



THE EXTRACTION AND TRANSPORT OF RADIONUCLIDES  
PRODUCED IN SOIL BY HIGH ENERGY HADRONS

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INTRODUCTION

Most of the high energy protons which stop in a dense medium initiate a cascade of secondary hadrons. These secondaries can induce radioactivity in the surrounding materials. Radioactivity produced in this fashion has been observed in the earth shielding adjacent to the C.E.R.N. Proton Synchrotron<sup>1</sup>.

Radionuclides produced underground may be leached from the soil by natural percolating ground water and transported downward to the silurian aquifer. The surviving long-lived radionuclides can then be carried beyond the boundaries of a controlled site by the horizontally flowing water in the aquifer, and thus contaminate the waters in uncontrolled areas.

For a given geological situation, it is possible to prevent ground water contamination beyond permissible levels by

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attenuating the secondary hadron flux with massive insoluble shields. However, this method is impractical because of the expense. Thus, in order to optimize the design of hadron shields or beam dumps one must know the amount of leachable radioactivity produced in the soil. With this information and knowledge of the geology<sup>2-3</sup> and hydrology<sup>4</sup> of the area, one may employ a more effective approach to efficient and inexpensive shielding designs.

Glacial till from the construction site of the National Accelerator Laboratory was exposed to a high energy hadron flux produced near an internal target of the Zero Gradient Synchrotron at the Argonne National Laboratory. Radiochemical analyses were performed to determine the concentrations of radionuclides produced in the irradiated soil. Leaching experiments were then carried out to obtain distribution coefficients from which transport rates were calculated.

#### Soil Irradiation

Approximately five kilograms of soil were collected from the construction site of the National Accelerator Laboratory. The sample consisted of glacial till retrieved from a depth just below the designed level of the proton beam (722.5 ft). The approximate chemical composition is listed in Table I<sup>5</sup>.

This soil was placed next to the L-3 target straight section of the Argonne National Laboratory's Zero Gradient Synchrotron. More specifically, it was located at beam

elevation and three feet downstream from the lead shielding surrounding the target. An aluminum disc was placed next to the soil as an activation detector for the purpose of integrating the incident hadron flux.

After a 75 day exposure under normal ZGS duty cycle, the soil and disc were removed from the accelerator enclosure and prepared for analysis.

#### Hadron Flux Determination

A determination of the  $^{22}\text{Na}$  induced in the aluminum disc was made several days after the end of the exposure when the background from short-lived isotopes was considerably reduced. The 560 g disc was counted for 10 minutes on a NaI(Tl) crystal. The measured  $^{22}\text{Na}$  activity after background subtraction was  $74 \pm 7$  dpm/g of aluminum.

The hadron flux incident on the soil and disc can be obtained from the relationship

$$R = \Phi * \sigma * N$$

where

R = rate of production of  $^{22}\text{Na}$  per g of Al

$\Phi$  = incident flux (hadrons/cm<sup>2</sup> . sec)

N = nuclei/g =  $N_0/A$

$\sigma$  = cross-section (cm<sup>2</sup>) for  $^{27}\text{Al}$  (N, 3p3n)  $^{22}\text{Na}$  (6)

Above threshold energy (30 MeV) the cross-section is assumed to be independent of energy and of the type of incident hadron. Barish has shown that the total flux (nucleons and charged pions) in a concrete block next to an

iron cylinder with 3 GeV incident protons is predominately due to neutrons<sup>7</sup>.

At saturation, the rate of production of <sup>22</sup>Na equals the rate of decay. Thus, the measured activity at time t after termination of the exposure is

$$\begin{aligned} A(t) &= {}^{22}\text{Na (sat)} (1 - e^{-\lambda t_i}) e^{-\lambda t} \\ &= \phi * \sigma * N * (1 - e^{-\lambda t_i}) e^{-\lambda t} \end{aligned}$$

where  $t_i$  is the length of irradiation (75 days) and  $t$  = decay time (13 days). From counting results of the aluminum disc

$$A(13 \text{ d}) = 1.23 \text{ dps/g} = \phi * 2.34 \times 10^{-5}$$

and

$$\phi = 5.25 * 10^4 \text{ hadrons/cm}^2 \cdot \text{sec}$$

with energy above 30 MeV.

### Soil Analysis

#### Preliminary Work.

In preparation for receipt of the activated soil, a series of preliminary tests were conducted on comparable non-activated soil. This soil was glacial till obtained from a location close to the area from where the irradiated sample was taken.

These preliminary studies included the measurement of (1) moisture content (by drying at 400-450°C); (2) natural radioactivity (using gamma spectrometry and liquid scintillation spectrometry; (3) density (by water displacement).

These results are listed in Table II. In addition, a series of experiments were performed to determine the most practical approach for measuring the leachability of elements from the soil. The techniques tested were: (1) columns made from cored samples of undisturbed glacial till; (2) columns packed with soil and mixtures of soil and washed sand; (3) batch processing by directly mixing soil and water in various ratios. Due to the extremely low porosity of the soil (natural water flow rate <10 ft/yr) the batch procedure was adopted as the most feasible method to determine reasonable leaching factors in a relatively short period of time.

It is assumed that natural percolating ground water has established equilibrium with respect to the soil for all ions and solids by the time it has passed through the upper strata of soil and reached the vicinity of the activated soil. Preferably, water of this equilibrium composition should be used as the leaching agent. Various samples of water were tested as leaching agents which would best represent actual environmental conditions. Water obtained from several sequential batch experiments and slow flowing columns, as well as surface water and deep well water from the NAL site were tested for total solid content and Na, Mg and Ca concentrations. Since the differences in composition between these synthesized waters and deep well water were small, the latter was chosen as the leaching water for the batch processing experiments. A summary of the properties of this water is given in Table III.

### Leaching Procedure

The usual batch procedure used a ratio of 10 parts water to 1 part soil - usually 1000 g H<sub>2</sub>O with 100 g soil. To determine the total activity in the soil, the sample was first mixed with 20 ml leaching water. The resulting slurry was centrifuged to a uniform geometry in an 8 oz polyethylene bottle. This mixture was then counted on both a 4" x 4" NaI (Tl) crystal and then on a Ge(Li) crystal for 100 minutes.

The soil was then transferred to a 1 liter flask with the remaining fraction of leach water. After vigorous shaking to disperse the soil in the liquid, the mixture was stirred (for usually 1 hour) to maintain good suspension of the soil in water. The equilibration was carried out at room temperature (22-25°C) at the pH(7.3-7.9) of the natural water.

The water was then separated (centrifuged) from the soil. This leached soil was recounted to measure the loss of activity. All soil activities were normalized to one gram of soil with normal water content. The hazy leaching water was filtered through a Millipore filter (0.45μ) and then evaporated to near dryness. During evaporation 15-20 ml condensate was collected for tritium measurement. The solids were then transferred with dilute HNO<sub>3</sub> to a 4 oz polyethylene bottle, diluted to 50 ml and counted on the 4" x 4" NaI (Tl) crystal. The activity was too low to be counted on the Ge(Li) detector in a reasonable length of time. In addition, the high resolution of the Ge(Li) system was not needed to identify the

activities of the leach water.

The leach water was also counted for activity by liquid scintillation spectrometry. From the latter measurements,  $^{45}\text{Ca}$  and  $^{54}\text{Mn}$  were found in the water. These two isotopes were then chemically separated. The  $^{45}\text{Ca}$  was measured by liquid scintillation counting and the  $^{54}\text{Mn}$  by gamma counting. The liquid scintillation pulse height spectra were examined by coupling the system to a multichannel analyzer<sup>8</sup>.

The chemical separation of the Mn and Ca was obtained by coprecipitating the  $^{54}\text{Mn}$  on  $\text{MnO}_2$  [Mn(II) and Mn(VII) carriers were added to the water] from dilute  $\text{HNO}_3$  at elevated temperatures ( $90^\circ\text{C}$ ). The  $\text{MnO}_2$  was filtered and mounted on a planchet for counting, and the filtrate was saved for the  $^{45}\text{Ca}$  activity determination. The  $^{45}\text{Ca}$  was coprecipitated with non-activated Ca carrier from the filtrate as the phosphate and hydroxide by addition of  $\text{H}_3\text{PO}_4$  and  $\text{NH}_4\text{OH}$ . The precipitate was dissolved in  $\text{HNO}_3$  and transferred to a liquid scintillation vial with water. Scintillation solution was then added. The sample was counted as a gel at  $4^\circ\text{C}$  in a Packard Model 3320 liquid scintillation spectrometer.

Separations and measurements were also made to determine the presence of  $^{55}\text{Fe}$  in the leach waters. The  $^{55}\text{Fe}$  was ultimately separated by extraction into HDEHP\* - toluene from 0.3N HCl. The resulting extract was counted by liquid scintillation methods.

\* di-2-ethylhexylphosphoric acid

Additional leaching experiments were performed after initial results were obtained. The variations in these leaching conditions will be explained under results and discussion.

All counting procedures were calibrated by the use of appropriate radioactive standards and controls.

#### Calculations

In order to design the insoluble part of the beam dump, one needs to know the behavior of the leachable radioactivity under actual soil conditions. Since batch processing is not a direct analog of water passing through compacted soil, it is necessary to calculate the distribution ( $K_d$ ) which under equilibrium conditions is the ratio of the concentration of an isotope remaining in the soil per unit weight of soil to the concentrations of isotope leached per unit volume of solution. The larger the distribution coefficient, the slower the flow of the radioactive element with respect to the flow of the solution.

The distribution coefficient for a given radioactive isotope is<sup>9</sup>

$$K_d = \frac{f_m * L_v}{f_s * M_w}$$

where

$$K_d = \text{ml/g}$$

$f_m$  = fraction of activity absorbed on the soil

$M_w$  = weight of the soil in grams

$L_v$  = volume of solution (ml) equilibrated with  $M_w$

$f_s$  = fraction of activity in solution =  $1 - f_m$

Using  $K_d$  one can calculate the rate of movement  $R$  of the ion relative to the water movement<sup>10</sup>

$$R = \frac{1}{(K_d * \rho_e) + 1}$$

$\rho_e$  = exchange ratio (i.e., weight of soil seen by a unit volume of solution) =  $\rho_b/p$

$\rho_b$  = bulk density = weight of soil dried at 105°C/  
volume occupied = 1.81 g/cc

$p$  = porosity = fraction of total volume occupied by water, air, etc., (i.e., portion of soil not occupied by solid particles) = 0.294.

For a comparison to column conditions, the batch  $K_d$  may be used to determine the peak position of activity; that is, the position in a column where the ratio of activity to the initial activity is a maximum:<sup>11</sup>

$$C_p = \frac{K_d * \rho * (1-p)}{p}$$

where

$C_p$  = position of maximum concentration in pore volumes minus one pore volume

$\rho$  = grain density (same as  $\rho_b$  above) in g/cc

$p$  = porosity (same as  $p$  above).

### Results

The concentrations of radionuclides with half-lives greater than 30 days detected in the activated soil are listed in Table IV. The results of the radiochemical analysis of the leach waters are listed in Table V. A discussion of each of the leachable elements follows.

$^{22}\text{Na}$ 

The peak position  $C_p$  for  $^{22}\text{Na}$  activity corresponds to 324 pore volumes of solution passing through a column. The values presented in Table V are valid only if the leached activity is due to a true equilibrium exchange process. However, when second and third leachings were performed on the same soil samples, much lower concentrations of  $^{22}\text{Na}$  were found in the water. Both the second and third leach waters contained only 2% of the total activity (i.e.,  $K_d \sim 490$  ml/g).

This consistency on subsequent leachings indicates that equilibrium leaching was being effected. Therefore, the first leaching results are not indicative of the ionic Na exchange rate, but are actually due more to wash out processes. This wash out was verified by varying soil to water ratios in further leaching experiments. It thus appears that  $\sim 10\%$  of the  $^{22}\text{Na}$  is created in the water content of the soil and would leach out at essentially the same rate as the water front, and an additional 2% is picked up by exchange processes. Assuming  $\sim 20$ -25 ft of till below the point of formation, and a flow rate of  $\sim 5$  ft/yr, then roughly 1-2 half-lives will have passed before the  $^{22}\text{Na}$  reaches the aquifer. Thus, neglecting further exchange  $\sim 2$ -3% of the  $^{22}\text{Na}$  formed would reach the aquifer at a steady rate. Based on the  $^{22}\text{Na}$  uptake experiments, re-exchange of the  $^{22}\text{Na}$  back into the "cold" soil below the point of activation is apparently very slow. This low rate of re-exchange is probably due to the relatively small concentration

of stable Na in the regular soil.

$^{54}\text{Mn}$  and  $^{45}\text{Ca}$

Since a relatively high total  $\beta$  activity (~130 cpm above control level) was observed in the leach water liquid scintillation samples, a spectral analysis was performed and it was determined that the  $\beta$  activity resulted from the presence of  $^{54}\text{Mn}$  and  $^{45}\text{Ca}$ . Consequently, the leach waters were analyzed for  $^{54}\text{Mn}$  and  $^{45}\text{Ca}$  by the chemical separation and liquid scintillation techniques discussed earlier.

$^3\text{H}$

Water collected during the bake out of a sample of soil yielded a  $^3\text{H}$  concentration of 190.5 dpm/ml which is equivalent to 26.6 dpm  $^3\text{H/g}$  of soil (water concentration of soil was 0.14  $\text{H}_2\text{O/g}$  of soil). A sample of water (excess moisture) which had evaporated from the irradiated soil and condensed on the container yielded a  $^3\text{H}$  concentration of 189 dpm/ml. When the leach waters were counted directly for  $^3\text{H}$  and corrections made for the amount of other activity present in the sample, the  $^3\text{H}$  in the leach water was calculated to be 184 dpm/ml.

Conclusions

Of the long-lived (>30 days) radionuclides identified in the soil and under batch processing extraction, the measured

- a) the measured  $^3\text{H}$  is totally leached
- b) approximately 12% of the  $^{22}\text{Na}$  is removed by a combination of wash out and exchange leaching

- c) approximately .29% of the  $^{54}\text{Mn}$  is leached, and
- d) the  $^{45}\text{Ca}$  leached was not measured as a fraction of the total  $^{45}\text{Ca}$  formed.

The leached  $^3\text{H}$  is expected to move with the same rate as the natural ground water as it passes through subsequent layers of soil. Very little of the leached  $^{22}\text{Na}$  is re-exchanged as it passes through "cold soil" and the same is expected for the leached  $^{45}\text{Ca}$  and  $^{54}\text{Mn}$ .

Table V gives the activity concentration of radionuclides leached into the water of the batch extraction process. These amounts may be used to calculate upper limits to the transferable radioactivity from the silt to the vertically flowing water.

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TABLE I

Elemental Composition of Soil

<u>Element</u>	<u>Z</u>	<u>% by Wt. of Dry Soil</u>
O	8	50.80
Si	14	25.70
C	6	3.73
Al	13	6.20
Ca	20	6.84
Mg	12	2.35
Fe	26	3.27
K	19	0.58
Na	11	0.45

TABLE II

Summary of Control Soil Measurements

Average Density	2.1 - 2.2 g/cm <sup>3</sup>
Moisture Content	0.2 g H <sub>2</sub> O/g soil
Natural Radioactivity	<sup>3</sup> H, Radium Daughters, <sup>40</sup> K

TABLE III

Properties of NAL Deep Well Water

<u>Element</u>	<u>µg/ml</u>	
Na (a)	57.5	Total Solids - 0.51 mg/ml
Ca (b)	70	pH - 7.3 - 7.9
Mg (b)	26	

(a) By flame spectroscopy

(b) By atomic absorption

TABLE IV

Radionuclides <sup>(a)</sup> in Activated Soil for an Incident Flux of  
 $5.2 \times 10^4$  Hadrons  $\text{cm}^{-2} \text{sec}^{-1}$  with  $E_H > 30$  MeV

Radionuclide	$T_{1/2}$	dpm/gm <sup>(b)</sup>	pCi/gm	Method of Measurement
<sup>7</sup> Be	53d	805	366	$\gamma$ Spectroscopy
<sup>22</sup> Na	2.6y	573	260	$\gamma$ Spectroscopy
<sup>45</sup> Ca	163d			Liquid Scintillation
<sup>54</sup> Mn	312d	164	74.5	$\gamma$ Spectroscopy
<sup>55</sup> Fe	2.4y			
<sup>46</sup> Sc	83.8d	83.8	38.1	$\gamma$ Spectroscopy
<sup>3</sup> H	12.26y	26.6	12.1	Liquid Scintillation <sup>(c)</sup>

(a) Half-lives  $>30$  days. Other induced nuclides with half-lives  $<30$  days were also identified: <sup>47</sup>Sc, <sup>48</sup>Sc, <sup>48</sup>V, <sup>51</sup>Cr, <sup>52</sup>Mn, <sup>24</sup>Na. Trace amounts of these longer lived isotopes were detected: <sup>57</sup>Co, <sup>58</sup>Co, <sup>59</sup>Fe, <sup>65</sup>Zn.

(b) Corrected to saturation levels.

(c) Measurable tritium present in the soil, as determined from the water in the soil.

TABLE V

Radionuclides <sup>(a)</sup> in Leach Water for Incident Flux of  
 $5.2 \times 10^4$  Hadrons  $\text{cm}^{-2} \text{sec}^{-1}$  with  $E_H > 730$  MeV

Radionuclide	pCi/g H <sub>2</sub> O	dpm/g Soil	pCi/g Soil	% Leached	K <sub>d</sub> (ml/g)
<sup>3</sup> H	86	26.6	12	100	
<sup>22</sup> Na	230	69	32	12	490 <sup>(c)</sup>
<sup>45</sup> Ca	43	13	6		
<sup>54</sup> Mn	21	5	2	.29	347

(a) Normalized to saturation equilibrium:

<sup>7</sup>Be, <sup>55</sup>Fe, <sup>46</sup>Sc and other trace isotopes were not found in the leach H<sub>2</sub>O.

(b) Measured moisture content of soil is 14% by weight.

(c) Calculated for the <sup>22</sup>Na leached by exchange processes (2%).