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MASTER

VOLATILIZATION FROM BOROSILICATE GLASS MELTS OF SIMULATED SAVANNAH RIVER PLANT WASTE*

MN ONLY

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Abstract

Laboratory scale studies determined the rates at which the semivolatile components sodium, boron, lithium, cesium, and ruthenium volatilized from borosilicate glass melts that contained simulated Savannah River Plant waste sludge. Sodium and boric oxides volatilize as the thermally stable compound sodium metaborate, and accounted for ~90% of the semivolatiles that evolved. The amounts of semivolatiles that evolved increased linearly with the logarithm of the sodium content of the glass-forming mixture. Cesium volatility was slightly suppressed when titanium dioxide was added to the melt, but was unaffected when cesium was added to the melt as a cesium-loaded zeolite rather than as a cesium carbonate solution. Volatility of ruthenium was not suppressed when the glass melt was blanketed with a nonoxidizing atmosphere.

Trace quantities of mercury were removed from vapor streams by adsorption onto a silver-exchanged zeolite. A bed containing silver in the ionic state removed more than 99.9% of the mercury and had a high chemisorption capacity. Beds of lead-, copper-, and copper sulfide-exchanged zeolite-X and also an unexchanged zeolite-X were tested. None of these latter beds had high removal efficiency and high chemisorption capacity.

I. Introduction

One process being studied for long term management of Savannah River Plant (SRP) high-level waste sludge is incorporation into a borosilicate glass matrix by spray calcination and electric melting. Several components of the melt will volatilize during the high temperature vitrification process. Savannah River Laboratory (SRL) has therefore initiated studies to determine the types and quantities of species that vaporize during fixation of SRP waste into glass. These studies provide basic data that are required to design an off-gas clean-up system for a vitrification process. This paper discusses laboratory-scale studies of the vaporization of sodium, lithium, boron, cesium, and ruthenium from glass melts. The chemical form in which these semivolatiles vaporize, the rates of vaporization, and some of the factors that influence volatility are discussed. All results were obtained with glasses that contained simulated nonradioactive sludges.

DISCLAIMER

Based on previous studies at SRL, all of the mercury in SRP waste is expected to volatilize during vitrification. A process was developed to remove trace quantities of mercury from gaseous streams by adsorption onto a bed of silver-exchanged zeolite. This process is discussed in the second part of this paper.

II. Experimental Procedure

Sodium, Lithium, Boron, and Cesium Compounds

The apparatus used to measure the volatility of Na, Li, B, and Cs is shown schematically in Figure 1. The crucible, collection tube, lid assembly, and hypodermic tubing were all fabricated from platinum. The transfer line from the collection tube to the scrubber was made of stainless steel, and the scrubber was made of glass. Volatility was determined by mixing the required proportions of glass frit/simulated sludge in the platinum crucible, which was then placed in the furnace. Normal melting conditions consisted of holding a 2-g sample at 1150°C for three hours. Nitrogen gas (750 mL/min) was introduced through the hypodermic tubing and across the melt. A vacuum was applied to the scrubber to insure that all volatilized species were removed from the crucible.

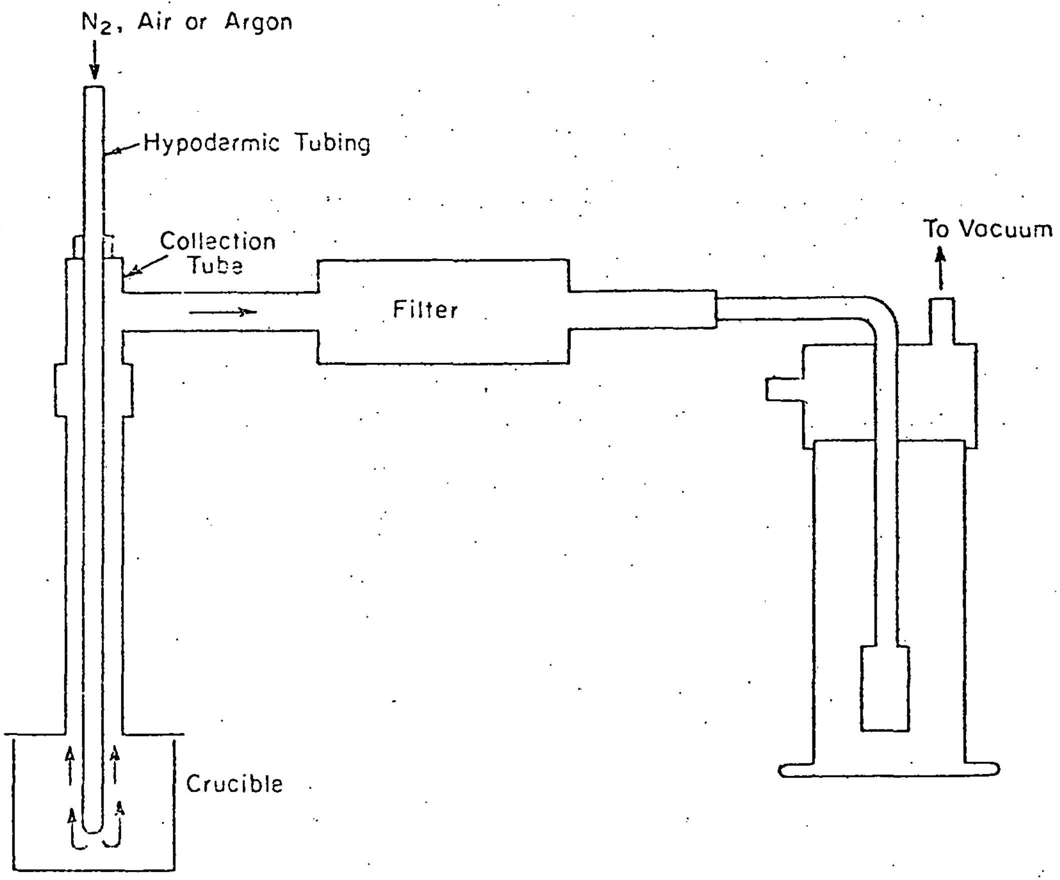

FIGURE 1
VOLATILITY APPARATUS

Compounds of Li, B, Na, and Cs condensed at the top of the collection tube, on the hypodermic tubing, in the transfer lines, and on the surface of the filter. Less than 1% of the semivolatiles penetrated through the filter; these were collected in the scrubber. The condensed gases were washed from the various parts of the apparatus and analyzed for Li, B, Na, and Cs by atomic absorption spectrophotometry (AA). A solution of 0.1M HNO_3 was used both for washing out the apparatus and as a scrubber solution.

Ruthenium Compounds

The apparatus and procedure described above were used to measure ruthenium volatility, except that a 6-g sample size was used and the in-line filter was removed. To minimize plating-out of ruthenium on the walls of the platinum collection tube, the inside of the tube was polished just prior to running each sample. This procedure prevented buildup of ruthenium in the transfer line. The collection tube was washed out after each sample was run, and residual ruthenium was removed from the walls. The washings containing the residual ruthenium were combined with the scrubber solution prior to analysis. This technique did not distinguish between particulate and volatile ruthenium, nor did it measure the extent to which ruthenium plates out.

The ruthenium was analyzed by a modification of the spectrophotometric technique developed by Woodhead.(1) This technique measures the absorbance at the isosbestic point (415 nm) of a RuO_4^{2-}/RuO_4^- mixture. Ruthenium was converted to the mixture by the action of $K_2S_2O_8$ in the presence of boiling KOH. The method detected ruthenium concentrations as low as 0.3 ppm in 100 mL of solution, which covered the range of ruthenium concentrations in the scrubber solutions.

III. Glass Compositions

Table I lists the two borosilicate glass-forming frits used in these studies. The high Fe, high Al, and average simulated calcined

Table I. Frit compositions.

Component	Concentration, wt % Frit 21	Frit 18
SiO_2	52.5	52.5
Na_2O	18.5	22.2
B_2O_3	10.0	10.0
TiO_2	10.0	10.0
CaO	5.0	5.0
Li_2O	4.0	—

sludges were prepared by mixing quantities of the dried metal oxides in the proportions required to give the compositions shown in Table II. The compositions are based on actual analyses of SRP waste sludge[2,3] and represent sludges from waste tanks with typically high Fe concentrations, Al concentrations, and an overall average for all tanks sampled.

Table II. Composition of simulated calcined sludges.

Metal Oxide	Metal Oxide in Sludge, wt %		
	High Fe	High Al	Average
Fe_2O_3	61.4	6.0	43.5
Al_2O_3	5.6	86.3	25.8
MnO_2	4.1	4.9	11.7
U_3O_8	14.2	1.5	11.0
CaO	4.2	0.4	3.0
NiO	10.5	0.9	5.0

The cesium content of SRP waste glass was calculated to be 0.36 wt % (as Cs_2O). Because this small amount of material could not be added in solid form to the 2-g samples, cesium was added by either adsorption of the cesium onto zeolite or by adding aliquots of a cesium carbonate solution to the glass-forming mixture. In cases where cesium was added from solution, the sample was dried to remove excess water before placing the loaded crucible into the furnace. Pre-drying prevented entrainment of particulates in the steam that would result from placing the wet mixture in the furnace heated to 1150°C.

Ruthenium was incorporated into the glass-forming mixture by adding the volume of a 3 g/L solution of $Ru(NO)(NO_3)_3$ required to give 0.05 or 0.15 wt % Ru in the final glass. The $Ru(NO)(NO_3)_3$ solution was prepared by dissolving $Ru(NO)(OH)_3$ in 4M HNO_3. After addition of the $Ru(NO)(NO_3)_3$ solution, the glass-forming mixture was dried at 115°C to drive off excess water to prevent entrainment of ruthenium.

IV. Specific Element Volatility

Sodium, Boron, and Lithium Volatilities

Volatilities of Na, Li, and B are discussed together because these species vaporized from the melt as alkali borates. The thermally stable compound sodium metaborate ($Na_2O \cdot B_2O_3$) accounted for ~90% of the semivolatiles that vaporized. Trace quantities of $LiBO_2$, $LiNaBO_2$, Na_2BO_2, and B_2O_3 were also detected in the vapor above the melt by Knudsen cell - mass spectrometer measurements. In the condensed phase, the species that volatilized were determined from the molar ratios of Na/B and (Li + Na)/B in the condensate. A ratio of one would indicate the metaborate, a ratio of two would indicate the diborate, and a mixture of the two compounds would be indicated by a ratio between one and two. The ratio of Na/B should be less than one when the melt contains lithium, because only part of the boron is associated with sodium; the remaining boron forms a lithium borate. The ratio of (Li + Na)/B would equal one, however, if $Li_2O{\cdot}B_2O_3$ and $Na_2O{\cdot}B_2O_3$ are the compounds that volatilize. A melt that contains sodium (but no lithium) should give a Na/B ratio of 1 if $Na_2O{\cdot}B_2O_3$ is the vaporizing species. When Frit 21, which contained both sodium and lithium, was used to prepare glasses (Table III), the molar ratio of Na/B was 0.89, and that of (Na + Li)/B was 1.02. Off-gasses from glasses prepared from Frit 18, a frit that contains no lithium, gave a Na/B ratio of 1.05 (Table IV). These three ratios are

Table III. Volatility of Na, Li and B from Frit 21 glass melts.

Code	Na_2O in Glass, mole %	Volatility, mg/cm²			Molar Ratios	
		Na_2O	Li_2O	B_2O_3	Na_2O/B_2O_3	$(Na_2O + Li_2O)/B_2O_3$
21-Avg-25		0.4	0.04	0.4	1	1.0
-35		0.4	0.05	0.5	1	1.1
-45	13.6	0.9	0.14	1.2	0.84	0.97
21-Fe-25	17.1	1.4	0.20	1.5	0.99	1.1
-35	15.7	1.4	0.20	2.0	0.82	0.93
-45	14.2	0.7	0.13	1.0	0.83	0.98
21-Al-25	16.1	1.3	0.16	2.0	0.74	0.84
-35	14.5	0.7	0.13	1.0	0.84	1.0
-45	12.6	0.5	0.08	0.5	1	1.2
				Avg	0.89	1.02

Table IV. Volatility of Na and B from Frit 18 glass melts.

Code	Na_2O in glass, mole %	Volatility, mg/cm²		Molar Ratio, Na_2O/B_2O_3
		Na_2O	B_2O_3	
18-Avg-25	21.2	2.6	3.0	0.97
-35	19.4	1.9	1.9	1.1
-45	17.1	1.5	1.6	1.1
18-Fe-25	21.6	1.8	1.9	1.1
-35	19.9	2.2	2.3	1.1
-45	17.7	1.0	1.4	0.86
18-Al-25	20.4	0.7	0.7	1.1
-35	18.2	1.5	1.9	0.93
-45	15.8	1.2	1.2	1.2
			Avg	1.05
Frit 18	22.7	4.0	4.5	
Frit 21	17.8	1.7		

consistent with a mechanism of alkali and boron volatilization as the compounds $Na_2O \cdot B_2O_3$ and $Li_2O \cdot B_2O_3$. Solomin(4) and Walmsley,(5) in their work on borosilicate glass volatility, also concluded that alkalis volatilize from borosilicate melts as thermally stable alkali borates.

The quantity of $Na_2O \cdot B_2O_3$ evolved increased exponentially when the mole % of sodium in the glass melt was increased (Figure 2). Measurements were made over a range of 12 to 23 mole % Na_2O in the glass. Volatility varied from 1.5 mg/cm^2 (at 12 mole % Na_2O) to 8.5 mg/cm^2 (at 23 mole % Na_2O). The linear relationship between the logarithm of weight loss and Na_2O content of the melt is similar to that obtained by Kolykov(6) when he studied the system Na_2O-B_2O_3-SiO_2. Barlow(7) also concluded that sodium volatilizes from a borosilicate glass melt as either sodium metaborate or sodium diborate, and that volatility increases as the logarithm of sodium concentration.

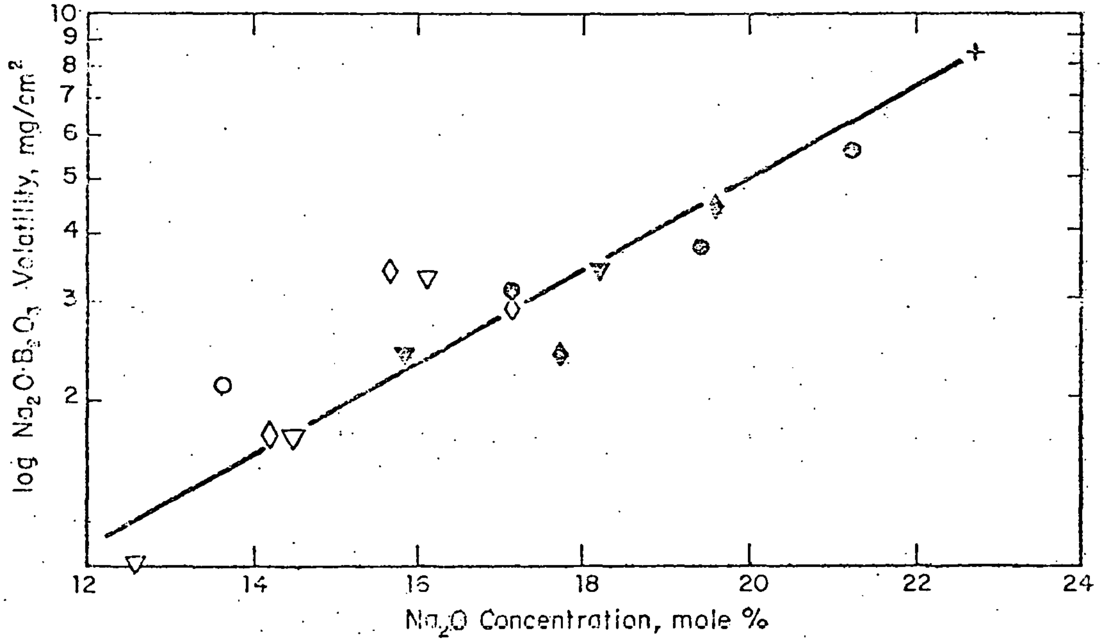

FIGURE 2
EFFECT OF Na_2O CONCENTRATION ON $Na_2O \cdot B_2O_3$ VOLATILITY

Lithium metaborate volatility was about 1/10 that of sodium borate. Changes in melt composition or in melting conditions had no appreciable effect on lithium volatility.

The type sludge, the type frit, and the concentration of other glass components affected volatility only to the extent that changes in these variables affected changes in the mole % of Na_2O in the glass melt.

Cesium

Cesium, which volatilized from the melt as either elemental cesium or as some oxide of cesium, is the most volatile of the three alkali metals studied. An average of 0.11 mg/cm^2 of cesium (as Cs_2O) volatilized from samples that contained a range of 0.03 to 0.09 wt %

cesium. Because previous workers(8) have reported that addition of TiO_2, B_2O_3, or MoO_3 to glass melts reduces cesium volatility, one part of the current work compared cesium volatilization from glass melts prepared from frits that contained 0, 5, and 10 wt % of TiO_2. Also, a comparison between cesium volatility from melts which contained cesium as a cesium-loaded zeolite and as a cesium carbonate solution was made.

Tables IV through VII summarize the effect on cesium volatility of the wt % TiO_2 added, the form of cesium addition, and the concentration of cesium in the melt. The high volatilities in these tests reflect the high surface-area-to-weight ratios for the small samples used and should not be interpreted as a direct measure of the amount of cesium expected to volatilize from a full-scale melter. If these levels of volatility are scaled up to a 2.2 ton/day melter, they

Table V. Effect of addition of TiO_2 on cesium volatility.

Cesium Added as	Cs_2O in Glass, wt %	TiO_2 in Frit, wt %	Volatility, mg/cm²
Zeolite	0.03	0	0.08
Zeolite	0.03	10	0.06
Carbonate	0.03	0	0.08
Carbonate	0.03	10	0.06

Table VI. Effect of form of addition on cesium volatility.

Cesium Added as	Cs_2O in Glass, wt %	TiO_2 in Frit, wt %	Volatility, mg/cm²
Zeolite	0.03	0	0.08
Carbonate	0.03	0	0.08
Zeolite	0.03	10	0.06
Carbonate	0.03	10	0.06
Zeolite	0.09	10	0.10
Carbonate	0.09	10	0.15

Table VII. Effect of Cs_2O concentration on cesium volatility.

Cs_2O in Glass, wt %	TiO_2 in Frit, wt %	Volatility, mg/cm²
0.03	0	0.08
0.03	10	0.06
0.06	5	0.11
0.06	5	0.13
0.09	0	0.21
0.09	10	0.15

represent volatilization of 0.05% of the cesium in the melter charge. Battelle Northwest Laboratories (BNWL), by comparison, measured ~0.3% volatility when they vitrified simulated light-water-reactor (LWR) waste that contained 0.2 wt.% of Cs_2O.(9) A melting temperature of 1050°C for 6 hours was used in the BNWL study.

The slight suppression of cesium volatility by titanium dioxide can be seen by comparing samples in Table V. The volatility is decreased so slightly that it would not significantly reduce problems of cesium vaporization during glass melting. The failure of titanium dioxide to significantly reduce cesium volatilization can be explained by the work of Rastogi, et al.,(10,11) who found that reductions in cesium volatility were obtained only at temperatures below 1000°C and for vitrification times ≤1 hour. They found, for example, that the compound $Cs_2O \cdot 4TiO_2$ does not volatilize at 400°C, but that 31% of this compound volatilizes at 1200°C. Other work by Rudolph, et al.(8) and by Kupfer and Schulz(12) report that titanium dioxide effectively suppresses cesium volatilization, but in the 1000 to 1050°C temperature range. Another probable cause of the failure of titanium dioxide suppress cesium volatility significantly is the large amounts of boric oxide present in the melt compositions used for SRP glasses. Rudolph, et al.(8) found that boric oxide, though not as effective as titanium dioxide, does reduce the volatility of cesium. The effect of titanium dioxide, then, is probably reduced when the melt contains boric oxide as a constituent.

Incorporation of cesium into the glass as cesium-loaded zeolite (0.02 g Cs/g zeolite), rather than as a cesium carbonate solution, did not increase cesium volatility from the glass melt. The insensitivity of cesium volatility to the form of cesium addition is shown in Table VI. Kelley, in his work on radionuclide vaporization from SRP waste,(13) also found that volatility of cesium was unchanged when cesium-loaded zeolite was substituted for direct addition of cesium carbonate.

Total cesium volatility increased when the total amount of cesium in the melt was increased (Table VII). The increase in volatility was proportional to the increased cesium concentration, suggesting that cesium vaporizes by diffusion from the melt surface.

The Knudsen cell studies conducted as a part of the experiments in this report did detect elemental cesium above the melt at a temperature of 1200°C. No cesium borates were detected.

Ruthenium

The high alumina, high iron, and composite sludges (Table II) along with Frit 21 were used to study ruthenium volatility. The two gases used to blanket the melt, air and argon, showed the effect of the oxygen on ruthenium volatilization. Each sludge-atmosphere combination was run in duplicate, and the result was interpreted by the analysis of variance method. For these experiments, nitrate-free simulated sludge was used. Neither the composition of the sludge nor the atmosphere over the melt affected the volatilization of ruthenium. Table VIII shows the per cent of ruthenium volatilized for the various combinations of sludges and atmospheres above the melt. The failure

Table VIII. Effect of sludge type and atmosphere over melt on ruthenium volatility.

Sludge Type	Cover Gas	Ru Volatilized, %
High Al	Argon	5.5
	Air	6.3
High Fe	Argon	2.8
	Air	7.4
Composite	Argon	7.5
	Air	5.3

of oxygen to increase ruthenium volatility, indicates that volatilization of ruthenium depends on the bulk rather than surface conditions of the melt. This result also indicates that atmospheric oxygen is not the only oxidant for ruthenium. This is consistent with previous work(13) that identified manganese dioxide as one component of SRP sludges that oxidizes ruthenium. All three sludges contained an excess of manganese dioxide relative to the ruthenium content.

The effect of nitrate concentration on ruthenium volatility depended on the level of ruthenium in the melt. Figure 3 summarizes

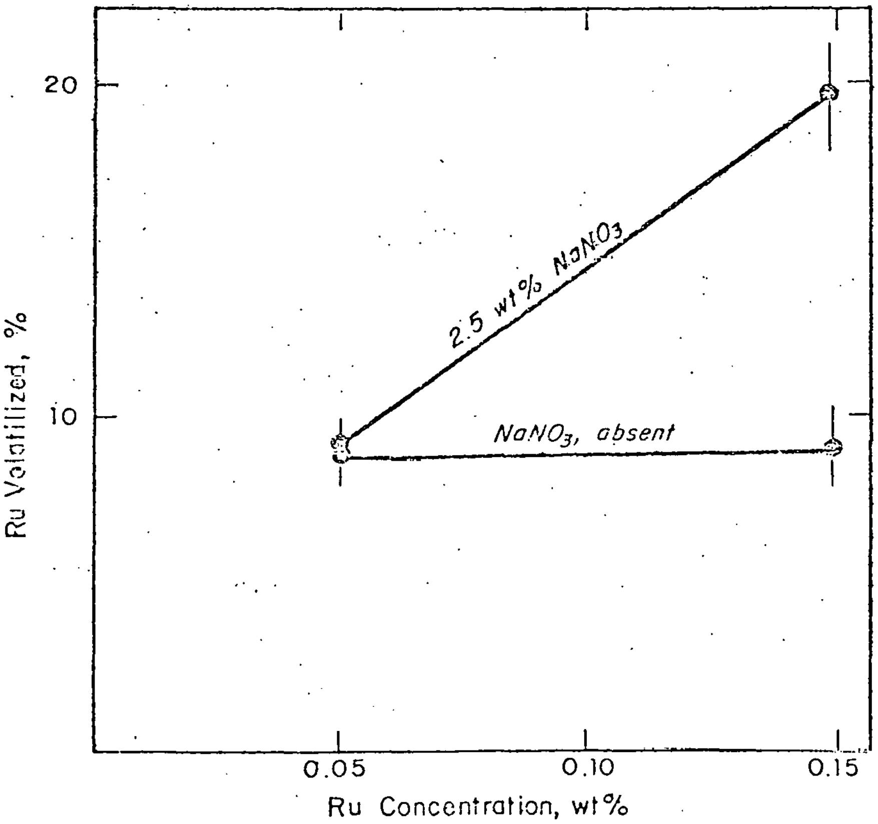

FIGURE 3
EFFECT OF SODIUM NITRATE CONCENTRATION ON RUTHENIUM

the volatility dependence on the level of ruthenium and the concentration of nitrate in the waste. Neither increasing the nitrate concentration at a low ruthenium concentration nor increasing the ruthenium concentration in nitrate-free melts caused increased ruthenium volatilization. However, a sharp increase in volatility was obtained when both the nitrate and ruthenium contents were increased. The nature of the nitrate/ruthenium concentration interaction has not been defined. These results do show, however, that acceptable nitrate levels for SRP waste sludges may depend on the amount of ruthenium present in composite (blended) SRP sludge.

V. Solid Sorbents for Mercury Vapor

It is estimated that 2.3 lbs/hr of mercury will be vaporized from the calciner/melter during vitrification of SRP waste. The calciner/melter off-gas system will include a quench column and a condenser that is cooled to 5°C to reduce the mercury vapor concentration to $\sim 3 \times 10^{-9}$ g/cm^3. Laboratory data show that the final traces of mercury can be removed by adsorption onto silver-exchanged zeolite. A bed of Ag^+ exchanged zeolite irreversibly chemisorbed 0.190 g Hg/g of bed at an adsorption efficiency of >99.9%.* Over the temperature range of 20 to 400°C, the efficiency of the silver zeolite bed remained >99.9%; at 500°C, efficiency dropped to 92%.

Preparation of Zeolite and Analytical Method

The Na, Ag^+, Ag^0, Pb^{2+} and the CuS forms of zeolite were available from previous studies.(14) The Cu^{2+} zeolite was prepared by exchanging Cu^{2+} from a saturated cupric acetate solution with *Linde Type 13X®* molecular sieve for 10 days at 80°C. After exchange, the Cu^{2+} zeolite was thoroughly washed to remove any residual cupric acetate solution and then dried.

Mercury vapor concentrations were measured with a mercury analyzer previously used in a study of the dispersion of buried elemental mercury.(15) The analyzer is shown schematically in Fig. 4 and is more fully described in Reference 15. In these experiments, the accessory mercury vapor source is replaced by the adsorption bed being tested. A septum, through which known amounts of air saturated with mercury vapor can be injected, is placed just upstream from the bed.

Capacities of adsorption beds were measured by passing mercury vapor through the bed at a face velocity of ~3 m/min and measuring the weight of the bed until no further weight gain was recorded. After constant weight was attained, argon was passed through the bed and the weight loss recorded. The weight lost to the argon stream was assumed to be physically adsorbed mercury, while the remaining weight gain by the bed was assumed to be chemisorbed mercury. During desorption of physisorbed mercury, the bed was placed in line with the specific mercury analyzer, and the evolution of mercury was measured.

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* Efficiency is defined as the % of mercury in the vapor stream that is trapped by the adsorbent bed.

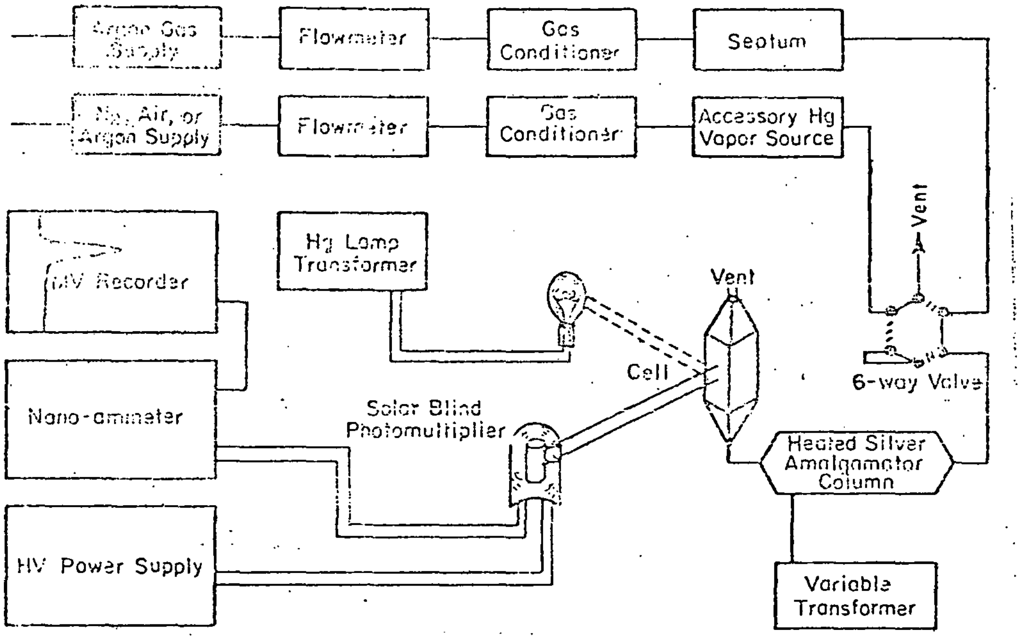

FIGURE 4
SCHEMATIC DIAGRAM OF MERCURY ANALYZER

Screening Tests

The adsorption efficiency of the beds was first measured at room temperature (∿20°C). The results in Table IX show that only Ag^+, Ag^0, and CuS exchanged beds have a high adsorption efficiency for mercury. Table IX also shows that apparent residence times* influence mercury adsorption efficiency. The importance of residence time is shown by comparing the efficiencies of the Ag^+ exchanged bed at various residence times. The efficiency of >99.9% at 0.04 seconds apparent residence time decreased to 80% at 0.0006 sec. In these experiments, the lower detection limit for mercury was 0.1%, so that an efficiency of at least 99.9% may be assigned for the cases where no mercury was detected in the vapor. This assumption gives a lower limit of $\sim10^3$ for the mercury decontamination factor for cases in which no detectable mercury vapor was found exiting the adsorption bed.

Effect of Temperature on Efficiency

The effect of bed temperature on adsorption efficiency for Ag^+, Ag^0, and CuS exchanged zeolite beds was measured over a temperature range of 20 to 500°C (Table X). Beds were first heated to the desired temperature, and then the mercury vapor was passed through the adsorbent. Of the three beds, the Ag^+ form was least affected by temperature, showing an adsorption efficiency of >99.9% up to 400°C. The Ag^0 bed had >99.9% efficiency up to 200°C, while the CuS bed had this level of efficeincy only up to 50°C. These results are consistent with work reported by Barrer and Whiteman,(16) who found that sorption of mercury onto metal-exchanged zeolites was inversely proportional to temperature.

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* Apparent residence time is defined as the bed volume divided by the volume flow rate of the vapor stream.

TABLE IX. Efficiency of mercury adsorption beds.

Sorbent[a]	Apparent Residence Time, sec	Hg Vapor Adsorbed, %
None	0.04	0
Shredded Rubber	0.04	0
Na-X	0.04	0
Pb-X	0.04	15
Cu-X	0.04	0
CuS-X	0.04	>99.9[b]
Ag^0-X	0.04	>99.9[b]
Ag^+-X	0.04	>99.9[b]
Ag^+-X	0.0002	98
Ag^+-X	0.001	95
Ag^+-X	0.0006	80

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[a] X = A near-faujasite type of zeolite.

[b] No mercury was detected in the gas exiting the bed; percent adsorption taken by using minimum detection level of 0.1%.

Table X. Effect of temperature on efficiency of mercury adsorption beds.

Bed Temperature, °C	Adsorption Efficiency, % Hg Adsorbed		
	CuS-X	Ag^+-X	Ag^0-X
20 to 25	>99.9	>99.9	>99.9
50	>99.9	>99.9	>99.9
100	97	>99.9	>99.9
200	79	>99.9	>99.9
300	59	>99.9	92
400	39	>99.9	88
500	-	92	-

Adsorption Capacity

The capacity of a zeolite adsorption bed depends on the bed depth, the face velocity of the gas stream entering the bed, and the nature of the sorbent. The capacities of Ag^+, Ag^0 and CuS beds were measured for a bed depth of 1.5 cm and a superficial face velocity of ∼3m/min.

The only bed with an appreciable adsorption capacity was the Ag^+ exchanged zeolite which chemisorbed 0.190 g of Hg/g of bed and physisorbed another 0.0264 g Hg/g of bed before a constant weight was achieved. The irreversible chemisorption of mercury is attributed to the reaction,

$$2Ag^{+} + Hg \rightarrow 2Ag + Hg^{2+}.$$

Barrer and Whiteman(16) studied adsorption of mercury onto several zeolites. At low mercury concentrations, the exchange between silver and mercury reached 63% of the value calculated for complete exchange. At mercury concentrations higher than those expected to be encountered in the calciner/melter off-gas system adsorption beds, the reactions,

$$Hg^{2+} + Hg \rightarrow Hg_2{}^{2+}$$

$$Ag + Hg \rightarrow Ag(Hg) \text{ amalgam}$$

and

$$Hg_2{}^{2+} + XHg \rightarrow Hg^{2+}_{(x+2)}$$

can also occur.

The adsorption capacities of Ag^0 and CuS exchanged zeolite beds are quite low under the conditions of these experiments (Table XI). No detectable weight gain was recorded for either bed. Therefore, the smallest measurable weight gain (0.1 mg) was used to calculate the upper limits on capacities shown in Table XI. Even though the capacities are very low, Ag^0 and CuS exchanged zeolite beds efficiently removed mercury vapor at low concentrations. However, Ag^+ zeolite beds are recommended for plant processing because less frequent replacement is required.

Table XI. Capacities of mercury adsorbent beds.

Sorbent	Bed Length, cm	Bed Weight, g	Mercury Adsorbed, g Hg/g Bed Total	Mercury Adsorbed, g Hg/g Bed Chemisorbed
Ag^+-X	1.5	0.1525	0.2164	0.190
CuS-X	1.5	0.1495	$<7 \times 10^{-4}$	-
Ag^0-X	1.5	0.1505	$<7 \times 10^{-4}$	-

VI. Acknowledgement

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Volatilization from Borosilicate Glass Melts of Simulated Savannah River Plant Waste

Keywords

Alkali volatility

Boron volatility

Borosilicate glass melts

Cesium volatility

Mercury adsorption

Metal-exchanged zeolites

Radioisotope waste storage

Ruthenium volatility

Savannah River Plant waste

Volatility of glass melts

Zeolites

Based on previous studies at SRL, all of the mercury in SRP waste is expected to volatilize during vitrification. A process was developed to remove trace quantities of mercury from gaseous streams by adsorption onto a bed of silver-exchanged zeolite. This process is discussed in the second part of this paper.

II. Experimental Procedure

Sodium, Lithium, Boron, and Cesium Compounds

The apparatus used to measure the volatility of Na, Li, B, and Cs is shown schematically in Figure 1. The crucible, collection tube, lid assembly, and hypodermic tubing were all fabricated from platinum. The transfer line from the collection tube to the scrubber was made of stainless steel, and the scrubber was made of glass. Volatility was determined by mixing the required proportions of glass frit/simulated sludge in the platinum crucible, which was then placed in the furnace. Normal melting conditions consisted of holding a 2-g sample at 1150°C for three hours. Nitrogen gas (750 mL/min) was introduced through the hypodermic tubing and across the melt. A vacuum was applied to the scrubber to insure that all volatilized species were removed from the crucible.

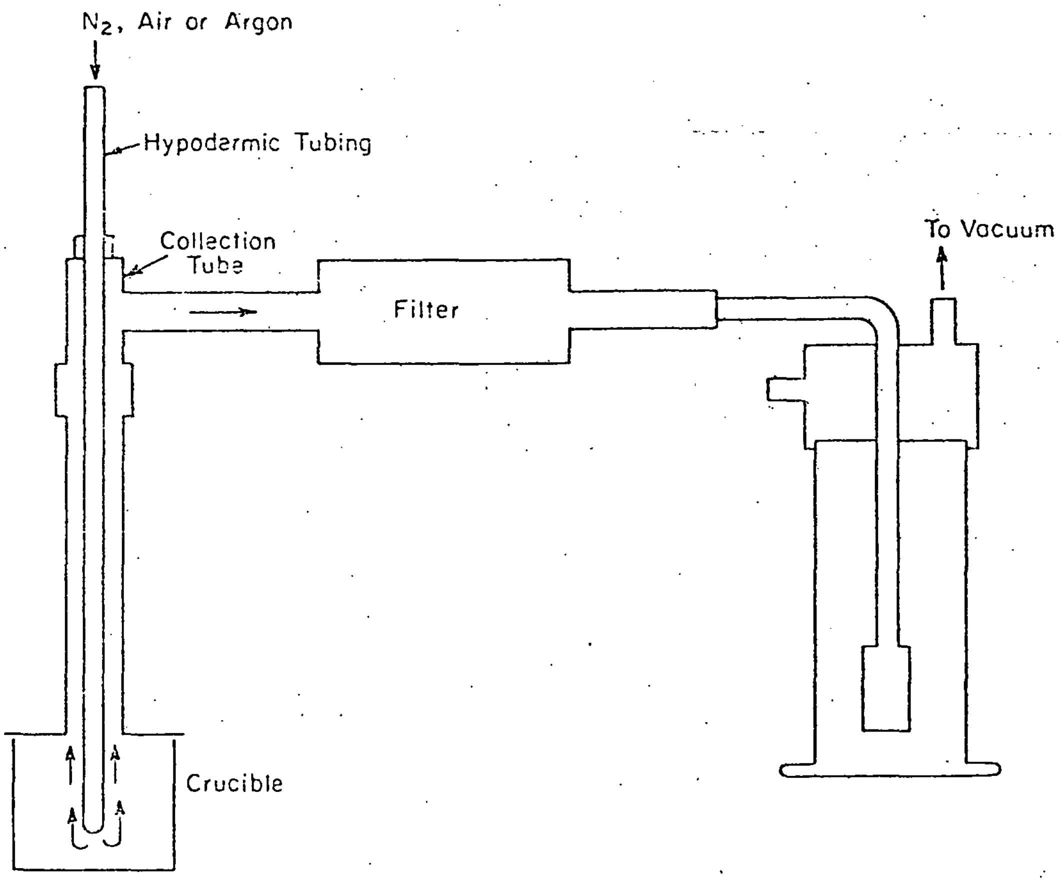

FIGURE 1
VOLATILITY APPARATUS

Compounds of Li, B, Na, and Cs condensed at the top of the collection tube, on the hypodermic tubing, in the transfer lines, and on the surface of the filter. Less than 1% of the semivolatiles penetrated through the filter; these were collected in the scrubber. The condensed gases were washed from the various parts of the apparatus and analyzed for Li, B, Na, and Cs by atomic absorption spectrophotometry (AA). A solution of 0.1M HNO_3 was used both for washing out the apparatus and as a scrubber solution.

Ruthenium Compounds

The apparatus and procedure described above were used to measure ruthenium volatility, except that a 6-g sample size was used and the in-line filter was removed. To minimize plating-out of ruthenium on the walls of the platinum collection tube, the inside of the tube was polished just prior to running each sample. This procedure prevented buildup of ruthenium in the transfer line. The collection tube was washed out after each sample was run, and residual ruthenium was removed from the walls. The washings containing the residual ruthenium were combined with the scrubber solution prior to analysis. This technique did not distinguish between particulate and volatile ruthenium, nor did it measure the extent to which ruthenium plates out.

The ruthenium was analyzed by a modification of the spectrophotometric technique developed by Woodhead.(1) This technique measures the absorbance at the isosbestic point (415 nm) of a RuO_4^{2-}/RuO_4^- mixture. Ruthenium was converted to the mixture by the action of $K_2S_2O_8$ in the presence of boiling KOH. The method detected ruthenium concentrations as low as 0.3 ppm in 100 mL of solution, which covered the range of ruthenium concentrations in the scrubber solutions.

III. Glass Compositions

Table I lists the two borosilicate glass-forming frits used in these studies. The high Fe, high Al, and average simulated calcined

Table I. Frit compositions.

Component	Concentration, wt % Frit 21	Frit 18
SiO_2	52.5	52.5
Na_2O	18.5	22.2
B_2O_3	10.0	10.0
TiO_2	10.0	10.0
CaO	5.0	5.0
Li_2O	4.0	—

sludges were prepared by mixing quantities of the dried metal oxides in the proportions required to give the compositions shown in Table II. The compositions are based on actual analyses of SRP waste sludge(2,3) and represent sludges from waste tanks with typically high Fe concentrations, Al concentrations, and an overall average for all tanks sampled.

Table II. Composition of simulated calcined sludges.

Metal Oxide	Metal Oxide in Sludge, wt %		
	High Fe	High Al	Average
Fe_2O_3	61.4	6.0	43.5
Al_2O_3	5.6	86.3	25.8
MnO_2	4.1	4.9	11.7
U_3O_8	14.2	1.5	11.0
CaO	4.2	0.4	3.0
NiO	10.5	0.9	5.0

The cesium content of SRP waste glass was calculated to be 0.26 wt % (as Cs_2O). Because this small amount of material could not be added in solid form to the 2-g samples, cesium was added by either adsorption of the cesium onto zeolite or by adding aliquots of a cesium carbonate solution to the glass-forming mixture. In cases where cesium was added from solution, the sample was dried to remove excess water before placing the loaded crucible into the furnace. Pre-drying prevented entrainment of particulates in the steam that would result from placing the wet mixture in the furnace heated to 1150°C.

Ruthenium was incorporated into the glass-forming mixture by adding the volume of a 3 g/L solution of $Ru(NO)(NO_3)_3$ required to give 0.05 or 0.15 wt % Ru in the final glass. The $Ru(NO)(NO_3)_3$ solution was prepared by dissolving $Ru(NO)(OH)_3$ in 4M HNO_3. After addition of the $Ru(NO)(NO_3)_3$ solution, the glass-forming mixture was dried at 115°C to drive off excess water to prevent entrainment of ruthenium.

IV. Specific Element Volatility

Sodium, Boron, and Lithium Volatilities

Volatilities of Na, Li, and B are discussed together because these species vaporized from the melt as alkali borates. The thermally stable compound sodium metaborate ($Na_2O \cdot B_2O_3$) accounted for $\sim$90% of the semivolatiles that vaporized. Trace quantities of $LiBO_2$, $LiNaBO_2$, Na_2BO_2, and B_2O_3 were also detected in the vapor above the melt by Knudsen cell - mass spectrometer measurements. In the condensed phase, the species that volatilized were determined from the molar ratios of Na/B and (Li + Na)/B in the condensate. A ratio of one would indicate the metaborate, a ratio of two would indicate the diborate, and a mixture of the two compounds would be indicated by a ratio between one and two. The ratio of Na/B should be less than one when the melt contains lithium, because only part of the boron is associated with sodium; the remaining boron forms a lithium borate. The ratio of (Li + Na)/B would equal one, however, if $Li_2O \cdot B_2O_3$ and $Na_2O \cdot B_2O_3$ are the compounds that volatilize. A melt that contains sodium (but no lithium) should give a Na/B ratio of 1 if $Na_2O \cdot B_2O_3$ is the vaporizing species. When Frit 21, which contained both sodium and lithium, was used to prepare glasses (Table III), the molar ratio of Na/B was 0.89, and that of (Na + Li)/B was 1.02. Off-gasses from glasses prepared from Frit 18, a frit that contains no lithium, gave a Na/B ratio of 1.05 (Table IV). These three ratios are

Table III. Volatility of Na, Li and B from Frit 21 glass melts.

Code	Na_2O in Glass, mole %	Volatility, mg/cm^2 Na_2O	Li_2O	B_2O_3	Molar Ratios Na_2O/B_2O_3	$(Na_2O + Li_2O)/B_2O_3$
21-Avg-25		0.4	0.04	0.4	1	1.0
-35		0.4	0.05	0.5	1	1.1
-45	13.6	0.9	0.14	1.2	0.84	0.97
21-Fe-25	17.1	1.4	0.20	1.5	0.99	1.1
-35	15.7	1.4	0.20	2.0	0.82	0.93
-45	14.2	0.7	0.13	1.0	0.83	0.98
21-Al-25	16.1	1.3	0.16	2.0	0.74	0.84
-35	14.5	0.7	0.13	1.0	0.84	1.0
-45	12.6	0.5	0.08	0.5	1	1.2
				Avg	0.89	1.02

Table IV. Volatility of Na and B from Frit 18 glass melts.

Code	Na_2O in glass, mole %	Volatility, mg/cm^2 Na_2O	B_2O_3	Molar Ratio, Na_2O/B_2O_3
18-Avg-25	21.2	2.6	3.0	0.97
-35	19.4	1.9	1.9	1.1
-45	17.1	1.5	1.6	1.1
18-Fe-25	21.6	1.8	1.9	1.1
-35	19.9	2.2	2.3	1.1
-45	17.7	1.0	1.4	0.86
18-Al-25	20.4	0.7	0.7	1.1
-35	18.2	1.5	1.9	0.93
-45	15.8	1.2	1.2	1.2
			Avg	1.05
Frit 18	22.7	4.0	4.5	
Frit 21	17.8	1.7		

consistent with a mechanism of alkali and boron volatilization as the compounds $Na_2O \cdot B_2O_3$ and $Li_2O \cdot B_2O_3$. Solomin(4) and Walmsley,(5) in their work on borosilicate glass volatility, also concluded that alkalis volatilize from borosilicate melts as thermally stable alkali borates.

The quantity of $Na_2O \cdot B_2O_3$ evolved increased exponentially when the mole % of sodium in the glass melt was increased (Figure 2). Measurements were made over a range of 12 to 23 mole % Na_2O in the glass. Volatility varied from 1.5 mg/cm^2 (at 12 mole % Na_2O) to 8.5 mg/cm^2 (at 23 mole % Na_2O). The linear relationship between the logarithm of weight loss and Na_2O content of the melt is similar to that obtained by Kolykov(6) when he studied the system Na_2O-B_2O_3-SiO_2. Barlow(7) also concluded that sodium volatilizes from a borosilicate glass melt as either sodium metaborate or sodium diborate, and that volatility increases as the logarithm of sodium concentration.

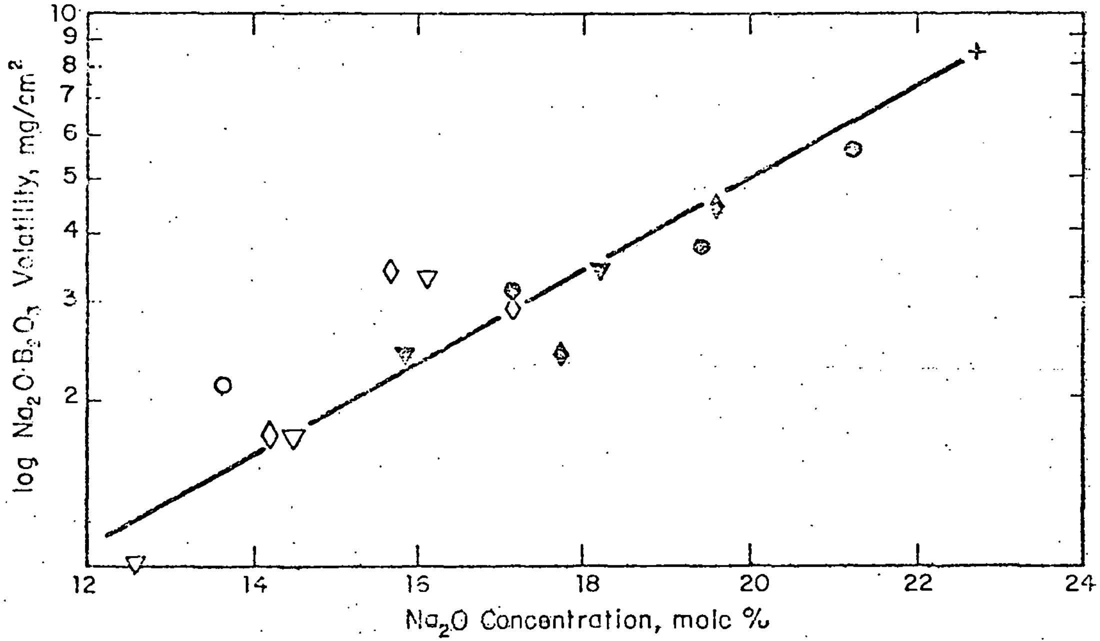

FIGURE 2
EFFECT OF Na_2O CONCENTRATION ON $Na_2O \cdot B_2O_3$ VOLATILITY

Lithium metaborate volatility was about 1/10 that of sodium borate. Changes in melt composition or in melting conditions had no appreciable effect on lithium volatility.

The type sludge, the type frit, and the concentration of other glass components affected volatility only to the extent that changes in these variables affected changes in the mole % of Na_2O in the glass melt.

Cesium

Cesium, which volatilized from the melt as either elemental cesium or as some oxide of cesium, is the most volatile of the three alkali metals studied. An average of 0.11 mg/cm^2 of cesium (as Cs_2O) volatilized from samples that contained a range of 0.03 to 0.09 wt %

cesium. Because previous workers(8) have reported that addition of TiO_2, B_2O_3, or MoO_3 to glass melts reduces cesium volatility, one part of the current work compared cesium volatilization from glass melts prepared from frits that contained 0, 5, and 10 wt % of TiO_2. Also, a comparison between cesium volatility from melts which contained cesium as a cesium-loaded zeolite and as a cesium carbonate solution was made.

Tables IV through VII summarize the effect on cesium volatility of the wt % TiO_2 added, the form of cesium addition, and the concentration of cesium in the melt. The high volatilities in these tests reflect the high surface-area-to-weight ratios for the small samples used and should not be interpreted as a direct measure of the amount of cesium expected to volatilize from a full-scale melter. If these levels of volatility are scaled up to a 2.2 ton/day melter, they

Table V. Effect of addition of TiO_2 on cesium volatility.

Cesium Added as	Cs_2O in Glass, wt %	TiO_2 in Frit, wt %	Volatility, mg/cm^2
Zeolite	0.03	0	0.08
Zeolite	0.03	10	0.06
Carbonate	0.03	0	0.08
Carbonate	0.03	10	0.06

Table VI. Effect of form of addition on cesium volatility.

Cesium Added as	Cs_2O in Glass, wt %	TiO_2 in Frit, wt %	Volatility, mg/cm^2
Zeolite	0.03	0	0.08
Carbonate	0.03	0	0.08
Zeolite	0.03	10	0.06
Carbonate	0.03	10	0.06
Zeolite	0.09	10	0.10
Carbonate	0.09	10	0.15

Table VII. Effect of Cs_2O concentration on cesium volatility.

Cs_2O in Glass, wt %	TiO_2 in Frit, wt %	Volatility, mg/cm^2
0.03	0	0.08
0.03	10	0.06
0.06	5	0.11
0.06	5	0.13
0.09	0	0.21
0.09	10	0.15

represent volatilization of 0.05% of the cesium in the melter charge. Battelle Northwest Laboratories (BNWL), by comparison, measured ~0.3% volatility when they vitrified simulated light-water-reactor (LWR) waste that contained 0.2 wt. % of Cs_2O.(9) A melting temperature of 1050°C for 6 hours was used in the BNWL study.

The slight suppression of cesium volatility by titanium dioxide can be seen by comparing samples in Table V. The volatility is decreased so slightly that it would not significantly reduce problems of cesium vaporization during glass melting. The failure of titanium dioxide to significantly reduce cesium volatilization can be explained by the work of Rastogi, et al.,(10,11) who found that reductions in cesium volatility were obtained only at temperatures below 1000°C and for vitrification times ≤ 1 hour. They found, for example, that the compound $Cs_2O \cdot 4TiO_2$ does not volatilize at 400°C, but that 31% of this compound volatilizes at 1200°C. Other work by Rudolph, et al.(8) and by Kupfer and Schulz(12) report that titanium dioxide effectively suppresses cesium volatilization, but in the 1000 to 1050°C temperature range. Another probable cause of the failure of titanium dioxide suppress cesium volatility significantly is the large amounts of boric oxide present in the melt compositions used for SRP glasses. Rudolph, et al.(8) found that boric oxide, though not as effective as titanium dioxide, does reduce the volatility of cesium. The effect of titanium dioxide, then, is probably reduced when the melt contains boric oxide as a constituent.

Incorporation of cesium into the glass as cesium-loaded zeolite (0.02 g Cs/g zeolite), rather than as a cesium carbonate solution, did not increase cesium volatility from the glass melt. The insensitivity of cesium volatility to the form of cesium addition is shown in Table VI. Kelley, in his work on radionuclide vaporization from SRP waste,(13) also found that volatility of cesium was unchanged when cesium-loaded zeolite was substituted for direct addition of cesium carbonate.

Total cesium volatility increased when the total amount of cesium in the melt was increased (Table VII). The increase in volatility was proportional to the increased cesium concentration, suggesting that cesium vaporizes by diffusion from the melt surface.

The Knudsen cell studies conducted as a part of the experiments in this report did detect elemental cesium above the melt at a temperature of 1200°C. No cesium borates were detected.

Ruthenium

The high alumina, high iron, and composite sludges (Table II) along with Frit 21 were used to study ruthenium volatility. The two gases used to blanket the melt, air and argon, showed the effect of the oxygen on ruthenium volatilization. Each sludge-atmosphere combination was run in duplicate, and the result was interpreted by the analysis of variance method. For these experiments, nitrate-free simulated sludge was used. Neither the composition of the sludge nor the atmosphere over the melt affected the volatilization of ruthenium. Table VIII shows the per cent of ruthenium volatilized for the various combinations of sludges and atmospheres above the melt. The failure

Table VIII. Effect of sludge type and atmosphere over melt on ruthenium volatility.

Sludge Type	Cover Gas	Ru Volatilized, %
High Al	Argon	5.5
	Air	6.3
High Fe	Argon	2.8
	Air	7.4
Composite	Argon	7.5
	Air	5.3

of oxygen to increase ruthenium volatility, indicates that volatilization of ruthenium depends on the bulk rather than surface conditions of the melt. This result also indicates that atmospheric oxygen is not the only oxidant for ruthenium. This is consistent with previous work(13) that identified manganese dioxide as one component of SRP sludges that oxidizes ruthenium. All three sludges contained an excess of manganese dioxide relative to the ruthenium content.

The effect of nitrate concentration on ruthenium volatility depended on the level of ruthenium in the melt. Figure 3 summarizes

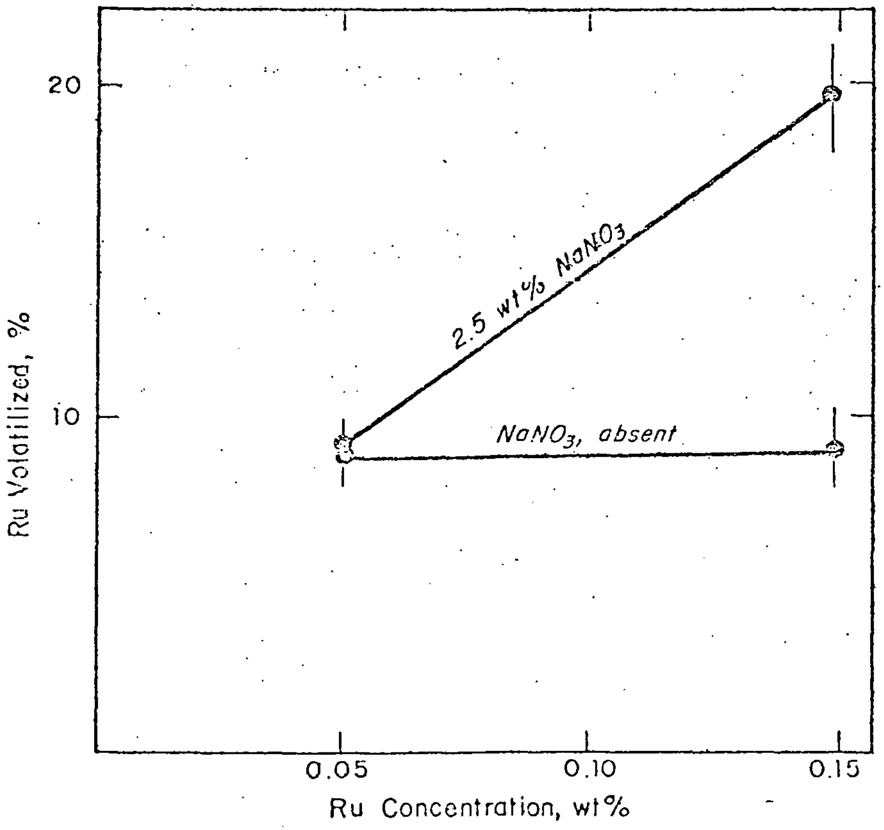

FIGURE 3
EFFECT OF SODIUM NITRATE CONCENTRATION ON RUTHENIUM

the volatility dependence on the level of ruthenium and the concentration of nitrate in the waste. Neither increasing the nitrate concentration at a low ruthenium concentration nor increasing the ruthenium concentration in nitrate-free melts caused increased ruthenium volatilization. However, a sharp increase in volatility was obtained when both the nitrate and ruthenium contents were increased. The nature of the nitrate/ruthenium concentration interaction has not been defined. These results do show, however, that acceptable nitrate levels for SRP waste sludges may depend on the amount of ruthenium present in composite (blended) SRP sludge.

V. Solid Sorbents for Mercury Vapor

It is estimated that 2.3 lbs/hr of mercury will be vaporized from the calciner/melter during vitrification of SRP waste. The calciner/melter off-gas system will include a quench column and a condenser that is cooled to 5°C to reduce the mercury vapor concentration to $\sim 3 \times 10^{-9}$ g/cm^3. Laboratory data show that the final traces of mercury can be removed by adsorption onto silver-exchanged zeolite. A bed of Ag^+ exchanged zeolite irreversibly chemisorbed 0.190 g Hg/g of bed at an adsorption efficiency of >99.9%.* Over the temperature range of 20 to 400°C, the efficiency of the silver zeolite bed remained >99.9%; at 500°C, efficiency dropped to 92%.

Preparation of Zeolite and Analytical Method

The Na, Ag^+, Ag^0, Pb^{2+} and the CuS forms of zeolite were available from previous studies.(14) The Cu^{2+} zeolite was prepared by exchanging Cu^{2+} from a saturated cupric acetate solution with *Linde Type 13X®* molecular sieve for 10 days at 80°C. After exchange, the Cu^{2+} zeolite was thoroughly washed to remove any residual cupric acetate solution and then dried.

Mercury vapor concentrations were measured with a mercury analyzer previously used in a study of the dispersion of buried elemental mercury.(15) The analyzer is shown schematically in Fig. 4 and is more fully described in Reference 15. In these experiments, the accessory mercury vapor source is replaced by the adsorption bed being tested. A septum, through which known amounts of air saturated with mercury vapor can be injected, is placed just upstream from the bed.

Capacities of adsorption beds were measured by passing mercury vapor through the bed at a face velocity of ~3 m/min and measuring the weight of the bed until no further weight gain was recorded. After constant weight was attained, argon was passed through the bed and the weight loss recorded. The weight lost to the argon stream was assumed to be physically adsorbed mercury, while the remaining weight gain by the bed was assumed to be chemisorbed mercury. During desorption of physisorbed mercury, the bed was placed in line with the specific mercury analyzer, and the evolution of mercury was measured.

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* Efficiency is defined as the % of mercury in the vapor stream that is trapped by the adsorbent bed.

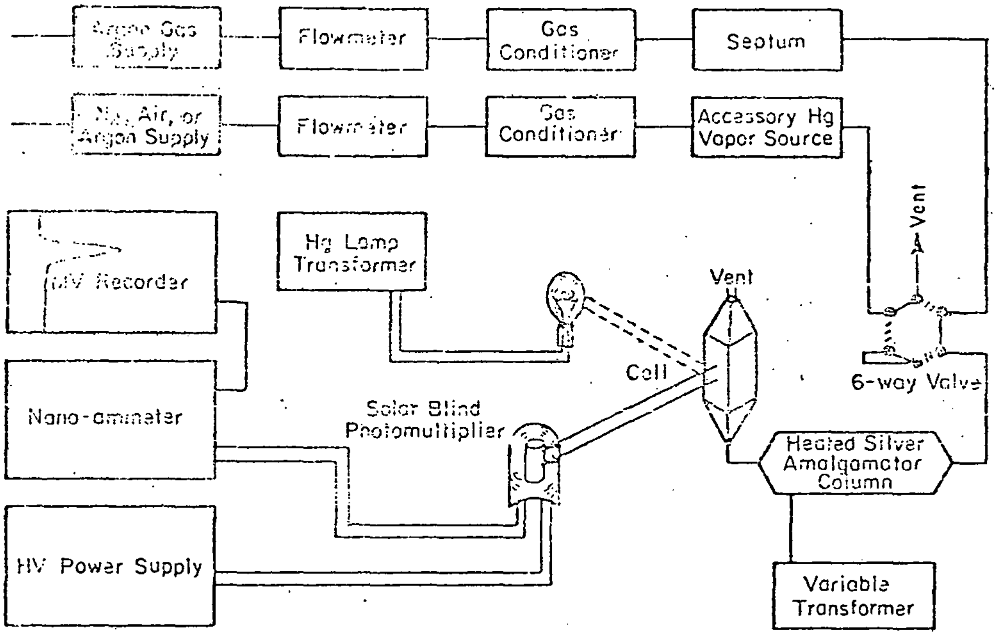

FIGURE 4
SCHEMATIC DIAGRAM OF MERCURY ANALYZER

Screening Tests

The adsorption efficiency of the beds was first measured at room temperature (~20°C). The results in Table IX show that only Ag^+, Ag^0, and CuS exchanged beds have a high adsorption efficiency for mercury. Table IX also shows that apparent residence times* influence mercury adsorption efficiency. The importance of residence time is shown by comparing the efficiencies of the Ag^+ exchanged bed at various residence times. The efficiency of >99.9% at 0.04 seconds apparent residence time decreased to 80% at 0.0006 sec. In these experiments, the lower detection limit for mercury was 0.1%, so that an efficiency of at least 99.9% may be assigned for the cases where no mercury was detected in the vapor. This assumption gives a lower limit of $\sim 10^3$ for the mercury decontamination factor for cases in which no detectable mercury vapor was found exiting the adsorption bed.

Effect of Temperature on Efficiency

The effect of bed temperature on adsorption efficiency for Ag^+, Ag^0, and CuS exchanged zeolite beds was measured over a temperature range of 20 to 500°C (Table X). Beds were first heated to the desired temperature, and then the mercury vapor was passed through the adsorbent. Of the three beds, the Ag^+ form was least affected by temperature, showing an adsorption efficiency of >99.9% up to 400°C. The Ag^0 bed had >99.9% efficiency up to 200°C, while the CuS bed had this level of efficeincy only up to 50°C. These results are consistent with work reported by Barrer and Whiteman,(16) who found that sorption of mercury onto metal-exchanged zeolites was inversely proportional to temperature.

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* Apparent residence time is defined as the bed volume divided by the volume flow rate of the vapor stream.

TABLE IX. Efficiency of mercury adsorption beds.

Sorbent[a]	Apparent Residence Time, sec	Hg Vapor Adsorbed, %
None	0.04	0
Shredded Rubber	0.04	0
Na-X	0.04	0
Pb-X	0.04	15
Cu-X	0.04	0
CuS-X	0.04	>99.9[b]
Ag^0-X	0.04	>99.9[b]
Ag$^+$-X	0.04	>99.9[b]
Ag$^+$-X	0.0002	98
Ag$^+$-X	0.001	95
Ag$^+$-X	0.0006	80

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a. X = A near-faujasite type of zeolite.

b. No mercury was detected in the gas exiting the bed; percent adsorption taken by using minimum detection level of 0.1%.

Table X. Effect of temperature on efficiency of mercury adsorption beds.

Bed Temperature, °C	Adsorption Efficiency, % Hg Adsorbed		
	CuS-X	Ag$^+$-X	Ag^0-X
20 to 25	>99.9	>99.9	>99.9
50	>99.9	>99.9	>99.9
100	97	>99.9	>99.9
200	79	>99.9	>99.9
300	59	>99.9	92
400	39	>99.9	88
500	-	92	-

Adsorption Capacity

The capacity of a zeolite adsorption bed depends on the bed depth, the face velocity of the gas stream entering the bed, and the nature of the sorbent. The capacities of Ag$^+$, Ag^0 and CuS beds were measured for a bed depth of 1.5 cm and a superficial face velocity of $\sim$3m/min.

The only bed with an appreciable adsorption capacity was the Ag$^+$ exchanged zeolite which chemisorbed 0.190 g of Hg/g of bed and physisorbed another 0.0264 g Hg/g of bed before a constant weight was achieved. The irreversible chemisorption of mercury is attributed to the reaction,

$$2Ag^{+} + Hg \rightarrow 2Ag + Hg^{2+}.$$

Barrer and Whiteman(16) studied adsorption of mercury onto several zeolites. At low mercury concentrations, the exchange between silver and mercury reached 63% of the value calculated for complete exchange. At mercury concentrations higher than those expected to be encountered in the calciner/melter off-gas system adsorption beds, the reactions,

$$Hg^{2+} + Hg \rightarrow Hg_2{}^{2+}$$

$$Ag + Hg \rightarrow Ag(Hg) \text{ amalgam}$$

and

$$Hg_2{}^{2+} + XHg \rightarrow Hg^{2+}_{(X+2)}$$

can also occur.

The adsorption capacities of Ag^0 and CuS exchanged zeolite beds are quite low under the conditions of these experiments (Table XI). No detectable weight gain was recorded for either bed. Therefore, the smallest measurable weight gain (0.1 mg) was used to calculate the upper limits on capacities shown in Table XI. Even though the capacities are very low, Ag^0 and CuS exchanged zeolite beds efficiently removed mercury vapor at low concentrations. However, Ag^+ zeolite beds are recommended for plant processing because less frequent replacement is required.

Table XI. Capacities of mercury adsorbent beds.

Sorbent	Bed Length, cm	Bed Weight, g	Mercury Adsorbed, g Hg/g Bed Total	Chemisorbed
Ag^+-X	1.5	0.1525	0.2164	0.190
CuS-X	1.5	0.1495	$<7 \times 10^{-4}$	-
Ag^0-X	1.5	0.1505	$<7 \times 10^{-4}$	-

VI. Acknowledgement

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Volatilization from Borosilicate Glass Melts of Simulated Savannah River Plant Waste

Keywords

Alkali volatility

Boron volatility

Borosilicate glass melts

Cesium volatility

Mercury adsorption

Metal-exchanged zeolites

Radioisotope waste storage

Ruthenium volatility

Savannah River Plant waste

Volatility of glass melts

Zeolites