vitrified at HLW facilities, while Γ-Zirconium Phosphate has successfully been sintered.<sup>20,15,22</sup> Preprocessing the LLWV stream with an ion exchange system provides a significant reduction of the amount of cesium in the melter feed. (See Table III.)

TABLE III

### Melter Feed Cesium Concentration

	Untreated Cs Concentration <sup>9</sup> (1000 MWe-yr)	Treated Cs Concentration
BWR LLW	8.640E-1 Ci/m <sup>3</sup>	8.64E-5 Ci/m <sup>3</sup>
PWR LLW	4.074E-1 Ci/m <sup>3</sup>	4.07E-5 Ci/m <sup>3</sup>

A continuous ion exchange pretreatment system using fully developed technology could be easily integrated into the LLWV process. An ion exchange PILLWV produces highly partitioned waste forms and effectively controls the volatility of cesium.

### CHEMICAL PRECIPITATION

A chemical precipitation system would be integrated in the LLWV process in the same way as shown in Fig. 2. This technique was successfully used to remove cesium from low-level waste salts prior to cementation and disposal at the Defense Waste Processing Facility (DWPF) at the Savannah River Plant (SRP).<sup>13</sup> However, for the waste streams at West Valley the required partitioning efficiency of the process was found to be lower than ion exchange. Sodium and Potassium tetraphenyl borate are both cited in the literature as having high cesium selectivity.<sup>11,13,24</sup> The thermal properties of the precipitates have not been reported, therefore these properties must be established prior to vitrification. Furthermore, individual waste stream characteristics can greatly impact the effectiveness of a chemical precipitation system.

### ELECTRODIALYSIS

Electrodialysis has received limited application within the nuclear industry in the U.S.,<sup>24</sup> the UK,<sup>25</sup> and the USSR.<sup>17</sup> The concept of a combined electro dialysis-ion exchange system is shown in Fig. 3.

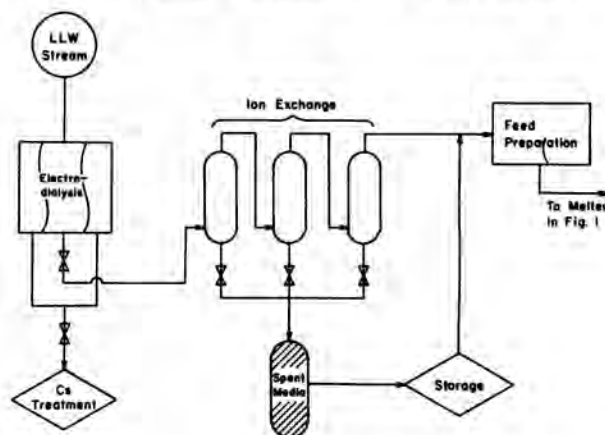


Fig. 3. Electrodialysis-Ion Exchange PILLWV

Electrodialysis has been shown to effectively, efficiently, and economically separate cesium,<sup>25</sup> but a follow-on immobilization process must be utilized to obtain a disposable waste form. This follow-on treatment decreases some of the volume reduction capability of the process, but significant overall system effectiveness is attainable. Cesium decontamination factors of 2000 for electrodialysis are reported.<sup>25</sup> Preliminary calculations indicate an increase of 2-3 orders of magnitude in DF's of an integrated electrodialysis-ion exchange system (EIE).<sup>26</sup>

Electrodialysis can initially decrease the cesium concentration of the LLW stream fed to ion exchange columns, which increases the life of the ion exchange media. The concentrated cesium waste from the electrodialysis must then be processed by an additional immobilization step. Possible steps include chemical precipitation, ion exchange, or solidification. Reference 17 briefly indicates preliminary success in a combined electrodialysis-ion exchange technique in preparation for cementation. The technique was reported to provide the desired cesium partitioning, however an immobilization technique for the partitioned waste stream was not reported.

#### PILLWV REGULATORY COMPLIANCE AND COST ESTIMATION

The glass of reported LLW process<sup>1</sup> meets all the regulatory requirements for stability stated in 10 CFR 61 and for transportation stated in 49 CFR 173. The PILLWV glass will also meet these regulatory requirements. Additionally, TABLE IV shows that the concentrated cesium LLW waste forms do not exceed Class C waste limits as defined in 10 CFR 61.

TABLE IV

Annual Vitrified Product 1100-MWe BWR\*1

Waste	Volume m <sup>3</sup>	Activity (Ci)	Drummed Products			
			Number	mrem/hr	Shipping Container <sup>†</sup>	Class
Resin	82	1,170	10.3	1.08	A	B
			31	10.8	B	B
			10.3	108	B	C
Conc. liquid	226	362	38	0.095	Unshielded	A
			114	0.95	Shielded	B
			38	9.5	B	B
Filter Sludge	152	1,364	34	2.08	A	B
			102	20.8	B	B
			34	208	B	C

\*Waste Classification in accordance with Federal Regulation 10 CFR 61 not included in Ref. 1.

†Shipping Container Type in accordance with Federal Regulation 49 CFR 173. The dose limits of Ref. 1 are correctly shown as mrem/hr instead of rem/hr.

Reference 1 gives an installation and operation cost comparison for LLW volume reduction techniques. Vitrification is shown to be the cheapest volume reduction technique.<sup>1</sup> Firm cost figures for installation and operation of nuclear grade ion exchange systems are not available in the open literature, but an estimated installation and operation cost is \$200,000.

This cost was calculated in the following manner. The 1970 installation and operation costs of a continuous zeolite ion exchanger (to selectively remove cesium) are \$95,000 and \$11,100 respectively.<sup>19</sup> These costs were summed and an annual equivalent installation and operation cost (AEC) was calculated with the standard interest formula<sup>27</sup>

$$AEC = P * (A/P)^i_n$$

The AEC is \$21,000, assuming a 15% interest rate. A 1984 AEC (\$74,000) was then calculated using the producer price index of Ref. 28. The 1984 AEC was increased by an arbitrary factor of 2.5 because past experience indicates that nuclear costs are routinely underestimated, and the source used to derive this figure is dated. Reference 29 provided a current 1986 installation cost estimate of \$71,000. It is assumed that the 1986 installation cost reflects considerable technological and economic improvement in the process, therefore an ion exchange LLWV system would be even more attractive. Table V summarizes the cost of volume reduction techniques and shows that the Ion Exchange PILLWV is cost competitive.

TABLE V

Volume Reduction Cost Comparison<sup>1†</sup>  
(\$1,000,000)

Vitrification	2.4
Vitrification with Ion Exchange*	2.6
Incineration/ Calcination	3.0
Evaporation	4.1
Incineration	4.7
Bituminization	5.5

\*Costs are for a 1100-MWe BWR, 1250 miles transportation, Barnwell, S.C.

†Vitrification with Ion Exchange not included in Ref. 1. Incineration/calcination, evaporation, and incineration all use cementation as the immobilization technique.

#### CONCLUSION

Currently used or proposed LLW immobilization options have been reviewed. An improved LLW process is proposed and compared to other techniques. This process, which relies on partitioning, virtually eliminates the loss of cesium from a LLW process. It is shown to yield a superior waste form that meets or exceeds all applicable regulatory requirements for transportation and disposal as Low-Level Waste. It is further shown that the proposed improved process is economically superior to cementation, and other LLW immobilization techniques. The improved waste product and the effective control of cesium are expected to greatly enhance the licensing procedure of a prospective LLW facility. Further investigation of cesium immobilization options appears warranted.

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## REFERENCES

1. D. E. Larson et al., Assessment of Power Reactor Waste Immobilization by Vitrification, EPRI-3225, Electric Power Research Institute, (1983).
2. J. M. Rusin et al., "Alternate Waste Forms--A Comparative Study," Scientific Basis for Nuclear Waste Management, 2, p. 255, (1980).
3. J. Arod, "Bituminization of Radioactive Wastes: Safety Studies," Nuclear and Chemical Waste Management, 3, p. 179, (1982).
4. J. R. Wiley, "Decontamination of Alkaline Radioactive Wastes by Ion Exchange," Ind. Eng. Chem. Process Des. Dev., 17, No. 1, p. 67, (1978).
5. D. Ebenhack, Chem-Nuc Systems Inc. personal communication, Columbia, South Carolina, November, 1985.
6. Spent Fuel and Radioactive Waste Inventories, Projections, and Characteristics, U.S. Department of Energy, Washington, D.C., (1983).
7. Licensing Requirements for Land Disposal of Radioactive Waste, U.S. Nuclear Regulatory Commission, Code of Federal Regulations, Title 10, Part 61.
8. J. Phillips et al., A Waste Inventory Report for Reactor and Fuel Fabrication Facility Wastes, ONWI-20 NUS-3314, NUS Corporation, (1979).
9. C. Forsberg, W. Carter, and A. Kibbly, Flowsheets and Source Terms for Radioactive Waste Projections, ORNL/RM-8462, Oak Ridge National Laboratory, (1985).
10. L. Klinger and K. Armstrong, An Evaluation of Operating Experience for Low-Level Nuclear Waste Processing, MLM-3229, Mound, (1985).
11. G. M. Hughes, et al., "Conceptual Design of High-Level Waste Vitrification Process at West Valley Using a Slurry-Fed Ceramic Melter," Advances in Ceramics, 8, p. 143, American Ceramics Society, Columbus, Ohio, (1984).
12. P. K. Baumgarten et al., "Development of an Ion-Exchange Process for Removing Cesium from High-Level Radioactive Liquid Wastes," Scientific Basis for Nuclear Waste Management, 2, p. 875, Plenum, New York, (1980).
13. C. A. Langton et al., "Cement-Based Waste Forms for Disposal of Savannah River Plant Low-Level Radioactive Salt Waste," Mat. Res. Soc. Proc., 26, p. 575, North-Holland, New York, (1984).
14. Treatment of Low- and Intermediate-level Liquid Radioactive Wastes, Technical Reports Series No. 236, IAEA, Vienna, (1984).
15. S. Forsberg et al., "Fixation of Medium-Level Wastes in Titanates and Zeolites: Progress Towards a System for Transfer of Nuclear Reactor Activities From Spent Organic to Organic Ion Exchangers," Scientific Basis for Nuclear Waste Management, 2, p. 867, Plenum, New York, (1980).
16. F. Kawamura and K. Motojima, "Using Copper Hexacyano-Ferrate (II) Impregnated Zeolite for Cesium Removal from Radioactive Waste," Nucl. Techno., 58, p. 242, ANS, (1982).
17. F. V. Rauzen et al., "Ion Exchange and Electro-dialysis in Liquid Radioactive-Waste Decontamination," Atomnaya Energiya, translated in Soviet Atomic Energy, 54, No. 6, p. 705, (1983).
18. B. E. Ryabchikov et al., "Treating Radioactive Waters with a Mixed Ion-Exchange Bed in a Continuous-Operation Plant," Atomnaya Energiya, translated in Soviet Atomic Energy, 55, No. 6, p. 815, (1984).
19. C. Dallman, "Four Years Operating Experience with Graver's Cl Process," The International Water Conference Thirty-Second Annual Meeting, p. 113, Engineer's Society of Western Pennsylvania, Pittsburgh, Pennsylvania, (1971).
20. P. K. Baumgarten et al., "Ion Exchange Processes for Decontamination Alkaline Radioactive Wastes," Waste Management '81, 2, p. 1057, ANS, New York, (1981).
21. D. K. Ploetz et al., "Conceptual Design of a Process for Removing Radioactivity from a Salt Solution," Advances in Ceramics Nuclear Waste Management, 8, p. 183, American Ceramics Society, Columbus, Ohio, (1984).
22. S. Komarneni and R. Roy, "Use of  $\Gamma$ -Zirconium Phosphate for Cs Removal from Radioactive Wastes," Nature, 299, p. 707, (1982).
23. S. Komarneni and R. Roy, " $\Gamma$ -Zirconium Phosphate as a Cs-Waste Form Form for Partitioned Wastes," Mat. Res. Soc. Symp. Proc., 15, p. 77, North-Holland, New York, (1983).
24. R. C. Roberts and M. K. Williams, Development of Low-Level Waste Treatment Systems: April-September 1982, MLM-3014, Mound, (1982).
25. A. D. Turner and R. M. Dell, "Electrochemistry and Radioactive Wastes," Atom, 327, p. 14, (1984).
26. W. S. Horton, "An Improvement to Low-Level Waste Vitrification," M.S. Thesis, University of Illinois, (1986).
27. G. W. Smith, Engineering Economy: Analysis of Capital Expenditures, 3rd Edition, Iowa State Univ. Press, Ames, Iowa, (1979).
28. U.S. Bureau of the Census, Statistical Abstract of the United States: 1985 (105th Edition), p. 469, Washington, D.C., (1984).
29. D. F. Malauskas, personal communication, Commonwealth Edison, Chicago, Illinois, January, (1986).