

VITROKELETM* COMPOSITIONS: NOVEL, HIGH AFFINITY, METAL SELECTIVE AND REGENERABLE MEDIA FOR THE REMOVAL OF RADIOACTIVE METALS FROM AQUEOUS NUCLEAR WASTE STREAMS

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ABSTRACT

Aqueous nuclear waste streams containing various amounts of fission and activation products, together with different amounts of non-radioactive metal ions, present a significant waste disposal problem. Such streams require substantial volume reduction or treatment to high decontamination factors for their effective handling. The variable levels of activity and amounts of competing non active metal ions present problems to the application of conventional ion exchange materials in the processing of these wastes.

This paper describes new technology, the DeVoe-Holbein Technology, which provides highly efficient and effective means for handling a variety of nuclear waste streams. DeVoe-Holbein Technology consists of a novel series of synthetic (VitrokeleTM) compositions and various processes for their use. The compositions are highly efficient at metal capture, are selective for individual or groups of metals, allow high flow throughputs, are mechanically stable, and can be regenerated with small amounts of regenerant, solidified or vitrified directly.

Field and laboratory studies with actual or simulated waste streams have demonstrated the virtual complete removal of Cs, Sr and Co from low level wastes, while in the presence of low to high concentrations of non-radioactive competing metal ions. Systems for the in-line processing of waste streams employing capture and regeneration cycles are presented.

INTRODUCTION

The operation of a nuclear reactor results in the generation of large volumes of aqueous wastes containing low levels or radionuclides. These nuclides are produced by neutron activation of metallic elements originating from reactor components, and to a lesser extent by leakage of fission products from fuel¹. The large volume of aqueous waste presents a significant waste disposal problem, and for effective handling, the terms concentrate and contain must be employed. Concentration, by volume reduction, must be followed by efficient containment since many of the nuclides generated have relatively long half-lives.

In addition to the nuclides present in aqueous wastes, small to large amounts of non-active competing metals are also present. The non-active competing metals limit the effectiveness of conventional ion-exchange media, since little or no selectivity exists, and non-active species are often present at concentrations several orders of magnitude greater than the total nuclide content.

The DeVoe-Holbein technology consists of a series of novel synthetic compositions (VitrokeleTM), and the processes for their use. Vitrokele products have a number of advantages over conventional ion-exchange resins; high affinity capture mechanism, selectivity for the target metal or group of metals, resistance to ionizing radiation, and for disposal

loaded composition can be solidified directly, vitrified, or regenerated with small volumes of regenerant. These features of Vitrokele products provide a more efficiently treated effluent stream, and a greater volume reduction factor than is normally achieved with ion-exchange resins.

This paper presents results on the application of DeVoe-Holbein technology to a number of nuclear problems. Results have been obtained through both laboratory and field studies employing actual or simulated nuclear waste solutions.

NUCLEAR APPLICATION OF DEVOE-HOLBEIN TECHNOLOGY

The principle requirements for the effective handling of nuclear wastes are concentrate and contain. Effective waste treatment procedures must employ high efficiency capture mechanisms. The large volumes of aqueous wastes present problems to existing technology since the actual concentration of radionuclides is often much less than parts per billion, but levels of radioactivity can be quite high. Techniques employed for the removal of trace radionuclides such as evaporation, precipitation and ion-exchange rarely achieve efficient removal of metals present in the parts per billion range. Although ion-exchange technology is employed extensively in the nuclear industry, wastes containing non-active competing metal ions limits its effectiveness.

The nuclear industry would benefit from a technology demonstrating a high affinity capture mechanism capable of removing radionuclides present in the parts per billion to parts per trillion range. A technology providing metal selectivity would be another benefit permitting a much greater volume reduction factor, since competition from non-active metal ions could be eliminated.

The DeVoe-Holbein technology^{2,3} has been evaluated both in the laboratory and in the field for its ability to remove radionuclides from a number of aqueous nuclear waste systems. A summary of a number of nuclear applications is given in Table I.

Vitrokele 566 has demonstrated high efficiency removal of ¹³⁷Cs, ⁶⁰Co and ⁹⁰Sr, from a simulated fuel bay waste water lagoon containing competing cation concentrations several orders of magnitude greater than the total nuclide content (Table I). The removal efficiency of each nuclide was in excess of 99.9%, and the composition could be fully regenerated with two bed volumes of regenerant. Vitrokele 520 performed similarly in the same waste water mock solution. Vitrokele 566 has been evaluated for the removal of ¹³⁷Cs and ⁶⁰Co from a primary coolant mock solution at 50°C, containing competing Li, Fe, Ni and Cr (Table I). The removal efficiency for both ¹³⁷Cs and ⁶⁰Co was in excess of 99.9% and the composition was readily regenerable. Similar

results were obtained on Vitrokele 566 using simulated fuel bay storage water as influent. Vitrokele 566 was also useful for the removal of ⁵¹Cr, ¹²⁵Sb, ⁹⁵Nb, and ⁶⁵Zn from floor drain radwaste generated at a PWR (Table I). Evaluation of Vitrokele 570 on the same floor drain radwaste sample demonstrated removal of ⁵¹Cr, ¹²⁵Sb and ⁹⁵Nb.

Vitrokele 553 is an Fe selective composition that has been evaluated in a number of nuclear and non-nuclear applications. With appropriate conditions, the composition is also capable of Cr removal (Table I). Vitrokele 553 has demonstrated the ability to bind Fe from citrate and EDTA complexes, and to selectively bind Fe from a complex solution containing both Fe and Co as citrate complexes (Table I). The selective removal of Fe, and in particular Fe³⁺, has obvious advantages in minimizing corrosion of metal fixtures.

An in-line processing system for the treatment of aqueous nuclear wastes is depicted in Fig. 1. Treated effluent can be re-cycled, or transferred to a holding tank prior to discharge. The loaded Vitrokele composition can be regenerated or alternatively, solidified or vitrified directly facilitating disposal.

TABLE I
Evaluation of Vitrokele Products for Various Nuclear Applications

Sample Description	Object	Results
1. Primary cooling loop (mock solution) 2000 ppm B, 5 ppm Li, 5ppb Fe, 1ppb Ni, 0.4 ppb Cr, 0.05 ppb ⁶⁰ Co, 0.02 ppb ¹³⁷ Cs, at 50°C	Removal of ¹³⁷ Cs and ⁶⁰ Co using Vitrokele 566	Capture of ¹³⁷ Cs and ⁶⁰ Co at >99.9% efficiency, fully regenerable
2. Fuel bay storage water ¹³⁷ Cs - 2.1 µCi/L ⁶⁰ Co - 20 µCi/L	Removal of ¹³⁷ Cs and ⁶⁰ Co using Vitrokele 566	Capture of ¹³⁷ Cs and ⁶⁰ Co at > 99.9% efficiency, fully regenerable
3. Floor drain radwaste (field test)	Nuclide removal: using Vitrokele 566 Vitrokele 570 Vitrokele 553	Removal of ⁵¹ Cr, ¹²⁵ Sb, ⁹⁵ Nb, ⁶⁵ Zn Removal of ⁵¹ Cr, ¹²⁵ Sb, ⁹⁵ Nb Removal of ⁵¹ Cr, ⁵⁹ Fe
4. ⁶⁰ Co and ⁵⁹ Fe as citrate complexes	Separation of ⁵⁹ Fe and ⁶⁰ Co on Vitrokele 553 and Vitrokele 570	Capture of ⁵⁹ Fe on Vitrokele 553 Capture of ⁶⁰ Co on Vitrokele 570
5. Floor drain radwaste (field test) large amounts of competing cations (TABLE II)	⁶⁰ Co capture on Vitrokele 571	Efficient capture of ⁵⁷ Co, ⁶⁸ Co and ⁶⁰ Co. No detectable interference from Na, Ca, Mg.
6. Fuel bay wastewater lagoon (mock solution) ¹³⁷ Cs, ⁶⁰ Co and ⁹⁰ Sr in the presence of competing cations	Capture of ¹³⁷ Cs, ⁶⁰ Co and ⁹⁰ Sr on Vitrokele 520 or Vitrokele 566	Capture of ¹³⁷ Cs, ⁶⁰ Co and ⁹⁰ Sr at > 99.9% efficiency.
7. ⁹⁹ Tc as anionic complex in the presence of competing cations and anions, at pH 2.0	Capture of ⁹⁹ Tc on Vitrokele 592	Efficient capture of ⁹⁹ Tc at > 99.9%

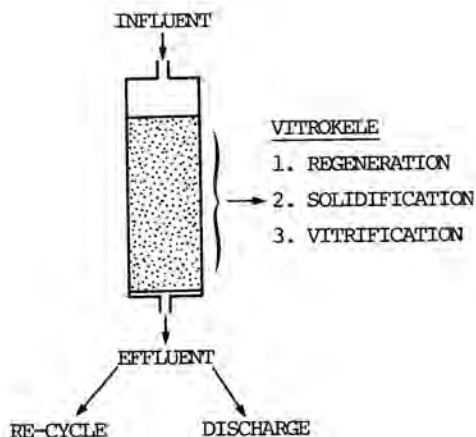


Fig 1. Simplified Scheme for the in-line processing of aqueous nuclear wastes.

COMPARATIVE EVALUATION OF VITROKELE 571 ON PWR RADWASTE

Background

Vitrokele 571 is a synthetic composition designed for the selective removal of Co. Laboratory experiments have demonstrated high affinity capture of Co from a variety of test solutions having both low and high concentrations of competing cations. A comprehensive field evaluation was initiated in conjunction with Chem Nuclear Systems Inc., Columbia S.C., to assess the composition on floor drain radwaste from a pressurized water reactor (PWR). A demineralization test unit was fabricated by Chem Nuclear Systems that could accommodate up to four columns in parallel. For comparative purposes Vitrokele 571, the polystyrene based strong cation exchanger HCR S-H, and a Co-specific synthetic zeolite X-61, were tested in parallel on the same sample of floor drain radwaste.

Columns were loaded and packed with 50 ml of hydrated resin, and the radwaste sample was applied at 50 bed volumes per hour. Effluent samples (1000 ml, 20 bed volumes) from each column were taken at the indicated time intervals (Fig. 2) for isotopic analysis (Ge-Li detector). After passage of 370 bed volumes (Vitrokele 571 and HCR S-H columns) or 220 bed volumes (zeolite X-61 column) of radwaste sample, the flow was interrupted for 14 hours before continuation of the experiment. This step was included to evaluate whether bound Co would egress after the media had remained static for several hours.

Floor Drain Radwaste Chemistry

The source of the radwaste utilized in the present study was a common pool comprising laboratory and equipment floor drains. The majority of nuclide activity (~90%) in the radwaste sample was in the form of Co isotopes. The sample had a conductivity of 790 $\mu\text{mhos/cm}$, the concentration of non-active competing ions being approximately nine orders of magnitude greater than the Co content (TABLE II).

Performance of Vitrokele 571

The elution profile of Co from the three test media is shown graphically in Fig 2. The performance of each of the media was evaluated by comparison of the 90% binding efficiency points. The cation exchange resin HCR S-H reached 90% after processing 110 bed volumes of radwaste, and the Co-specific synthetic zeolite exceeded 200 bed volumes. Vitrokele 571 reached 90% binding after processing nearly 1000 bed volumes, and based on the rate of exhaustion of the composition was capable of processing a great deal more before complete exhaustion occurred. This evaluation has been suggested by laboratory experiments run under similar conditions. Chemical evaluation of the pooled effluent from the Vitrokele 571 column showed virtually no change in the concentrations of the major competing cations Na, Mg and Ca (TABLE II). Vitrokele 571 did not alter the conductivity or pH significantly, also an indication of the high degree of selectivity of the composition for Co.

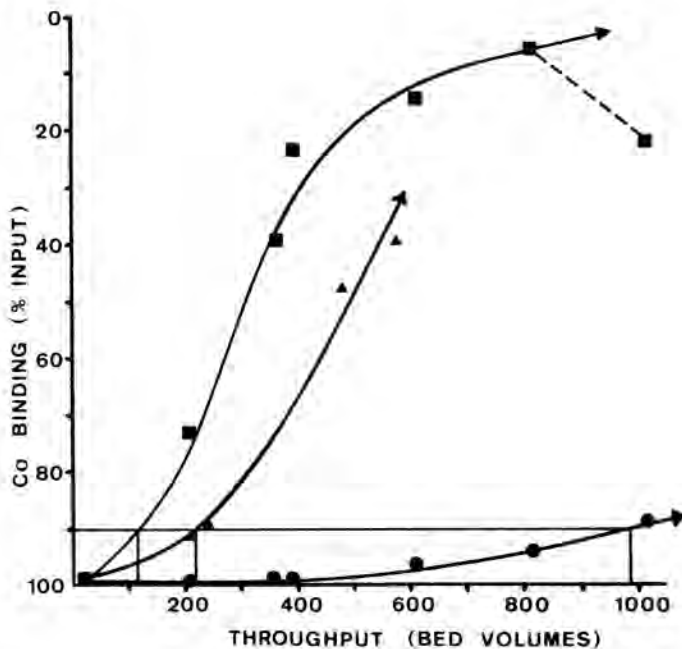


Fig. 2. Removal of cobalt (Co) from floor drain radwaste at a PWR. Vitrokele 571 (●) strong cation exchanger, HCR S-H (■), and Co-specific synthetic zeolite X-61 (▲).

TABLE II

Parameter	PWR Floor Drain Radwaste Chemistry	
	Influent	Vitrokele 571 Effluent (pool)
pH	7.80	7.9
Conductivity ($\mu\text{mhos/cm}$)	790	775
¹ TOC (ppm)	3.70	-
² TSS (ppm)	1000	0.25
Na (ppm)	173.5	176.0
Ca (ppm)	91.0	86.0
Mg (ppm)	22.5	19.7
B (ppm)	76.0	-
Total Co (ppt)	0.9 (8×10^{-4} $\mu\text{Ci/ml}$)	0.03 (3.2×10^{-5} $\mu\text{Ci/ml}$)

¹ Total organic carbon (TOC)

² Total suspended solids (TSS)

COMPARISON OF ION-EXCHANGE AND VITROKELE

A comparison of the properties of ion-exchangers and Vitrokele compositions is presented in Table III. In addition to the properties listed in the table, Vitrokele compositions are resistant to ionizing radiation. The high binding efficiency and selectivity of Vitrokele compositions result in a greater net volume reduction, and a higher decontamination factor than is achieved with ion exchange resins. Vitrokele compositions showing selectivity are especially

useful in the treatment of nuclear wastes containing low level radioactivity, and high concentrations of competing ions. The physical and chemical properties of Vitrokele compositions permit the option of regeneration, and removal of the captured metal in a small volume of regenerant, or they be solidified or vitrified directly for disposal.

TABLE III

Comparison of Vitrokele and ion-exchange processes.

Parameter	Vitrokele	Ion-Exchanger
1. Selectivity	Selective for target metal or group of metals.	Generally non-selective
2. Regeneration	Regeneration cycle can be accomplished in 1.5 to 4 bed volumes	Usually greater than 4 bed volumes required per cycle.
3. Conservation	Conditioners and regenerants can be reused, requiring occasional topping up.	Regenerants generally not reused, large volumes generated
4. Physical stability in column	No swelling or shrinking No bead breakage	Swelling and shrinking generally observed, beads break-up.
5. Handling and disposal	1) Metals can be recovered from regenerant solution. 2) Composition/regenerant solution can be solidified directly 3) Compositions can be vitrified.	1) Metal recovery often not practical due to large volumes of sludge that are generated containing non-target metals 2) Resins can be solidified directly
6. Volume Reduction	Due to selectivity, net volume reduction can be orders of magnitude greater than ion-exchange	Net volume reduction limited due to competition from non-target metals.

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