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Äspö Hard Rock Laboratory

Tracer Retention Understanding Experiments

Continued sampling and tracer measurements in the TRUE-1 experiment and TRUE Block Scale experiment, Phase C

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October 2002

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

Abstract

Results of an additional sampling and measurement programme within the Tracer Understanding Experiment (TRUE) are presented in this report. At the two different sites at Äspö Hard Rock Laboratory, TRUE-1 site and at the TRUE Block scale site, experiments with radioactive tracers had been performed earlier and this work gives complementary data to the earlier works.

At the TRUE-1 site, sampling was performed after ~3 years of stationary phase of no pumping or sampling at the site. The results of the measurements showed that the tracers remaining from the earlier injections, i.e., $^{134}\text{Cs}^+$ and $^{137}\text{Cs}^+$, was only found in the borehole sections in connection to the Feature A (i.e., the fracture that had previously been used for the STT1 and STT2 tracer experiments). No traces of migration of these tracers to the adjacent features could be measured which can be seen as a support of the assumptions applied in the structural model of the TRUE-1 site.

The continued sampling and measurement of the TRUE Block Scale Phase C experiment gave continuous breakthrough data for the tracers $^{134}\text{Cs}^+$ (injection C1), $^{22}\text{Na}^+$ (injection C3) together with $^{54}\text{Mn}^{2+}$ and $^{57}\text{Co}^{2+}$ (injection C4). Additionally, enrichments were performed in order to decrease the detection limits for tracers that not could be measured in the previously reported γ -spectrometry measurements. Cs^+ and Rb^+ were selectively separated on ammonium-molybdenum phosphate (AMP) which increased the detectability of the $^{137}\text{Cs}^+$ (injection C2) and $^{83}\text{Rb}^+$ (injection C3) tracers. By applying AMP separation, a breakthrough curve was obtained for $^{137}\text{Cs}^+$ which is presented in this report. A single data-point indicating a breakthrough for $^{83}\text{Rb}^+$ was also obtained; the relatively short half-life of this tracer made further studies of this tracer impossible.

Sammanfattning

Resultat av kompletterande provtagning och mätningar inom ramen för Tracer Retention Understanding Experiments (TRUE) redovisas i denna rapport. Det aktuella arbetet ger kompletterande resultat till undersökningar som tidigare genomförts på TRUE-1-siten och TRUE Block Scale-siten i Äspölaboratoriet.

På TRUE-1-siten genomfördes provtagning c:a 3 år efter en stationär period då ingen pumpning eller provtagning genomförts. Resultatet av de efterföljande mätningarna visade att spårämnen, $^{134}\text{Cs}^+$ och $^{137}\text{Cs}^+$, endast fanns kvar i sektioner i kontakt med Feature A. (Denna struktur har tidigare utnyttjats för spårförsök STT1 och STT2). Inga spår av migration av dessa spårämnen till närliggande strukturer kunde noteras. Detta kan betraktas som ett stöd för de antaganden som ligger till grund för den strukturella modellen över TRUE-1-siten.

Den fortsatta provtagningen och mätningen av Phase-C experimentet inom ramen för TRUE Block Scale har på kontinuerlig basis givit genombrottsdata för $^{134}\text{Cs}^+$ (Injektion C1), $^{22}\text{Na}^+$ (Injektion C3) tillsammans med $^{54}\text{Mn}^+$ och $^{57}\text{Co}^{2+}$ (båda injicerade under C4). Vidare genomfördes anrikningar för att sänka detektionsgränsen för spårämnen som inte kunde mätas i de tidigare rapporterade γ -spektroskopimätningarna. Cs^+ och Rb^+ separerades selektivt med hjälp av ammonium-molybdenfosfat (AMP) som ökade detekterbarheten för $^{137}\text{Cs}^+$ (Injektion C2) och $^{83}\text{Rb}^+$ (Injektion C3). Genom utnyttjande av AMP-separation har en genombrottskurva erhållits för $^{137}\text{Cs}^+$ som presenteras i denna rapport. En enskild datapunkt som indikerade genombrott även för $^{83}\text{Rb}^+$ erhöles också. Den korta halveringstiden för den senare tracern omöjliggjorde dock fortsatta studier av detta möjliga genombrott.

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1 Introduction

Within the some of the TRUE project experiments, TRUE-1 (Winberg et al. 2000) and TRUE Block Scale experiment, phase C (Andersson et al. 2002) injections of different radioactive tracers were done. Since most of the radioactive tracers used were sorbing species, the breakthrough of these tracers were comparatively slow and, consequently, complete recovery for these tracer had not been obtained when the final reporting of these projects was performed. In fact, for some tracers, no breakthrough whatsoever had been obtained. It was thus decided to continue the pumping and measurements in a low-intense stage. This report will give the results of the continued sampling and measurements of the project; activities performed during 2001-2002

1.1 TRUE-1

Injections of radioactive tracers within the TRUE-1 project at the Feature A were performed in three different campaigns, June 1997, December 1997 and June 1998. The last sample was taken 1998-10-11 and since then no experimental activities have been performed in that site. During 2001, some experimental activities were initiated in the “TRUE-1 continuation programme” (Winberg 200X) which included some sampling of the different boreholes at the TRUE-1 site. During this sampling, γ -spectrometry measurement of the sampled water was performed and up-dated information of the present status of concentration of radioactive tracers was obtained. These results will be presented in this report.

1.2 TRUE Block Scale

For the TRUE-Block Scale phase C tracer experiment (Andersson et al. 2002) four different injections of radioactive tracers were performed during the period June 2000 – September 2000. An intensive sampling was performed during the whole fall 2000 and it was decided to continue the pumping in 2001, combined with an extensive sampling and measurement programme. In this note, the results of the measurements will be presented and the results will be given as an up-date of the different breakthrough curves of the experiment. Besides that, results of different selective enrichment experiments (aimed to decrease the detection limits for tracers that had not been recovered earlier) will be presented in this report.

2 Experimental results and discussion

2.1 TRUE-1

2.1.1 Sampling 2001-10-17

The sampling 2001-10-17 was aimed for obtaining measurements of the concentration of radioactive tracers and measurements of the chemical conditions at the different borehole sections in the TRUE-1 site after the long stationary phase of no pumping or sampling at the site. Unfortunately, only three samplings had been performed when a packer failure caused an uncontrolled flow out of the KXTT1 borehole. This failure was suspected to have caused a large flow and mixing of the water in the Feature A boreholes so a continuation of the samplings at that moment was considered as meaningless. However, measurement of the radioactive tracers in the sampled water was performed and the results are presented in Table 2-1. As can be seen, there is a small indication of $^{137}\text{Cs}^+$; otherwise, no tracer could be quantified with the rather short γ -spectrometry measurements time applied. (i.e., 0.5-1 h)

Table 2-1 Results of γ -spectrometry measurements of samples taken 2001-10-17. The concentrations are given in Bq/kg and decay correction to the sampling time has been performed.

Borehole section	KXTT1:2	KXTT2:2	KXTT3:2
Fracture system	Feature A	Feature A	Feature A
Na-22	<1.9	<1.8	<2.7
Ba-133	<2.3	<3.2	<2.4
Cs-134	<1.8	<2.0	<2.7
Cs-137	<2.0	1.9±0.9	<2.4

2.1.2 Sampling 2001-11-22

One week after the packer failure the borehole KXTT4 was re-instrumented; involving that the former borehole section KXTT4:R2 was split up into two new sections, KXTT4:S1 and KXTT4:S2. Approximately one month after the re-instrumentation, sampling of the Feature A borehole sections as well as all the borehole sections in KXTT4 were sampled. In the sampling and γ -spectrometry measurements, the newly constructed Marinelli steel-beaker device was used (cf. Byegård et al. 2002). The results of the γ -spectrometry measurements are given in Table 2-2. As expected, a comparative high concentration of the Cs isotopes can be found in the sections corresponding to the old injection section in the STT1 and STT2 experiment. Small amounts of $^{137}\text{Cs}^+$ can also be seen in all of the borehole sections that have contact with the Feature A section.

Table 2-2 Results of the γ -spectrometry measurements of samples taken 2001-11-22. The concentrations are given in Bq/kg and decay correction to the sampling time has been performed.

Borrhole section	KXTT1: R2	KXTT2: R2	KXTT3: R2	KXTT4: S2	KXTT4: S3	KXTT4: S4	KXTT5: R2
Fracture system	Feature A	Feature A	Feature A	Feature A	Feature A	Feature B	Feature A
Na-22	<2.5	<1.9	<2.1	<2.5	<2.1	<2.2	<1.0
Ba-133	<4.2	<3.7	<2.8	<3.8	<2.6	<2.2	<2.1
Cs-134	<3.6	<2.3	3.1±0.9	146±4	46±2	<2.1	<3.6
Cs-137	3±1	6±1	2.8±0.9	218±4	59±2	<2.1	<2.3

2.1.3 Sampling in the period 2001-12-10 to 2001-12-12

In the period 2001-12-10 to 2001-12-12 the vast majority of the borehole section in the TRUE-1 target area was sampled and measured. The procedures applied were the same as mentioned for the sampling 2001-11-22. The results are presented in Table 2-3 and they are in line with the observations made in the earlier samplings. Traces of $^{137}\text{Cs}^+$ is found in all Feature A borehole sections; except for KXTT5:R2 which has been interpreted to be upstream of the injection section with respect to the natural gradient in Feature A. No traces of tracers can be observed in any borehole section associated to any other fracture system than Feature A.

Table 2-3 Results of the γ -spectrometry measurements of samples taken 2001-12-10 to 2001-12-12. The concentrations are given in Bq/kg and decay correction to the sampling time has been performed.

Borehole section	KXTT1: R2	KXTT2: R2	KXTT3: R2	KXTT4: S2	KXTT4: S3	KXTT5: R2	KA3005 A:R3
Fracture system	Feature A	Feature A	Feature A	Feature A	Feature A	Feature A	Feature A
Na-22	<1.6	<4.9	<2.8	<2.3	<1.4	<3.9	<4.5
Ba-133	<3.4	<4.8	<3.2	<5.5	<2.5	<5.7	<5.8
Cs-134	3±1	<3.9	<3.2	135±5	43±3	<5.0	<4.6
Cs-137	3±1	7±2	4±1	209±4	57±4	<4.6	6±2

Borehole section	KXTT1: R1	KXTT3: R1	KXTT5: R1	KXTT2: R1	KXTT2: R5
Fracture system	NW-2'	NW-2'	NW2, NW-2'	?	Feature D
Na-22	<3.1	<3.7	<4.9	<4.5	<2.5
Ba-133	<2.6	<5.8	<6.7	<4.8	<2.7
Cs-134	<3.0	<3.8	<5.0	<5.1	<3.1
Cs-137	<3.2	<3.8	<3.4	<3.7	<2.5

Borehole section	KXTT1: R3	KXTT2: R3	KXTT3: R3	KXTT4: R4	KA3004 A:R2
Fracture system	Feature B	Feature B	Feature B	Feature B	Feature B
Na-22	<2.0	<3.1	<4.3	<1.8	<3.0
Ba-133	<2.4	<2.9	<4.7	<6.5	<2.3
Cs-134	<2.9	<3.0	<3.5	<5.3	<3.3
Cs-137	<1.8	<2.2	<3.7	<3.6	<2.8

2.2 TRUE Block Scale Experiment

2.2.1 Sampling and γ -spectrometry measurements, 2001-2002

The last data-set delivered for the Phase C part of the TRUE Block Scale includes data from samples until 2000-11-01 (Andersson et al. 2002). An extensive sampling from the withdrawal water was continued after that and the results of the γ -spectrometry measurements are illustrated in Figures 2-1 to 2-4. The detailed database is given in Appendix A. As can be seen, the tracers that were possible to follow during this entire period were $^{134}\text{Cs}^+$ (injection C1), $^{22}\text{Na}^+$ (injection C3) and $^{54}\text{Mn}^{2+}$ (injection C4). Besides that, the tracer $^{57}\text{Co}^{2+}$ could be followed for a part of the period.

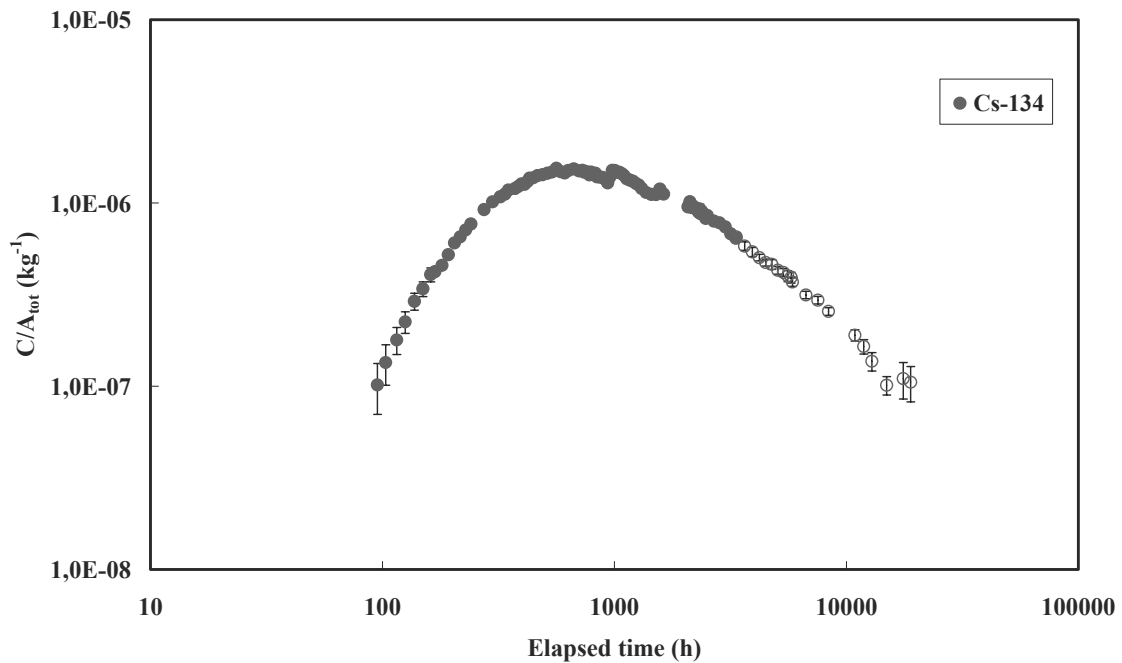


Figure 2-1 Results of the continued sampling and γ -spectrometry measurements of $^{134}\text{Cs}^+$, injection C1. The results are given as the measured tracer concentration, C , (Bq/kg) in the withdrawal water divided by the total amount of tracer, A_{tot} , (Bq) used in the injection. The filled circles refer to the result given in the previous report (Andersson et al 2002) and the open circles refer to results measured during the continuation part of the TRUE Block Scale Phase C experiment.

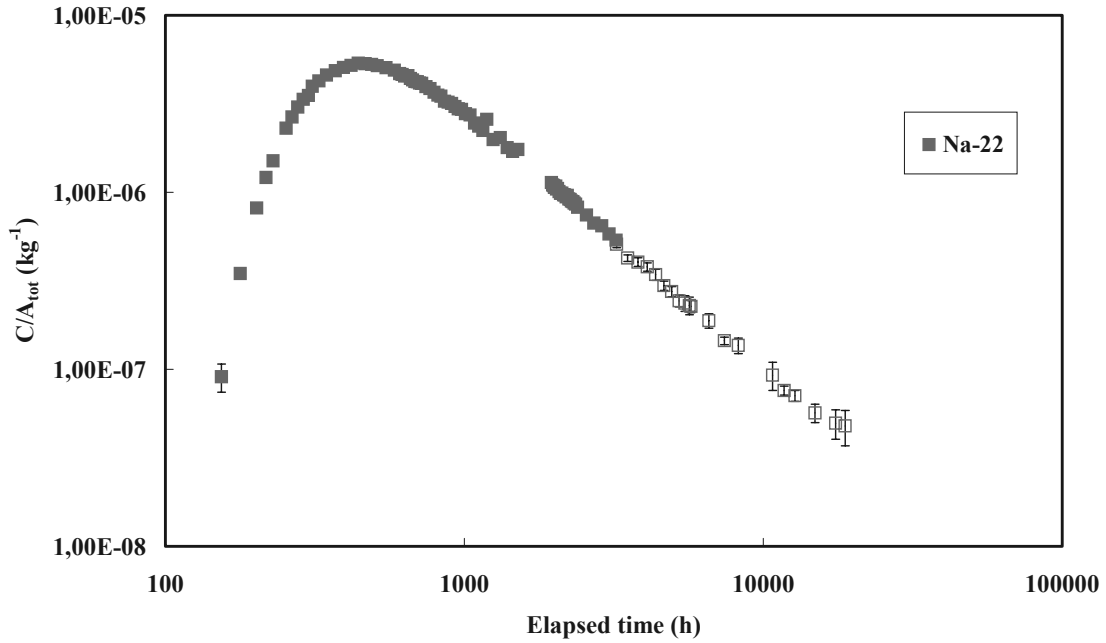


Figure 2-2 Results of the continued sampling and γ -spectrometry measurements of $^{22}\text{Na}^+$, injection C3. The results are given as the measured tracer concentration, C , (Bq/kg) in the withdrawal water divided by the total amount of tracer, A_{tot} , (Bq) used in the injection. The filled squares refer to the result given in the previous report (Andersson et al 2002) and the open squares refer to results measured during the continuation part of the TRUE Block Scale Phase C experiment.

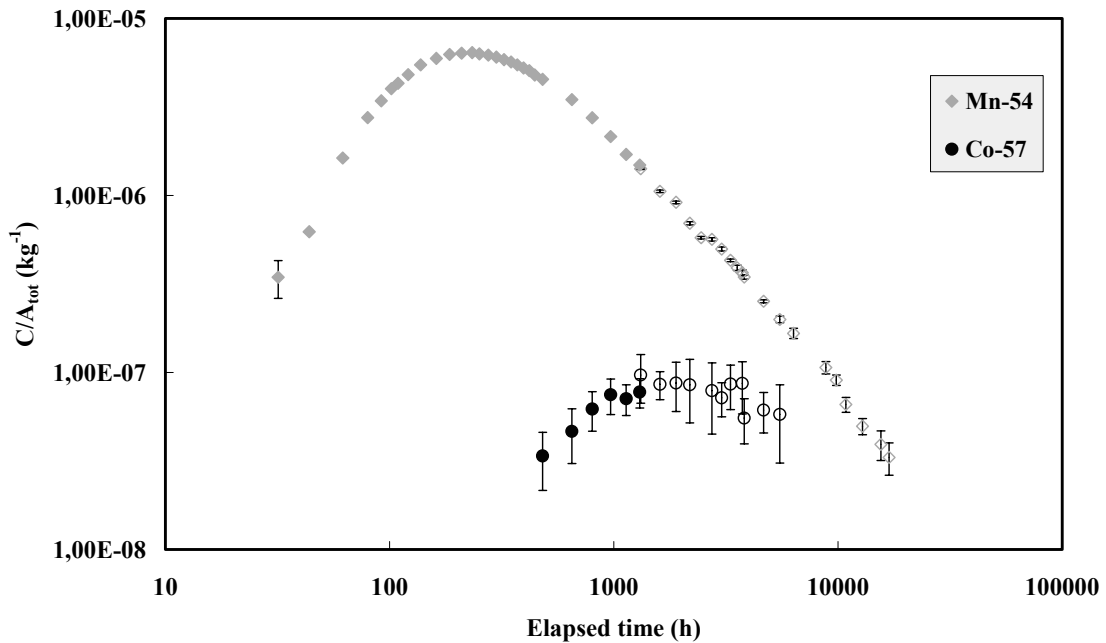


Figure 2.3 Results of the continued sampling and γ -spectrometry measurements of $^{54}\text{Mn}^{2+}$ and $^{57}\text{Co}^{2+}$, tracers used in injection C4. The results are given as the measured tracer concentration, C , (Bq/kg) in the withdrawal water divided by the total amount of tracer, A_{tot} , (Bq) used in the injection. The filled dots refer to the result given in the previous report (Andersson et al 2002) and the open dots refer to results measured during the continuation part of the TRUE Block Scale Phase C experiment.

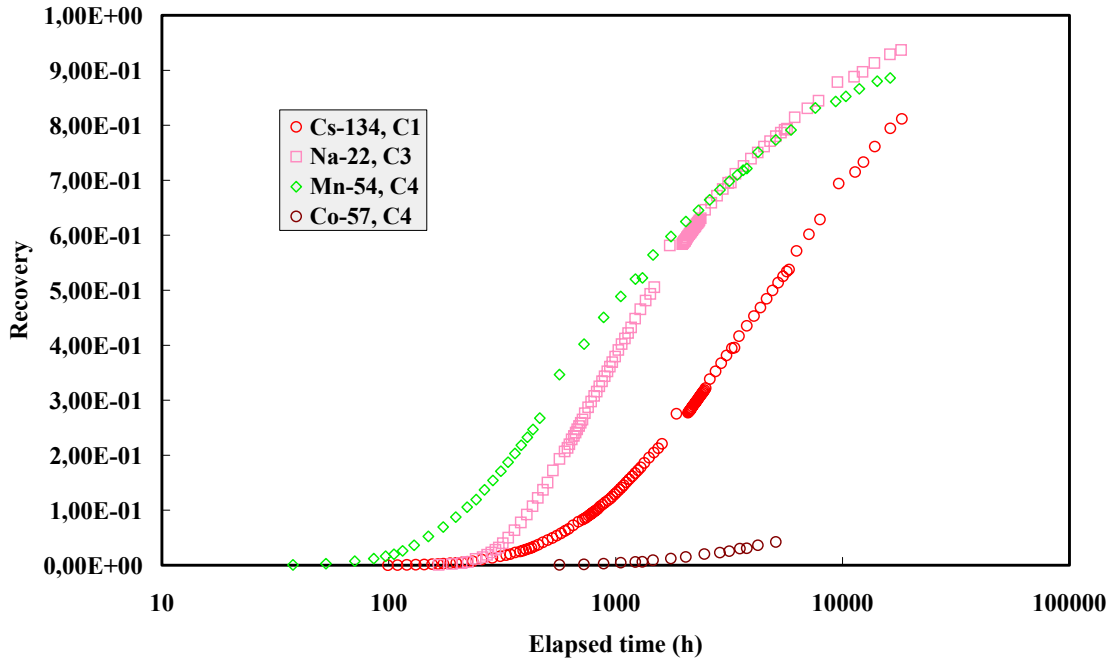


Figure 2.4 Updated recovery plots of the tracers measured using γ -spectrometry in the continuation part of the TRUE Block Scale phase C experiment.

2.2.2 Enrichments

In the TRUE Block Scale phase C experiment, no breakthrough had been measured for $^{131}\text{Ba}^{2+}$ and $^{137}\text{Cs}^+$ (injection C2), $^{83}\text{Rb}^+$ and $^{133}\text{Ba}^{2+}$ (injection C3) and $^{65}\text{Zn}^{2+}$ (injection C4) at the time for data delivery. The reason for the absence of a measurable breakthrough for these tracers was probably the pronounced retardation of these tracers, causing them to arrive in very low concentrations. By a direct application of γ -spectrometry measurement of the sampled groundwater (i.e., without any chemical separations) it was found that the background activity of ^{60}Co at BASLAB/CLAB together with the presence of e.g., $^{22}\text{Na}^+$ (injection 3) and $^{54}\text{Mn}^{2+}$ (injection 4) caused a pile-up of Compton events in the lower energy part of the γ -spectrum. This pile-up significantly decreased the possibilities of doing low activity measurements. A need was therefore identified to selectively separate the radioactive tracers that were suspected to be present in a low concentration and measure them without interferences from other tracers.

Among these tracers, $^{131}\text{Ba}^{2+}$ (used in injection C2) has a half-life of 11 days and could be considered as totally decayed in the beginning of the fall 2000. $^{83}\text{Rb}^+$ (injection C3) has a half-life of 86.2 days and this comparatively short half-life urged a need to rather quickly start a separation and measurement campaign for this tracer.

Pretest

Ammonium molybdophosphate (AMP) is known to act as a Cs selective ion exchanger and has therefore often been used to enrich Cs if very low concentrations are present in a sample (e.g., to detect a breakthrough of ^{137}Cs in a through diffusion experiment, Byegård et al. 1998). It is, however, not very many studies available on the possibilities of using AMP to enrich Rb.

In the C2 and C3 injections, $^{137}\text{Cs}^+$ and $^{83}\text{Rb}^+$, respectively, were injected. Using the normal sampling and γ -spectrometric procedures no detection of these tracers could be performed in the sampled pump water. However, the background activity in the water samples (mainly radon daughter products ^{214}Pb and ^{214}Bi) and due to the surrounding background activity of ^{60}Co at Baslab/CLAB had clearly interfered and increased the detection limits. It may be possible that a breakthrough of $^{83}\text{Rb}^+$ and $^{137}\text{Cs}^+$ actually has occurred in very low concentrations, but it has not been possible to detect it because of the background activities. An AMP enrichment of Cs and Rb from the water samples, followed by γ -spectrometric at a low-background laboratory, was therefore performed in order to increase the possibilities to quantify a breakthrough of these tracers.

Sample #C368, sampled October 18 2000, was measured in 1 l Marinelli beaker using the γ -spectrometric equipment at Baslab/CLAB. No extra treatment was performed for that sample.

0.01g of AMP (powder) was added to sample #C383, sampled November 2, and the sample was thoroughly shaken mechanically several times during a 3 hours period. After that, the solution was filtered through a 0.45 μm syringe filter in which process the AMP was fully removed from the solution. The syringe filter was taken to the Department of Nuclear Chemistry, Chalmers University of Technology, Göteborg and was measured using γ -spectrometry.

The γ -spectra in the region 500-670 keV for sample #C368 (no treatment) and for sample #C383 (AMP-treated) are presented in Figure 2-5 and 2-6, respectively. Due to the decreased total background level in sample #C383, the peaks originating from the decay of $^{83}\text{Rb}^+$ can clearly be observed. For sample #C368, the peaks from $^{83}\text{Rb}^+$ cannot be seen since the much higher background level interferes. An indication of a peak at 661.6 keV can also be observed in sample #C383; in that case it would originate from the decay of $^{137}\text{Cs}^+$. However, further studies were needed before it could be verified that a breakthrough of $^{137}\text{Cs}^+$ really had occurred.

A rough estimation (based on the assumption that the enrichment process was quantitative both for Rb and Cs) yields that the concentration of $^{83}\text{Rb}^+$ in sample #C383 should be around 1Bq/l (decay-corrected to the time of injection, corresponding to a C/A_{tot} of $2\text{e-}8 \text{ kg}^{-1}$). Similarly, the concentration of $^{137}\text{Cs}^+$ is 0.05 Bq/l, corresponding to a C/A_{tot} of $3\text{e-}9 \text{ kg}^{-1}$. These estimations are based on a very rough calibration of the detector done using the activity of $^{134}\text{Cs}^+$ in the sample as an internal standard. The numerical value of the $^{134}\text{Cs}^+$ activity used in the calibration are based on the γ -spectrometry measurement performed on Baslab/CLAB a groundwater sample estimated to have the same concentration of $^{134}\text{Cs}^+$ as the enriched sample. The calibration is illustrated in Figure 2-7.

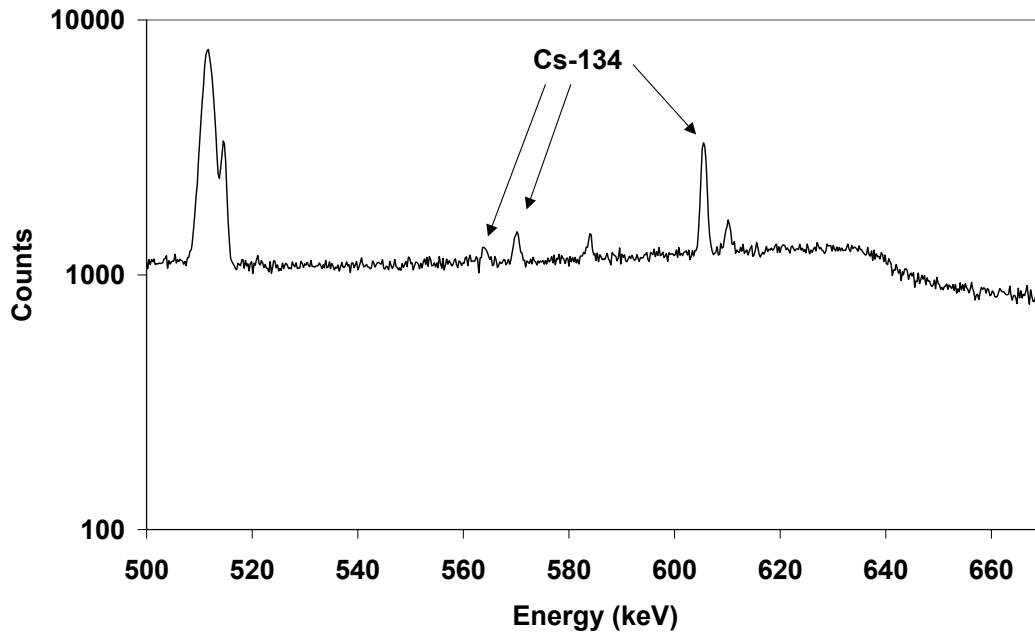


Figure 2-5 γ -spectrum in the region 500-670 keV of sample #C368. No separation was performed and the sample was measured in 1 l Marinelli beaker geometry 48 hours at the Baslab/CLAB.

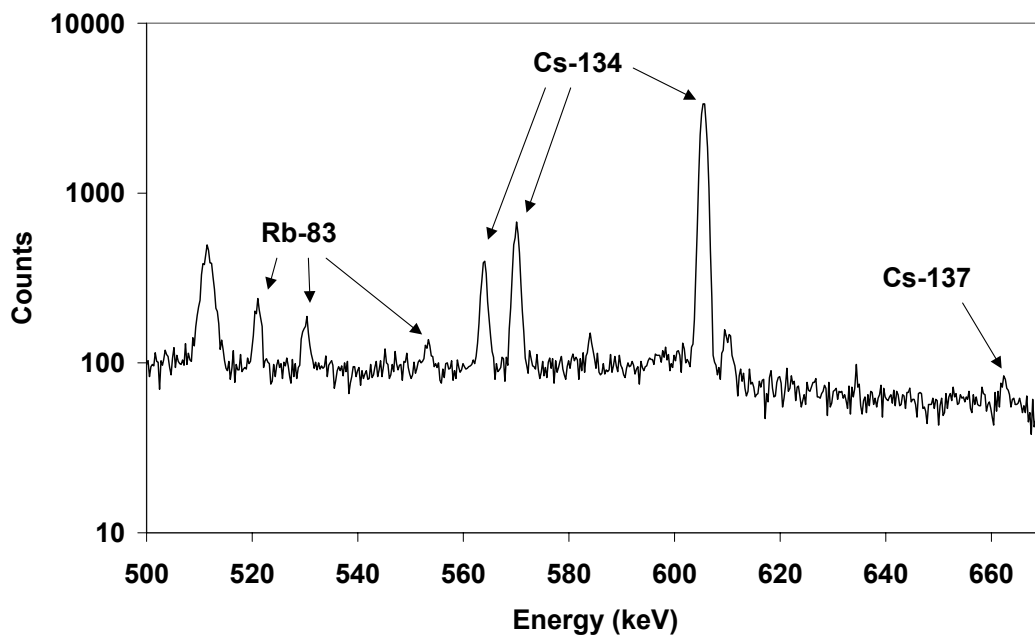


Figure 2-6 γ -spectrum in the region 500-670 keV of sample #C383. AMP separation was performed and the sample was measured in a syringe filter geometry 72 hours at the Department of Nuclear Chemistry, Chalmers University of Technology, Göteborg.

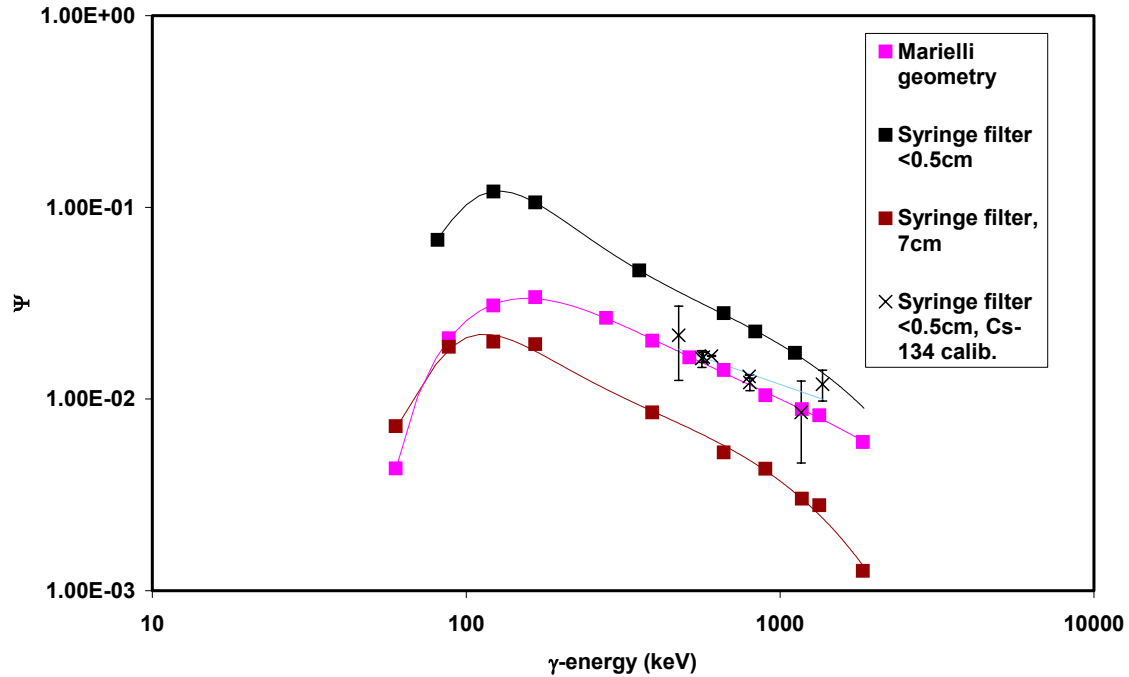


Figure 2-7 Efficiency curves for some positions used by the γ -spectrometry measurements using different HPGe detectors (see text for details).

Selective enrichments, 2001

Based on the experiences of enrichments, a campaign of AMP enrichments was performed in the spring 2001. A total number of XX 1 liter samples were selected and were processed in the same way as described above, except for that a $2\mu\text{m}$ filter was used instead of a $0.45\mu\text{m}$ filter. Besides the groundwater samples, small known amounts of the tracers $^{83}\text{Rb}^+$, $^{134}\text{Cs}^+$ and $^{137}\text{Cs}^+$ were spiked into groundwater samples and processed with the same procedure as above. These tracers were obtained from the samples obtained during the sampling of the injection solution, i.e., the concentrations of the tracers were known from the γ -spectrometry measurements done at Baslab/CLAB. In this way, it was aimed to determine the efficiency of the separation process. A calibration of the measurement geometry was performed by spiking a small amount of QCYB41 calibration solution (AEA Technology) in a syringe filter analogous to the syringe filter used in the enrichment procedure.

Each sample was measured with γ -spectrometry (HPGe-detector, 17.1% relative efficiency, EG&G Ortec) for ~ 21 hours. Evaluation of the γ -spectrum was performed using GammaVision (EG&G Ortec).

The measured efficiency of the separation procedure is given in Table 2-4. The values presented for $^{134}\text{Cs}^+$ and $^{137}\text{Cs}^+$ show apparent efficiencies significantly over 100%, a result that is difficult to explain. It should be mentioned that the present evaluation is calculated using both on the data obtained from the calibration of the HPGe-detector at Chalmers and the calibration of the detector at BALAB/CLAB. It can be suspected that this procedure may give some general uncertainty to the measured values. It is also likely that the way the measurements have been performed for the enriched samples,

i.e., two small point sources placed close to the detector, may give additional calibration problem. Further investigations of these calibration problems are probably necessary for the implementation of this enrichment method.

The efficiency for the separation of the $^{83}\text{Rb}^+$ is somewhat lower than 100%. However, having in mind that the corresponding values for Cs^+ were $>100\%$, this may indicate that the separation process of Rb^+ is somewhat non-quantitative. Further investigations of that topic are probably necessary.

For the samples measured, only the tracer $^{134}\text{Cs}^+$ can be identified in the spectrum. The detection limits for $^{83}\text{Rb}^+$ and $^{137}\text{Cs}^+$ are given in Table 2-5. As can be seen, the detection limits are somewhat higher than the values given obtained in the earlier performed pre-test. Three explanations for this observation can be identified:

- The samples were placed in a position about 7cm from the detector compared to the pre-test where a position almost adjacent to the detector was used. A longer distance gives less efficiency uncertainty but decreases the efficiency for the measurement (cf. Figure 2-7)
- A shorter measurement time was applied (21 hours compared to 3 days in the pre-test).
- The measurements were performed months after the pretest measurement. During this time, an $\sim 60\%$ decrease of the $^{83}\text{Rb}^+$ activity had occurred. (For the relatively long-lived Cs isotopes, this is not an important factor)

A summary of the results obtained for the $^{83}\text{Rb}^+$ tracer in injection C3 are given in Figure 2-8. The results of the pre-test and examples of the detection limits obtained in the 2001 campaign are presented together with the all the breakthrough data for injection C3.

Table 2-4 Efficiencies for the AMP-separation process for the different tracers. The reasons for the efficiencies higher than 100% are discussed in the text.

Tracer	$^{83}\text{Rb}^+$	$^{134}\text{Cs}^+$	$^{137}\text{Cs}^+$
Measured separation efficiency (%)	91±17	143±6	121±3

Table 2-5 Estimated detection limits for the different tracers using the AMP separation procedure combined with γ -spectrometry measurements. The detection limits are given provided a separation from a 1 kg groundwater sample and given without any decay correction to the injection date.

Tracer	$^{83}\text{Rb}^+$	$^{134}\text{Cs}^+$	$^{137}\text{Cs}^+$
Detection limit (Bq/kg)	0.78	0.12	0.17

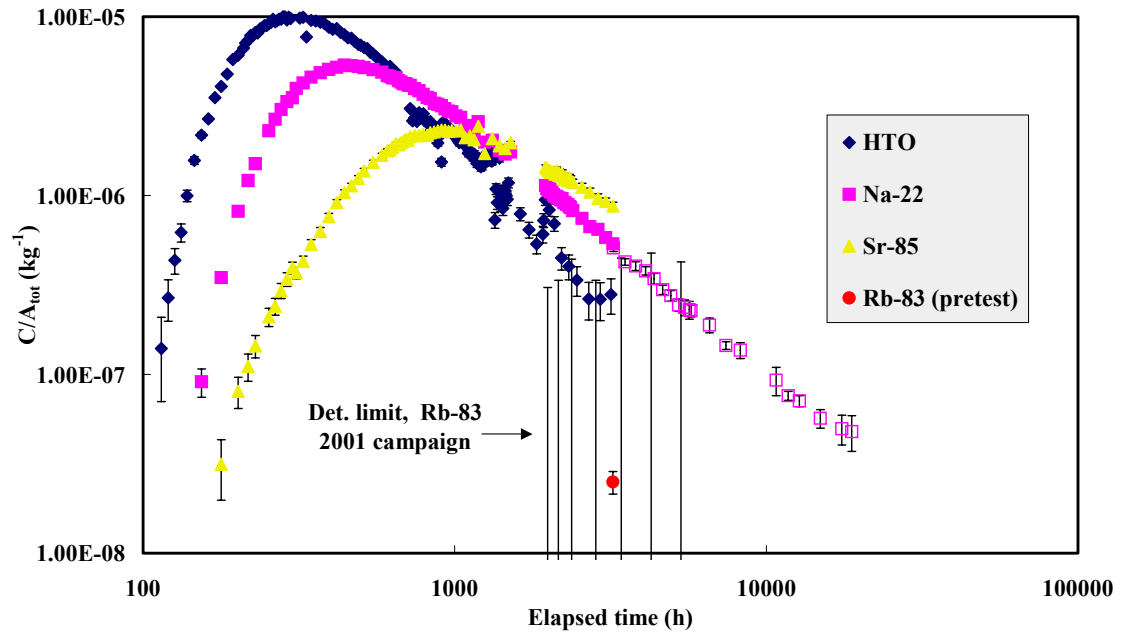


Figure 2-8 Breakthrough data obtained for injection C3. The single data point obtained for $^{83}\text{Rb}^+$ in the enrichment pretest together with examples of the detection limit obtained in the 2001 enrichment measurements

Selective enrichments, 2002

During 2002, 10 additional samples were prepared and measured the way as is described in the previous section. However, the sensitivity of the measurements was increased by applying a measurement time of 6-7 days instead the earlier used of 21 hours. Furthermore, the measurement was performed in a position extremely close ($<0.5\text{cm}$) to the detector (cf. Figure 2-7 for the efficiency curve). Combined with the fact that the $^{134}\text{Cs}^+$ isotope had undergone a significant decay, the sensitivity in these measurements was improved very much compared to the similar measurements performed in 2001. However, the $^{83}\text{Rb}^+$ tracer could now be considered as completely decayed so only results for the $^{134}\text{Cs}^+$ (injection C1) and $^{137}\text{Cs}^+$ (injection C2) could be obtained in these measurements.

The results (cf. Figures 2-9 and 2-10) show that a breakthrough curve for the $^{137}\text{Cs}^+$ tracer used in the C2 injection can be measured using this selective enrichment technique. From the very limited number of samples measured, it can be concluded that the first observation of breakthrough is observed 5-6 months after the injection and a peak concentration of $\sim 0.15\text{ Bq/kg}$ (corresponding to a C/A_{tot} of $6\text{e-}9\text{ kg}^{-1}$).

The evaluation of the measurement of $^{137}\text{Cs}^+$ indicates that a small breakthrough is observed already 4000h after the injection. However, it is somewhat contradictory that a sample taken at ~ 7000 hours show that the amount of $^{137}\text{Cs}^+$ is below the detection limit. Both these measurements are quit uncertain, but regarding the uncertainty levels it could be indicated that a small background level was present before the main breakthrough took place $\sim 7000\text{-}8000$ hours after injection. The result of the pre-test indicated that a C/A_{tot} -value of $3\text{e-}9\text{ kg}^{-1}$ 3240 h after injection, which also is an indication of a small background concentration already at that time. The reason for this observation is not fully understood and must be investigated further before any conclusions can be made.

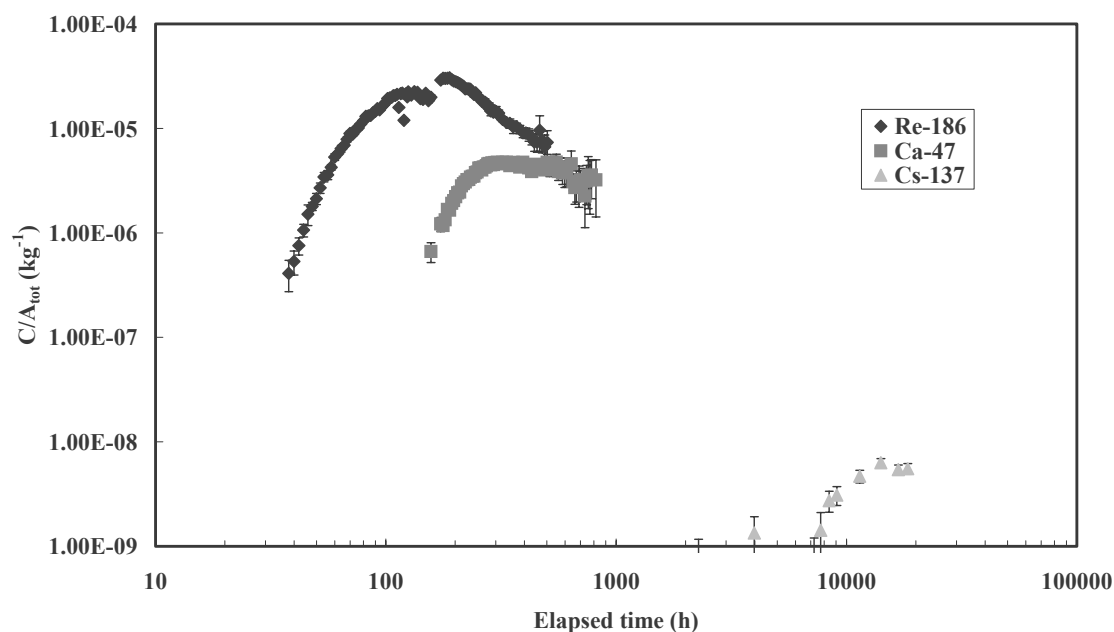


Figure 2-9 Breakthrough of $^{137}\text{Cs}^+$ given in comparison with the other tracers ($^{186}\text{ReO}_4^-$ and $^{47}\text{Ca}^{2+}$) used for injection C2.

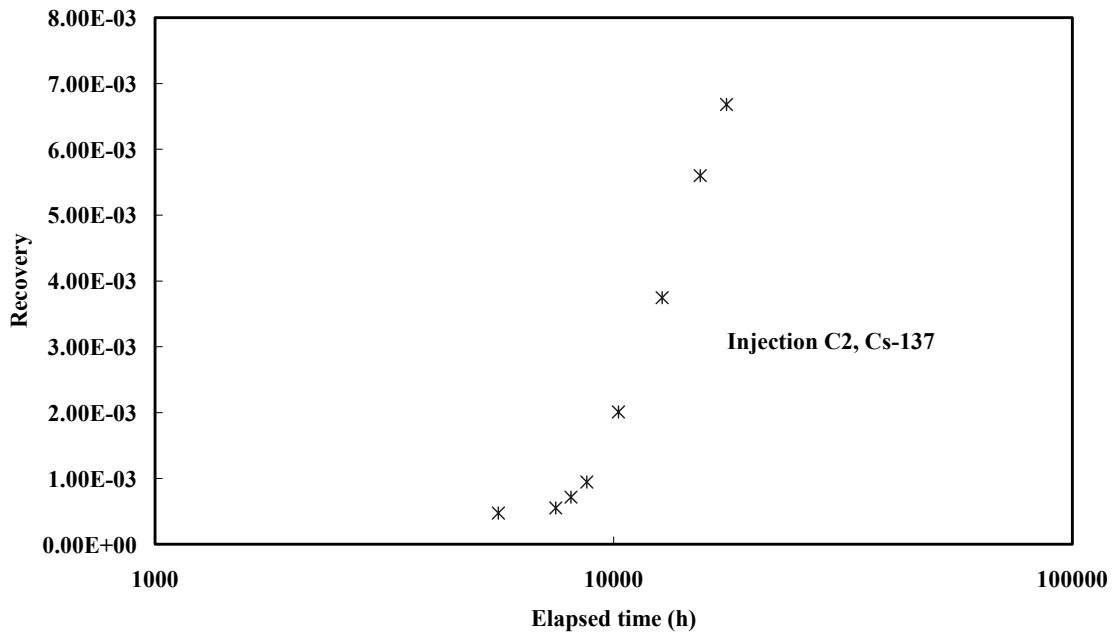


Figure 2-10 Cumulative recovery of $^{137}\text{Cs}^+$ used for injection C2.

During this 2002 campaign, a new effort was made in order to estimate the efficiency of the separation procedure. After the AMP separation had been performed, the filtered water was put in a Marinelli beaker and measured using γ -spectrometry. The results of these measurements were compared with samples measured without any separation performed. No $^{134}\text{Cs}^+$ could be found in the water exposed for the separation procedure. Based on the detection limit compared to the result of a sample not exposed for the separation, it could be calculated that the separation efficiency was >89%.

The data obtained for $^{134}\text{Cs}^+$ was compared to the data obtained in the separation campaign in 2001 and also to the measurements performed on Baslab/CLAB without application of any separation procedure. The results (Figure 2-11) indicate some deviations between the results obtained using the separation procedure and the results obtained by direct measurement. The reason for this is not fully understood. One possible explanation for the deviations is that the measurements of enriched samples are done with a point source quite close to the HPGe detector probe. It is well known that such measurements are very sensitive to small geometrical deviations. It is possible that the calibration source was not exactly in the same geometrical form as the sample and that this could be the reason for the observed deviations. As been mentioned earlier, no indication of a non-complete separation in the AMP enrichment procedure could be observed in the experiment.

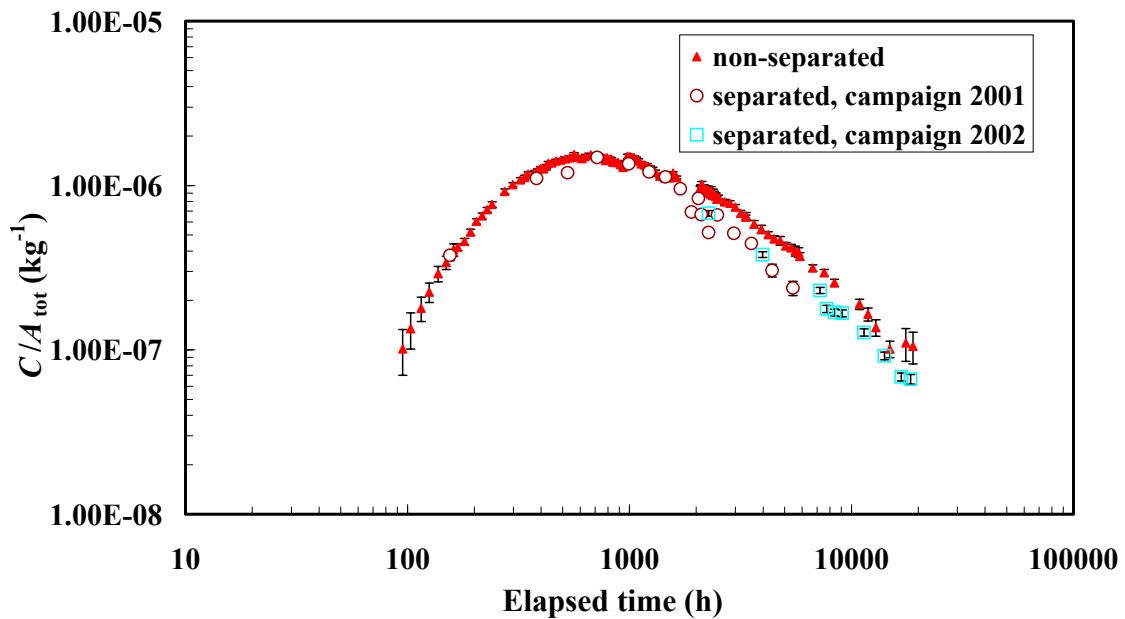


Figure 2-11 Breakthrough curve for $^{134}\text{Cs}^+$ used in injection C1. Results are given both for the γ -spectrometry measurements performed without any separation (Baslab/CLAB) and for the two different campaigns with selective separation of Cs^+ followed by γ -spectrometry measurements at Chalmers.

2.2.3 Future sampling perspective

Regarding a potential continued sampling and measurement in the TRUE Block Scale tracer experiment (phase C) it can be concluded that:

Injection C1

For the tracers used in the C1 injection, $^{134}\text{Cs}^+$ is the only tracer that is not completely decayed. The breakthrough curve of this tracer can probably be followed for some additional time. It is interesting that the high recovery of this much higher than the corresponding Cs^+ in the TRUE-1 experiment and it can probably be argued that it will be interesting to see if a pronounced decline will be observed when the recovery approaches 100%. However, because of the low activity level in the most recent samples, the uncertainty has become rather high. It is likely that if continued measurement will be done, one will have to use the enrichment results also for $^{134}\text{Cs}^+$.

Injection C2

For the tracers used in the C2 injection, $^{137}\text{Cs}^+$ is the only tracer that is not completely decayed. It is likely that more information of the breakthrough characteristics of this tracer by a continued use the AMP enrichment technique. However, a complete study of the breakthrough curve (including the tail) is from the time perspective of course not a realistic task.

Injection C3

For the tracers used in the C3 injection, $^{83}\text{Rb}^+$ and $^{85}\text{Sr}^{2+}$ are the only tracers that have decayed more or less completely. $^{22}\text{Na}^+$ is presently measured; however, the uncertainty is becoming rather pronounced.

HTO is presently not being measured; the background level of the counting rate at the liquid scintillation counter is too high to enable any low level measurement of tritium. One possibility could be to send selected preserved water samples to laboratories specialized in low-level tritium measurements.

$^{133}\text{Ba}^{2+}$ has never been recovered, probably because of the low activity used (0.5 MBq) and the generally high dilution of the tracers in this flow path. However, similar to the Cs^+ separations described in this report, it is also possible to do similar selective separations of Ba^{2+} to improve the detectability of $^{133}\text{Ba}^{2+}$. One possible way would be to add BaCl_2 to some preserved groundwater samples and thereby form a $\text{BaSO}_4(\text{s})$ precipitation. These precipitations would then be filtered through a syringe filter which thereafter would be measured by γ -spectrometry. In the C4 injection, the C/A_{tot} peak concentration of $^{131}\text{Ba}^{2+}$ was ~ 10 times lower than the corresponding peak concentration of the non-sorbing tracers used. If a similar retardation is expected for $^{133}\text{Ba}^{2+}$ in the C3 injection, a C/A_{tot} of $1\text{e-}6 \text{ kg}^{-1}$ would be obtained which would correspond to a activity concentration of $\sim 0.5\text{Bq/l}$. The detection limit for $^{133}\text{Ba}^{2+}$ in syringe filter geometry $< 0.5\text{cm}$ close to the detector has been estimated to 0.03Bq which indicates a possibility to quantify a breakthrough of $^{133}\text{Ba}^{2+}$ if optimized methods are used, i.e., complete separation of $^{133}\text{Ba}^{2+}$ from a one liter sample.

Injection C4

The only tracer from the C4 cocktail that is presently measured is $^{54}\text{Mn}^{2+}$ for which 89% of the injected tracer has been recovered. Considering that the uncertainty has become rather pronounced in the latest samples and that the half-life is 312 days, one can estimate that that the breakthrough of this tracer can be followed for additionally one year. $^{57}\text{Co}^{2+}$ ($t_{1/2}=271 \text{ d}$) has not been able to detect in the latest sample and it is not considered likely that any more measurement of this tracer will be possible. $^{65}\text{Zn}^{2+}$ ($t_{1/2}=244 \text{ d}$) has never been recovered and the relatively short half-life indicates that no measurable breakthrough can be expected. Both $^{57}\text{Co}^{2+}$ and $^{65}\text{Zn}^{2+}$ were significantly sorbed already in the injection borehole; an observation which also decrease the probability of measuring these tracers at this late stage.

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