DISTRIBUTION OF TRACER COMPOUNDS DURING IN SITU VITRIFICATION TESTS*

C. A. Loehr and R. A. Callow
Idaho National Engineering Laboratory
EG&G Idaho, Inc.
Idaho Falls, Idaho 83415

ABSTRACT

Rare-earth tracers were buried in two test pits that were vitrified in situ at the Idaho National Engineering Laboratory. The results indicated that the majority of each tracer was retained in the vitrified products. Also, the tracer concentrations were relatively homogeneous throughout the glass and crystalline products. In one test, up to several percent of the amounts initially added to the pit were released into the off-gas system. Further work is needed to quantify element release from the melt, and to correlate tracer release with expected plutonium release from the melt.

INTRODUCTION

Two in situ vitrification (ISV) field tests were conducted on simulated buried waste pits during June and July, 1990, at the Idaho National Engineering Laboratory (INEL). ISV, an emerging technology for in-place conversion of contaminated soils into a durable glass and crystalline waste form, is being investigated as a potential remediation technology for buried waste. The field tests were a cooperative effort between INEL and Pacific Northwest Laboratories (PNL), using PNL intermediate-scale processing equipment and are documented in Ref. 1.

ISV is a thermal treatment process that is initiated by a square array of four graphite electrodes inserted a few inches into the ground, as shown in Fig. 1. Because soil is not electrically conductive, a mixture of flaked graphite and glass frit is placed between the electrodes to serve as a starter path. Once an electrical potential is applied to the electrodes, an electrical current is started in the starter path beginning the melt. The graphite starter path is eventually consumed by oxidation, and the current is transferred to the molten soil, which is processed at temperatures between 1 723 and 2 273 K (1 450 and 2000°C). As the molten zone grows, it incorporates or encapsulates radionuclides and nonvolatile hazardous elements, such as heavy metals. The high temperature of the process destroys organic components by pyrolysis. Pyrolyzed by-products migrate to the surface of the treated zone and combust in the presence of air. A hood placed over the area being vitrified directs the gaseous effluent to an off-gas treatment system. The waste is then allowed to cool, trapping waste in the vitrified product.

As part of the 1990 field tests at the INEL, a tracer study was conducted during testing to provide qualitative assessment of the potential for radionuclide release during ISV processing of buried waste. During preparation of the test pits, rare-earth tracer elements were added to selected waste containers. The added tracers were oxides of dysprosium, terbium, and ytterbium (Dy_2O_3, Tb_4O_7, Yb_2O_3). This paper presents data on the distribution of tracers resulting from ISV processing of buried waste during the tests.

TEST EQUIPMENT

The intermediate-scale test system used for the tests consists of four graphite electrodes, a power control unit, an off-gas containment hood over the test site, and an off-gas treatment system housed in a portable semi-trailer (see Fig. 2). The power system uses a Scott-Tee connection to transform a 3-phase input to a 2-phase secondary load on diagonally opposed electrodes in a square pattern. This provides the energy source for the melting process.

The off-gas containment hood is designed to collect off-gases emanating from the melt and to direct them to an off-gas treatment system. The containment hood is an octagonal pyramid and is constructed from 304L stainless steel sheet metal, with the side panels constructed from 18 gauge sheet metal and the top constructed of 14 gauge sheet metal. The hood is sealed to the ground by piling soil around the base. Typical operating conditions in the hood range from 249 to 498 Pa (vacuum), created by an induced draft blower, and 473 to 673 K (200 to 400°C). The hood has a volume of approximately 28.3 m^3 to provide a surge capacity that minimizes vacuum loss during periods of sudden gas release. Air is drawn into the hood via an air inlet line, providing oxygen for combustion of pyrolysis gases released from the melt. Normal flow direction in the inlet air line is into the hood; however, the inlet line contains a high-efficiency particulate air (HEPA) filter as a safety feature to provide filtering of air exiting the hood through this line if the hood plenum pressure becomes positive.

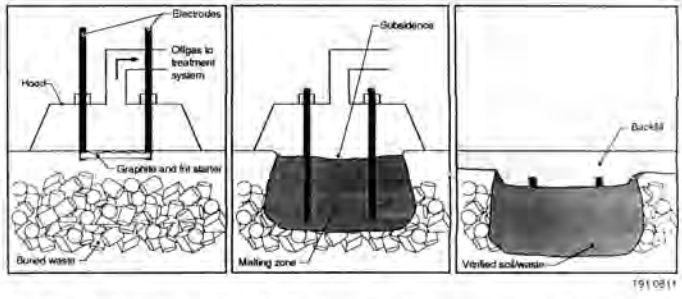

Fig. 1. Schematic of ISV process components and process steps.

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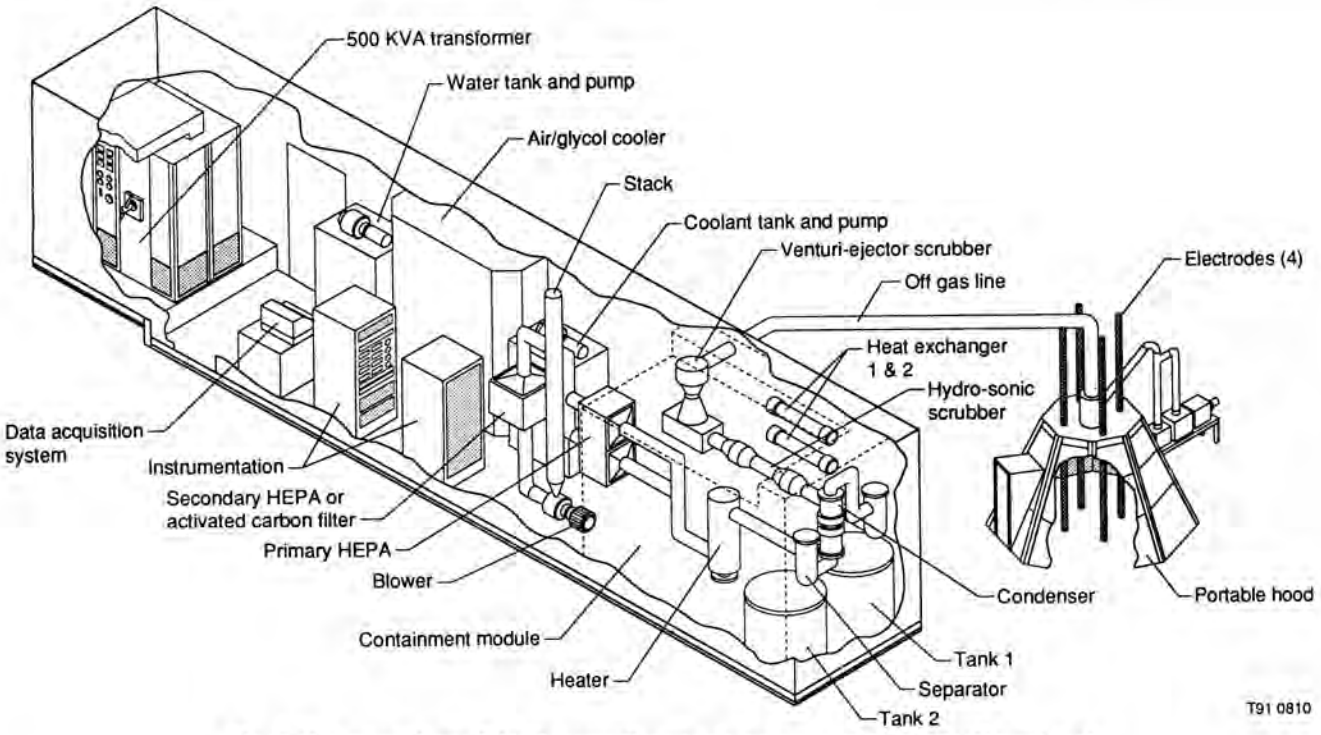

Fig. 2. Cutaway view of the intermediate-scale process trailer and off-gas hood.

Off-gases collected in the hood are directed to the off-gas treatment system via a 0.203-m diameter off-gas pipe as shown in Fig. 2. The off-gas treatment system consists of a Venturi-Ejector scrubber and separator, a Hydro-Sonic scrubber, a separator, a condenser, another separator, a heater, two stages of HEPA filtration, and a blower. Liquid to the two wet scrubbers is supplied by two independent scrub recirculation tanks, each equipped with a pump and heat exchanger. The first stage of HEPA filtration consists of two 0.61 x 0.61 x 0.29-m HEPA filters in parallel. During operation, the primary filter is used and the other remains as a backup in case the primary filter becomes loaded. The induced draft blower provides a total off-gas flow of between 10 to 20 m^3/min and creates a vacuum of approximately 24,900 Pa.

TRACER STUDY OBJECTIVES

The retention of an element within the ISV melt is dependent on multiple factors. Transport factors such as direct entrainment of elements into melt gases are of particular concern for ISV processing of buried waste, since these mechanisms offer the potential to increase the amount of released material in spite of equilibrium thermodynamic properties that may favor retention in the melt.

The tracer study was initiated to provide some insight into off-gas transport mechanisms and to provide qualitative indications of the potential for element release from the melt. Rare-earth elements (lanthanides) were used in the study because of chemical similarities to actinides, specifically Pu. It is recognized that direct quantitative correlation of lanthanide and Pu behavior is not possible, particularly under ISV processing conditions.

The objectives of the tracer study focused on characterizing the distribution of the tracers throughout the ISV process equipment and product. Specifically examined were (a) the distribution of tracers in the product block, (b) the presence or absence in the hood, off-gas treatment system, and adjacent soil, (c) tracer release patterns over time, and (d) the relative amounts found within the block, on the hood and off-gas line surfaces, within the scrub system, and on exit and inlet HEPA filters. In some cases, because of uncertainties introduced by sampling and analysis, only order of magnitude estimates or qualitative information on tracer amounts were obtained.

TEST DESIGN AND TRACER ANALYSIS

Two test pits were constructed at the INEL and contained simulated waste with no hazardous or radioactive material. The simulated waste was comprised of carbon steel containers and cardboard boxes filled with silicate and calcium silicate sludges, combustibles, concrete, glass, and scrap metal. Test Pit 1 was designed to simulate a waste region of randomly disposed drums and boxes intermixed with fill dirt. The test pit contained three tracers at three depths: 1.336 kg Dy_2O_3 at 0.76 m, 1.337 kg Tb_4O_7 at 1.07 m, and 1.331 kg Yb_2O_3 at 1.52 m. Each tracer was equally divided and placed into six cans to be vitrified. Test Pit 2 was designed to simulate a region of stacked drums and a stacked box region containing high metal content waste. Only one tracer material was placed in Pit 2; 2.282 kg of Dy_2O_3 was placed a depth of 1.61 m in ten of the cans to be vitrified. All cans containing tracer materials were placed near the center of the pits to ensure that they would be processed by the melt.

To meet the tracer study objectives, samples were collected and tracer amounts were measured in the (a) glass products, (b) confinement hood, (c) off-gas piping, (d) off-gas scrub solutions, (e) off-gas primary HEPA and hood inlet filters, (f) soil and sand used in pit preparations, and (g) soil adjacent to the glass product. Grab and core samples were collected from the product, pretest and posttest smears from the hood and off-gas pipe, samples during processing from the off-gas scrub solutions, samples from posttest HEPA filters, grab samples of soil used in the pits, and composite soil

samples at two distances from the solidified test products. Samples were analyzed for Dy, Tb, and Yb using inductively coupled plasma (ICP) atomic emission spectrometry (AES) or mass spectrometry (MS) methods. Laboratory quality control measurements were performed with all analyses.

RESULTS

Test 1

Glass, crystalline, and metal phases of the test product were analyzed for Dy, Tb, and Yb. The tracers were detected in virtually every sample. Table I gives estimates of the mean (or average) and 90% confidence limits for the mean based on seven glass and crystalline product samples. The confidence intervals indicate that nonmetal product materials from different block locations have relatively similar tracer amounts.

The mean tracer concentrations for nonmetal product phases reported in Table I correspond to respective amounts of 1 538, 1 968, and 3 009 g Dy, Tb, and Yb in the 8 267 kg total product. The amounts substantially exceed the amounts actually buried (1 164 g for Dy, 1 137 g for Tb, and 1 169 g for Yb), even when the confidence intervals for the mean concentrations are considered. The calculation of total product amounts is based on the entire product mass, including the metal phase, and assumes that the metal phase exhibits concentrations similar to nonmetal phases. However, there are indications that the metal phase, estimated as approximately 15% of the product mass, may have reduced concentrations of tracers. Although data from core samples show homogeneity of nonmetal phases of the product, it is possible that areas near the edges of the melt, where convective mixing is less, may also contain reduced concentrations of tracers.

Tracers were found deposited in the hood during Test 1 and no significant difference was detected between the top and bottom smear averages (see Table II). The 90% confidence intervals for the mean total amounts, using an interior hood surface area of 34.5 m^2 and assuming each of six smears represents an area of approximately 0.01 m^2, are (1.73, 3.17) g for Dy, (0.63, 1.93) g for Tb, and (2.05, 3.3) g for Yb. The tracer Dy was found on the air inlet filter in the hood. The mean concentration of three samples analyzed was 236 mg/kg; the 90% confidence interval for the mean is (92.8, 311.2) mg/kg. The tracer is believed to have been deposited during positive pressure events in the hood that were sufficient to cause air backflow down the air inlet line.

TABLE I

Nonmetal Product Tracer Analyses Means and 90% Confidence Limits in $\mu g/g$
Questionable and Less-than-detection Data Removed

Location	Tracer	Mean	Lower Limit	Upper Limit
Test 1	Dy	186.25	171.89	200.61
Test 1	Tb	238.20	208.93	267.47
Test 1	Yb	360.75	325.48	396.02
Test 2	Dy	175.56	169.76	181.35
Test 2	Yb	7.00	0.69	13.31

Tracers were also found deposited in the off-gas pipe between the hood and off-gas trailer. Order of magnitude calculations indicate that approximately 3 g of Dy, 28 g Tb, and 9 g of Yb may have accumulated in the off-gas pipe during Test 1.

Results of tracer analysis of Test 1 off-gas scrub solutions are illustrated in Fig. 3. The results are believed to reflect substantial noise and possibly bias because of laboratory analysis problems, tank volume measurement insensitivities, and nonuniform mixing and particulate settling in the tanks. Figure 3 shows tracer amounts in scrub solutions plotted against hours from the start of the test, the depth of the melt front, and tracer burial depths for each tracer. The data show that tracers occurred in the scrub solution as the melt reached the depth of tracer burial. The amount of tracers transported beyond the scrub solution in the off-gas system is believed to be small or none, since two samples from the primary HEPA filter downstream were measured as having less-than-detectable levels of Dy and Tb, and low concentrations (0.11-0.28 mg/kg) of Yb. Apparent evidence that the tracer levels in the tanks dropped off after peak releases, indicating that some amount of the tracers continued past the scrub solution, is believed to be caused in part by the nonuniform mixing and

TABLE II

Hood Tracer Analysis Statistics in μg

Location	Media	Area	Tracer Dy Concentration Mean	Tracer Dy Concentration Standard Deviation	Tracer Tb Concentration Mean	Tracer Tb Concentration Standard Deviation	Tracer Yb Concentration Mean	Tracer Yb Concentration Standard Deviation
Test 1	Hood Smear	Side	772.33	384.03	485.33	275.70	807.00	100.50
		Top	647.33	42.57	257.00	131.73	741.33	325.05
Test 2	Hood Smear	Side	232.17	367.94	180.13	294.33	226.57	352.87
		Top	750.00	531.13	277.33	19.66	719.00	339.17

particulate settling in the tanks. The amounts that were retained in the scrub solution were on the order of 4, 6, and 13 g for Dy, Tb, and Yb, respectively.

All tracers were detected in all six pretest soil samples and Dy and Yb were detected in all four Posttest 1 composite soil samples, with one exception. The average of pretest soil concentrations was compared with the average concentration of each set of posttest composite splits. Averages are given in Table III. No significant differences between pretest and individual posttest sample mans were detected.*

Test 2

As in Test 1, the Dy concentration of the nonmetal phases of product appears to be relatively evenly distributed in the product. The 90% confidence interval for Dy mean concentration based on 13 samples was (170, 181) μg/g, which corresponds to 2 929-3 155 total grams of Dy in the 17 430 kg Test 2 product. Also, as in Test 1, the amount of Dy in the product is considered to be a poor estimate, considering that it substantially exceeds the buried amounts. The observed concentrations do not appear to be different from those observed in Test 1, although the amount added to Test Pit 2 was greater than that added to Test Pit 1.

All three tracers were detected in six smears of the hood after Test 2. As for Test 1, no significant difference was found between averages of the top and sides of the hood. A 90% confidence interval for the mean of smears in the hood in μg is (82, 900) for Dy. Using hood interior surface area calculations and the Posttest 2 hood smear data, a 90% confidence interval for the mean amount of Dy in the hood after Test 2 is (0.28, 3.1) g. This amount ranges lower than the amount calculated for Posttest 1. Since Dy was added to the Test 2 pit, either Dy did not accumulate in the hood during Test 2 or the movement of the hood between tests caused Dy to be removed from hood panels and a comparable amount was added during the test.

The off-gas pipe smear data for Test 2 measured amounts of Dy comparable to Tb and Yb, which were not added to the test pit. The data are insufficient to determine whether or not

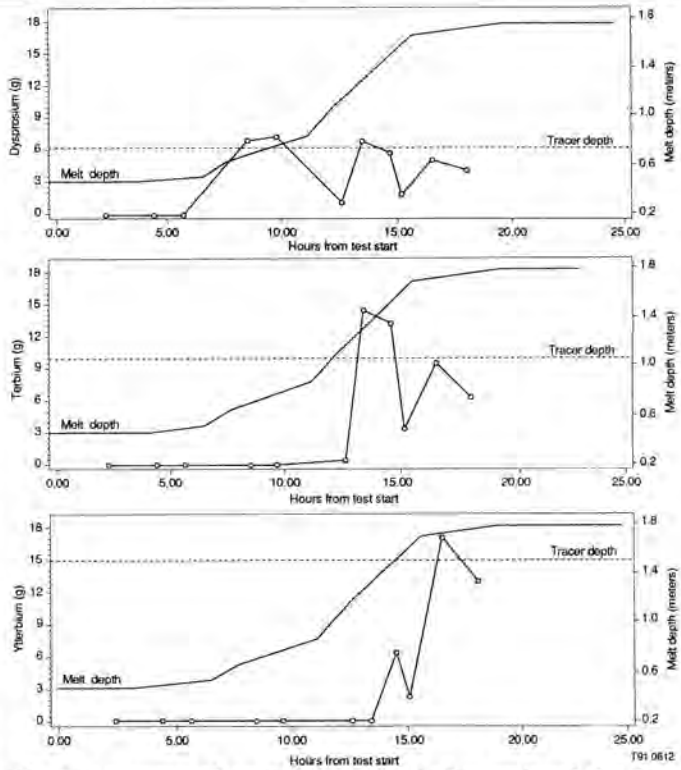

Fig. 3. Amounts of tracer in scrub solution and melt depth as a function of time during Test 1 for Dysprosium, Terbium, and Ytterbium. Dashed line shows depth of burial of tracer.

there is a difference between amounts measured in Posttest 1 and Posttest 2.

The tracer amounts measured in the scrub solutions during Test 2 are plotted in Fig. 4 against hours from the start of the test. The depth of the melt front and Dy burial depth are also shown. There is no apparent release of Dy during the test, and all three tracers exhibit a similar pattern. There is also no apparent difference** between pretest and posttest (actually last available data point) values. The magnitudes of the

TABLE III

Soil Tracer Analysis Means and Standard Errors for the Means in mg/kg

Location	Time	Media	Soil Location	Dy Mean	Dy Standard Error	Yb Mean	Yb Standard Error
Test 1	Pretest	Soil		2.08	0.091	0.90	0.036
Test 1	Posttest	Soil	Bottom, 12 in	2.40	0.100	2.15	0.650
Test 1	Posttest	Soil	Bottom, 6 in	2.65	0.050	1.15	0.050
Test 1	Posttest	Soil	Side, 12 in	2.50	0.100	3.00	1.901
Test 1	Posttest	Soil	Side, 6 in	2.45	0.050	1.05	0.050
Test 2	Posttest	Soil	Bottom, 12 in	2.60	0.058	.	.
Test 2	Posttest	Soil	Bottom, 6 in	2.45	0.150	.	.
Test 2	Posttest	Soil	Side, 12 in	2.20	0.000	.	.
Test 2	Posttest	Soil	Side, 6 in	2.00	0.000	.	.

* Student's t tests were performed using a family confidence level of 95% for Dy for both tests and also for Yb for Test 1.
** No direct estimates of uncertainty are available to test this hypothesis.

amounts in the scrub tanks during the test are all much less than peak values for Test 1. The data appear to represent residual tracer amounts from Test 1.

All of the tracers were detected in three samples of the primary HEPA filter for Test 2, even those added to Test Pit 1 and not Test Pit 2. The tracer added to Test Pit 2 (Dy) was present at levels comparable to those added to Test Pit 1 and not Test Pit 2, indicating that Test 2 may not have contributed to HEPA filter tracer amounts. The upper 90% confidence limit for the mean concentration of Dy, 1.28 mg/kg, implies that only about 4.3 mg of Dy was retained on the 3.36 kg filter.

Dy was detected in all four Posttest 2 composite soil samples. However, as for Test 1, there were no significant differences between pretest tracer concentrations in soil and concentrations measured in soil samples collected at specific distances from the Test 2 product block.

Discussion

Differences in pit configuration and unplanned differences in test operations could have influenced the released tracer amounts. Test Pit 1 was processed more rapidly than Pit 2 and Test 2 processing was characterized by a uniform heating of the buried waste region with few transient spikes as compared to Test 1. Comparison between tests is confounded by the test design; three different tracers were used in Test 1, but only one tracer in Test 2 and the one common tracer between the two tests (Dy_2O_3) was buried at different depths in the two tests.

The data suggest that Dy may not have entered the hood and off-gas system in Test 2, whereas tracer release occurred in Test 1. This may be due to the test operational differences; the Test 2 process strategy may act to promote retention of elements in the glass while a less quiescent melt with more active gas releases, such as in Test 1, may promote more tracer compound entrainment and release into the off-gas system.

CONCLUSIONS

The results indicated that the majority of each tracer was retained in the vitrified products. Also, the tracer concentrations were relatively homogeneous throughout the glass and crystalline products. Tracer concentrations in soil adjacent to the products were not significantly different from pretest measurements.

In Test 1, tracers were detected in the hood and off-gas system. Order-of-magnitude estimates for amounts of tracer materials released into the off-gas system for Test 1 were several grams to several tens of grams. This corresponds to up to several percent of the amounts initially added to the pit.

Tracers were detected in Test 1 off-gas scrub solutions as the melt reached the depth of tracer burial. The relative amounts of tracers measured, Yb > Tb > Dy, did not correspond to the relative amounts buried.

The detection of tracer on the air inlet filter indicates that mechanisms such as entrainment may be significant contributors to tracer element release from the melt. Tracer material could only be transported to the air inlet filter during the short time periods when the hood experienced positive pressure transients sufficient to cause reverse air flow in the inlet line. During both tests, a number of positive pressure spikes were detected in the hood plenum (1).

The results of tracer analysis of the hood and off-gas system in Test 2, although somewhat ambiguous, indicate that the tracer added to the test pit, Dy, did not enter the system. It is possible that this is because the melt was a more quiescent one, but the evidence is not conclusive.

The results of the tracer study suggest the need for further effort to estimate the potential for radionuclide release. The tracer data suggest that retention of tracers may be less than retention previously reported for plutonium (2) (i.e., plutonium retention >99.9%). It is not certain if the differences are due to chemical differences between tracers and plutonium, or differences in element release for buried waste ISV processing as compared to processing of contaminated soil. The more dynamic melt off-gasing processes observed in these tests may enhance element release from the melt. Further work is needed to quantify element release from the melt, and to correlate tracer release with expected plutonium release from the melt. Work is being conducted (3) to understand the likely mechanisms of tracer release and to improve the theoretical basis for predicting tracer and Pu behavior and transport during ISV. This information is needed to optimize equipment design for large-scale production processing equipment that will remove and contain any released fractions from the off-gas stream for processing in subsequent melts.

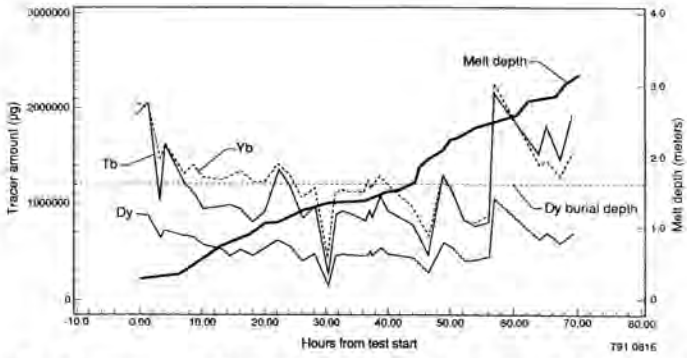

Fig. 4. Amounts of tracers Dy, Tb, and Yb in scrub solution and melt depth during Test 2. Burial depth of Dy is indicated.

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