

Intermediate and Low Level Nuclear Waste Stabilisation

Carbonation of Cement-based Wasteforms

by

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Abstract

Carbonation is a naturally-occurring process whereby Ca-containing cement phases lose their hydration water and are converted to carbonate minerals by reaction with atmospheric CO₂. As these secondary minerals develop in the microstructure of hydrated cement, porosity, pore-size distribution and permeability are decreased. These are all considered desirable properties in a wasteform. The objective of this study was to examine the effect of carbonation and different pozzolans on the leach performance and mechanical strength of ordinary Portland cement (OPC) wasteforms. Two methods of accelerated cement carbonation were used:

1. A “vacuum” carbonation method, where wasteforms are placed in an evacuated, sealed cell and subjected to small additions of CO₂ over several days at near vacuum conditions; and
2. A “one-step” carbonation method, where CO₂ gas is added to the wasteform paste as it is being mixed.

Thirteen elemental constituents of interest to the safety assessments of long-term management of Ontario Power Generation's radioactive waste (Cl, N, S, Se, ¹³C, Th, Pb, Co, Ni, Cu, Sr, Ba and Cs) were stabilised/solidified via cement mix water. Wasteforms were produced with only OPC, OPC and fly ash, or OPC and silica fume. Most wasteforms were carbonated using one of the carbonation methods. Some wasteforms were not carbonated and served as controls. Wasteforms were subjected to either standard leach tests or compressive strength tests.

The extent of carbonation was found to be about 20% for vacuum carbonation method, substantially higher than that for one-step treatment (up to about 10%). For vacuum carbonated wasteforms, carbonation occurred at the outer selvages of the wasteforms, whereas one-step treatment resulted in homogenous carbonation.

Generally, compared to uncarbonated OPC wasteforms, vacuum carbonation increased leaching of elements that are anionic in cementitious conditions (Cl, N, S, Se, ¹³C, Th), decreased leaching of large metal cations (Sr, Ba, Cs, Pb) and had negligible effect on the leaching of the

elements that form hydroxyl complexes (Co, Ni, Cu). ^{13}C was the only anionic element whose leachability was reduced by vacuum carbonation, as it may be precipitated in the form CO_3^{2-} in the large quantity of secondary carbonate minerals produced during the vacuum carbonation process.

One-step carbonation did not result in substantial reductions in leachability, compared to uncarbonated OPC wasteforms. However, it had an interesting inverse effect on large metal cation leachability from fly ash- and silica fume-containing wasteforms. A model is presented that proposes that porewater pH changes can have an effect on waste element leachability because 1) the C-S-H Ca/Si ratio is dependent on the equilibrating porewater pH and 2) the degree of ion sorption on C-S-H is dependent on the C-S-H Ca/Si ratio. This model should be tested experimentally as it has important implications on wasteform design. Because of this inverse behaviour, overall neither pozzolan outperformed the other with respect to leachability.

Generally, for uncarbonated wasteforms, OPC retained the elements more effectively than OPC with pozzolans. For pozzolans, the leachability of these elements from OPC with fly ash was lower than that of OPC with silica fume. Leaching of Cs was anomalously low from uncarbonated OPC wasteforms, but follow-up experimentation did not corroborate this anomaly. Further testing of these wasteforms to determine how the mineralogical fate of Cs can differ between wasteforms is recommended.

All wasteforms tested were of acceptable strength (<0.689 MPa). Fly ash, and, to a greater degree, silica fume, improved wasteform strength when compared to OPC wasteforms. Carbonation treatments had little effect on wasteform strength.

This study has provided much information about the leaching characteristics of a representative set of waste elements from several cement-based wasteform treatments. Although it has not indicated a wasteform design that is ideal for all elements studied, it does suggest that some treatments may be effective for certain groups of elements. Most notably, vacuum carbonation

shows promise in improving the immobilisation of isotopes of large metal cations such as Sr, Ba, Cs and Pb as well as ^{14}C (as suggested by ^{13}C here) in cement-based wasteforms.

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Glossary

Components of Ordinary Portland Cement

Alite	Ca_3SiO_5
Belite	Ca_2SiO_4
Aluminate	$\text{Ca}_3\text{Al}_2\text{O}_6$
Ferrite	$\text{Ca}_2\text{AlFeO}_5$
Anhydrite or Gypsum	$\text{CaSO}_4, \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Periclase	MgO
Free lime	CaO

Components of Hydrated Ordinary Portland Cement

C-S-H	$x\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$
Portlandite	$\text{Ca}(\text{OH})_2$
Ettringite	$\text{Ca}_6\text{Al}_2\text{O}_6(\text{SO}_4)_3 \cdot 32\text{H}_2\text{O}$
Monoaluminosulphate	$\text{Ca}_4\text{Al}_2\text{O}_6\text{SO}_4 \cdot 12\text{H}_2\text{O}$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Hydrogarnet	$\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$
Brucite	$\text{Mg}(\text{OH})_2$

Other Terms

OPC	Ordinary Portland Cement
w/s	water/solid ratio
AFm	Monoaluminosulphate-like solid-solution
Pozzolan	High silica cement additive

1. INTRODUCTION

1.1 Background

Nuclear waste has many sources. Hospital wastes and industrial processes produce significant amounts, but the largest contributor is the nuclear power generation industry (Glasser, 2001). The need for effective methods for the disposal of nuclear waste has stimulated much research. In recent years research has converged on stabilisation/solidification techniques for low-level waste (LLW) and intermediate-level wastes (ILW). Stabilisation involves physicochemical processes that act to detoxify waste, while solidification involves processes that improve the mechanical and handling characteristics of the waste (Cote, 1986; Cocke and Mollah, 1993). The United States Environmental Protection Agency has established that cementitious solidification is the best-demonstrated available technology for the land disposal of most toxic elements (Gougar et al, 1996). Cement-based stabilisation/solidification technology is preferable because of the low cost of materials and equipment, availability, adaptability, tolerance to wet conditions, non-flammability and durability under typical environmental conditions. Ordinary Portland cement (OPC) is the most common cement binder used in stabilisation/solidification technology. Although OPC-based wasteforms have been tested extensively for waste compatibility, waste loading potential and standard leach test performance, the complete history of OPC-wasteform technology development is difficult to piece together. The reason is that much of the information is either published in hard-to-obtain government and industry documents, or made proprietary because of some researchers' concern over intellectual-property protection (Hills, 2002).

Several radionuclides, namely, ^3H , ^{14}C , ^{36}Cl , ^{59}Ni , ^{79}Se , ^{94}Nb , ^{99}Tc , ^{129}I , ^{237}Np , and isotopes of U, Th, Ra, Pu, Pa and Am are of interest to safety assessments of long-term management options of Ontario Power Generation's Low and Intermediate Level Waste (L&ILW). Carbon-14, a low-energy beta emitter, is of particular interest, because it has a relatively long half-life, 5730 years, and is readily absorbed into the cell tissue of living organisms. In general, CANDU reactors produce larger quantities of ^{14}C than other types of commercial nuclear reactors, such as Light Water Reactors or Gas Cooled Reactors. The majority of ^{14}C is produced in the reactor

moderator system and is captured on ion exchange resins in the moderator purification system. Currently, cementation is the reference process for immobilising contaminants in the spent ILW resins. Improved cement wastefrom properties, and more specifically, the potential for enhanced retention of ^{14}C and other key radionuclides, are therefore of relevance to Ontario Power Generation in the context of its longer-term requirements for conditioned spent resins.

Reaction with carbon dioxide gas (CO_2) may be a way of improving OPC-based wastefrom properties. Calcium-bearing phases in hydrated (“cured”) OPC are susceptible to dehydration and conversion to calcium carbonate (CaCO_3) (“carbonation”) upon reaction with carbon dioxide (CO_2). Precipitation occurs in the cement pore network thereby reducing permeability. Co-precipitation of carbonates of elements that have similar ionic sizes and charges to Ca can also occur. Therefore, carbonated cement is potentially superior to uncarbonated cement in terms of waste retention.

Many materials that are not cementitious in their own right can be blended with OPC and can enhance certain cement properties. Fly ash and silica fume are two such materials that are readily available as industrial by-products. These are often called pozzolans, because they contain very high contents of reactive silica (SiO_2). Silica encourages the conversion of portlandite ($\text{Ca}(\text{OH})_2$) to calcium silicate hydrates (C-S-H) in OPC. While both portlandite and calcium silicate hydrates are normally present in hardened OPC as the dominant phases, it is the calcium silicate hydrates that are responsible for most of the strength exhibited by OPC.

The objective of this study was to examine the effect of carbonation and different pozzolans on the leach performance and mechanical strength of OPC-based wastefroms. Although similar studies have been conducted on either carbonated OPC-based wastefroms (Sweeny et al., 1998) or pozzolan-containing OPC-based wastefroms (Asavapisit et al., 2001), this is the first to look at the effects of both at once. Standard leach tests (ANSI/ANS 16.1; American Nuclear Society, 1986) were performed on wastefroms made with OPC, OPC and fly ash, or OPC and silica fume. The mix water contained non-radioactive isotopes of Cl, N, S, Se, C, Th, Pb, Co, Ni, Cu, Sr, Ba and Cs (chosen to represent the range of the key radionuclides discussed above). The wastefroms were carbonated by one of the following two methods:

1. **Vacuum carbonation method**, where wasteforms are placed in an evacuated, sealed cell and subjected to small additions of CO₂ over several days at near vacuum conditions. This method was developed to address the problem of build-up of water (by-product of carbonation), which normally shuts down the carbonation reaction.
2. **One step carbonation method**, where CO₂ gas is added to the wasteform paste as it is being mixed. It is a variation on a patented, one-step carbonation technique (Jennings and Hodsons, 1993). A successful one-step technique would be more economical and safer to implement than the vacuum carbonation method.

A similar set of wasteforms produced with de-ionised mix water was subjected to compressive strength tests (ASTM, 1999b). Possible physico-chemical behaviours of the cement and cement wasteforms are discussed.

1.2 General Cement Chemistry

1.2.1 Cement Composition and Manufacture

There are probably as many compositions of cement as there are applications of this unique material. However, OPC, the originally-developed material, is a standard reference and still in use today. It contains 60% CaO, 20% SiO₂, and 2 to 5 % each of Al₂O₃, Fe₂O₃ and MgO; with small (but not unimportant) amounts of Na, K and SO₄. Many different phases can be found in OPC, although alite (Ca₃SiO₅), belite (Ca₂SiO₄), aluminite (Ca₃Al₂O₆), and ferrite (Ca₂AlFeO₅) are the four principal phases. Periclase (MgO), free lime (CaO), anhydrite (CaSO₄) or gypsum (CaSO₄•H₂O) – additives that slow OPC setting and alkali sulphates (Na₂SO₄ and K₂SO₄) are minor phases, usually less than 1 mass %.

OPC is produced by heating an approximate 70/30 mass ratio of powdered (< 90 micron) limestone and clay or other aluminosilicate material in a rotary kiln to a temperature in excess of 1400°C for ten to fifteen minutes. The mixture partially melts and recombines in the semi-solid state into a mass of 3 to 20 mm nodules called a *clinker*. The clinker is then cooled and crushed to a particle size of <63 microns and mixed with several percent anhydrite.

1.2.2 Cement Hydration

Upon the addition of water, the soluble constituents of cement - free lime, anhydrite and alkali sulphates – start to dissolve and precipitate portlandite and gypsum. The bulk of the Na and K, contributed from the soluble alkali sulphates, partition into the solution phase but a portion is associated with newly-formed calcium silicate hydrates (C-S-H), and in high K cements precipitated with the mineral syngenite ($\text{K}_2\text{Ca}(\text{SO}_4)_2$).

In contrast to the high reactivity of many of the minor phases in cement and their control over the porewater composition at early times, the major phases - alite, belite, aluminate and ferrite, along with periclase, react more slowly with the porewater. For alite, belite and periclase, the percent transformed to hydrated alteration products in one day would be about 10, 15 and 40%, respectively. Aluminate and ferrite are the most reactive major phases; trivalent aluminium has a high affinity for water. In pure water systems, 70% or more of these phases will be transformed into hydrated alteration products in one day. This rapid hydration is undesirable as it can result in a flash set. However, the high initial SO_4^{2-} content of the paste porewater - ensured by the addition of anhydrite to the clinker - causes ettringite ($\text{Ca}_6\text{Al}_2\text{O}_6(\text{SO}_4)_3 \cdot 32\text{H}_2\text{O}$) crystals to form a layer at the surfaces of hydrating aluminate particles, impeding further hydration.

The reaction products of the hydration of alite and belite are C-S-H and portlandite. C-S-H can be represented by the formula $x\text{CaO} \cdot y\text{SiO}_2 \cdot n\text{H}_2\text{O}$, where x/y varies between 0.6 and 1.7 (Pointeau, 2001) and n is variable. A greater proportion of alite in the unhydrated cement results in more C-S-H upon hydration (Hills et al, 1996). The hydration of aluminate and ferrite results in the formation of iron-bearing calcium aluminates such as $\text{Ca}_2\text{Al}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ and $\text{Ca}_4\text{Al}_2\text{O}_7 \cdot 13\text{H}_2\text{O}$. However, these phases are unstable and convert to hydrogarnet ($\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$) over many days. With the high SO_4^{2-} content present, other hydrated calcium aluminate phases can form. Additional ettringite forms initially but within 24 hours begins to convert to monoaluminosulphate ($\text{Ca}_4\text{Al}_2\text{O}_6\text{SO}_4 \cdot 12\text{H}_2\text{O}$) as SO_4^{2-} becomes depleted in the porewater. Dissolution of gypsum and syngenite can buffer this depletion, but once these phases are consumed, all ettringite converts to monoaluminosulphate (Reardon, 1992). The structure of monoaluminosulphate is one of stacked sequences of portlandite-type layers, where one out of three Ca^{2+} are replaced by Al^{3+} . Thus, the layers have a positive charge that attracts SO_4^{2-} to the

interlayer regions. In cement/water systems many different anions are present that can substitute for SO_4^{2-} and Fe^{3+} can substitute for Al^{3+} resulting in a phase that does not have the exact composition of monoaluminosulphate. These monoaluminosulphate-like phases are therefore often referred to as AFm (“aluminium/ferrous mono”).

As hydrated reaction products develop on the anhydrous cement particles, further hydration becomes limited by diffusion and the rate of water uptake decreases markedly. A typical cement paste with a water/cement ratio of 0.4 becomes about 40% hydrated within one day, 70% within one month, and 80% after six months. Years are then required for the percent hydration to increase substantially beyond this point and without deliberate drying some porewater will remain until complete hydration. Hydration rates can vary considerably, however, depending on cement fineness, curing temperature and the addition of chemicals to accelerate the process. It should also be noted that OPC hydration behaviour is not always consistent when waste is incorporated (Hills and Pollard, 1997).

1.2.3 Cement Additives

Considerable research effort has been focused on formulating cement blends that improve the physical and/or chemical properties of cement wasteforms. Fly ash and silica fume are industrial waste products that are often blended with OPC. Fly ash has been used to reduce the heat of hydration and increase strength of concrete in construction applications since the 1940s (Naik et al., 1995) and silica fume since the 1970s (Bentz, 2000). These materials are sources of reactive silica or pozzolans. Silica encourages the conversion of portlandite to C-S-H during hydration resulting in cement with a denser microstructure (Kawamura and Torii, 1989) and reduced chloride diffusivity (Ampadu et al., 1999). This conversion is especially advantageous in wasteforms because portlandite is easily dissolved in natural environments (Faucon et al., 1998). This can lead to a more open pore network in cement wasteforms and thus greater leachability of waste constituents. A 10% addition of silica fume was found to increase the compressive strength of a wasteform up to 33% while having no negative impact on Cr and Pb leaching (Asavapisit et al., 2001). Venhuis and Reardon (2001) found that OPC wasteforms produced with 20% fly ash showed no evidence of shrinkage cracking during carbonation.

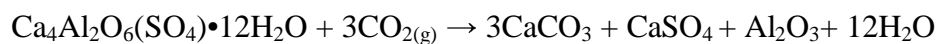
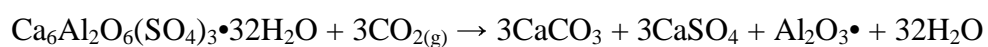
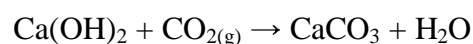
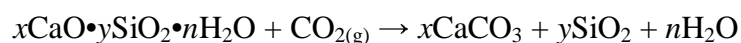
Addition of various other natural materials can result in improved wastefrom properties:

Matsuzuru and Ito (1978) found that a 25% OPC replacement with mordenite and clinoptilolite (zeolite minerals) resulted in a 100-fold reduction in Cs leachability; Osmanlioglu (2002) found that a 5% OPC replacement with kaolin clay reduced the rate of Cs and Co leaching by 50% without loss of wastefrom strength; Olsen et al., (1997) noted apatite and zeolite formation in cement/fly ash based wastefroms that had 11% replacement by attapulgite clay, which they ascribed to the observed reduction in alkali metal leachabilities.

1.2.4 Cement in the Environment and Carbonation

Most hydrated cement phases are not stable below pH 10. Because many natural waters have near-neutral pHs and may have low mineral content, there is concern over the effect that cement mineral destabilisation and dissolution would have on the leachability and long-term stability of stabilised/solidified wastes (Kirk, 1996; Faucon et al., 1998).

One of the more important processes that cement materials undergo in natural environments is reaction with CO₂, which is present in air and dissolved in subsurface waters. The reactions involved in this “carbonation process” are shown below:



These reactions induce a drop in porewater pH, often to below 9. Because steel rebar corrosion products can become depassivated at lower pH (Ihekweba et al., 1996), much of the early work in this area was concerned with the effect naturally occurring carbonation can have on the strength of cement structures. However, this early work demonstrated that as carbonation progresses, secondary carbonate minerals precipitate in the cement pore network. Carbonate solid solutions exist between Ca²⁺ and ions of similar charge and size such as Pb²⁺, Cd²⁺, Sr²⁺

and Ba^{2+} and have been used to immobilise such ions (Miyake et al, 1988). Smith and Walton (1991) suggested that carbonation, therefore, could reduce the leachability of certain waste elements from cement wasteforms. Dewaele et al. (1991) showed that carbonation, by precipitation of secondary minerals, reduces porosity and pore-size distribution in a selvage around the wasteform, thus providing a lower permeability outer barrier.

Carbonation can, therefore, convert soluble cement hydrates to relatively insoluble phases, significantly alter the microstructure of hydrated cement and relocate certain elemental constituents to different solid phases. The leachability of waste constituents from a carbonated wasteform is potentially reduced. A wide investigation by Lange et al. (1996a, b, c., 1997) found that cement cured in a CO_2 environment had a higher content of calcite (a polymorph of calcium carbonate), greater strength and reduced leachability for 12 common waste metals (Sr, Cr, Cu, Mn, Ni, Pb, Sb, Zn, Cd, Ba, As and Hg) by as much as 80% when compared to cement cured in a N_2 environment.

1.2.4.1 Mechanism of Carbonation from an External CO_2 Source

Reardon et al. (1989) suggested a three-stage interpretation of the cement carbonation process (Figure 1, page 38). All stages are diffusion-controlled reactions involving gas, liquid and mineral phases present in cement. The first stage is the rapid dissolution of CO_2 in the alkaline films coating cement grains. This stage is limited by the rate that CO_2 can diffuse through the gas phase as there is a steep concentration gradient across the films. When the film becomes saturated with respect to the CO_2 concentration, the gradient disappears. Uptake of more CO_2 can only occur by the addition of hydroxide ions (OH^-) to the solution, which increases the solubility of CO_2 in the film water. This new OH^- is principally furnished by the dissolution of portlandite. Thus, carbonation is then limited by the rate hydroxide ions can diffuse outwards and CO_2 can diffuse inwards towards reaction sites within cement particles. As shown above, each of the carbonation reactions produces water that builds up in the pore network. The third and final stage is initiated when the local pore network becomes completely saturated with liquid water, which effectively closes-off the previously interconnected gas phase. The rate of reaction is then controlled by the diffusion of CO_2 through a water phase that is continuous from the outside boundary of the cement specimen to the reaction site. As CO_2 diffusivity is

approximately four orders of magnitude slower in water than in air ($1.91 \times 10^{-5} \text{ cm}^2/\text{s}$ versus $2.08 \times 10^{-1} \text{ cm}^2/\text{s}$ respectively), the rate of CO_2 uptake is very slow during this stage. The carbonation process progresses as a front, moving inwards from the outside of a cement. The depth that carbonation occurs depends on how far the front progressed before the third phase arises.

1.2.4.2 Accelerated Carbonation and Its Application to Cementitious Wasteforms

Early work on carbonation was carried out at low pressures. Young et al. (1974) found that the rate of reaction could be increased by increasing CO_2 pressure up to 2 atm. However, further increases to 4 atm had little additional effect once pores became water saturated. More recent studies involved the use of CO_2 pressures of up to 40 atm (Dewaele, 1989; Reardon et al., 1989 and Zhang et al., 1998). It was reasoned that greater carbonation could be achieved if greater amounts of CO_2 were introduced into the cement before pore closure occurred. These studies showed that while pore closure is still a problem, high pressure carbonation held promise. However, high pressure carbonation may pose undue hazards during the treatment of radioactive wastes and would require rigorous safeguards to prevent leakage and/or rapid depressurisation.

Also investigated was the use of supercritical CO_2 – a phase of CO_2 that is twice as dense as gaseous CO_2 and is a solvent for water (Jones, 1996; Rubin et al., 1997; and Hartmann et al., 1999). It was suggested that supercritical CO_2 would dissolve porewater and replace portlandite- and C-S-H-bound water with CO_2 . However, detailed experiments by Venhuis and Reardon (2003) found no substantial enhancement of carbonation extent from the use of supercritical CO_2 versus high pressure CO_2 conditions.

Reardon et al. (1998) also investigated carbonation of wasteforms using CO_2 clathrate hydrates - CO_2 molecules completely enclosed by a sheath of water molecules ($\text{CO}_2 \cdot 6\text{H}_2\text{O}$). The idea was to overcome the problem of pore closure by expelling the water accumulated during carbonation by decomposing CO_2 clathrate hydrates. In this procedure, wastefrom samples are pressurised in CO_2 to 3.45 MPa and brought to 5 °C. Under these conditions, CO_2 clathrate hydrate is the stable form of CO_2 in water. So as CO_2 pervades the pore network and converts cement minerals to calcium carbonate and aluminosilicates, the water produced from the reaction is present as both liquid water and clathrate hydrate water. Because the CO_2 content of clathrate hydrates is

several times higher than that dissolved in the water phase at the same pressure and temperature, a large reservoir of CO₂ is trapped as clathrates within the pores once pore closure occurs. The clathrate hydrates are then destabilised by lowering the pressure in the cell. Their transformation back into gas and water increases internal porewater pressures, which results in an expulsion of both water and gas, thus clearing the pore network. Depressurisation with CO₂ enables a new cycle of carbonation reaction. A sequence of these CO₂ pressurisation/depressurisation cycles was thought to promote extensive carbonation. A pilot study indicated the method produced carbonation extents similar to high pressure carbonation and has not been studied further.

In an attempt to avoid high pressure carbonation, Venhuis and Reardon (2001) developed a new “vacuum” carbonation technique. The method enabled deeper carbonation by preventing accumulation of reaction water in the pore network. The water is removed as it is produced by conducting the experiment at very dry and very low pressure conditions. The low pressure (near-vacuum) conditions results in a greater mean free path of water molecules as they diffuse towards a desiccant. They found that vacuum carbonation applied to cementitious wastefoms resulted in carbonation depths up to 11 mm – more than twice those obtained with high pressure methods. Cationic waste elements showed lower leachabilities from vacuum carbonated wastefoms than from uncarbonated wastefoms during ANSI/ANS 16.1 leach tests (see Section 2.2, page 18). Anionic waste constituents, however, showed the opposite effect.

Reardon et al. (1987) and Dayal and Reardon (1992) investigated the use of cement as a matrix for ¹⁴C isolation. ¹⁴C in the form of ¹⁴CO₃²⁻/H¹⁴CO₃⁻, adsorbed to ion exchange resins, was mixed with a cement paste. The ¹⁴CO₃²⁻/H¹⁴CO₃⁻ was liberated from the resins by exchange with porewater OH⁻ and precipitated as calcium carbonate. The large reservoir of relatively soluble Ca-bearing phases in cement, especially portlandite and C-S-H, promoted the reaction. Chemical modelling showed that very little ¹⁴CO₃²⁻/H¹⁴CO₃⁻ would remain in solution and thus an almost total transfer of adsorbed ¹⁴C took place. ¹⁴C release behaviour then reflected calcium carbonate dissolution characteristics (i.e. low solubility at high pH).

1.3 Cement Wasteform Chemistry

1.3.1 Hydrolysis of Waste Elements in Cement Porewater

The dominant hydrolysis species of waste elements at pH levels representative of cement porewater are important to consider, as they may affect the solubility of waste element-containing minerals. In addition, the charge of a species (cation versus anion) has a fundamental influence on its transport properties in solid/water systems and whether it can be taken up in a particular crystallographic site or not. For example, AFm can take up only anions in its crystal structures to form solid solutions, whereas C-S-H can take up both cations and anions (Gougar et al, 1996). The hydrolysis species of the waste elements are shown in Figure 2 (page 38; based on Baes and Mesmer, 1976).

From Figure 2 the waste elements studied here, as they occur in cement porewater, can be classified into three groups:

1. **Cl and oxyanions (Cl, N, S, Se, C and Th).** With the exception of Cl, these are cationic elements with sufficient positive field strength (ion charge: ion surface area) to cause the detachment and ejection of all protons from their hydration water when they are placed in solution. If the solution is not pH-buffered, these protons will cause a drop in pH. The remaining oxygen atoms are covalently bonded to the waste element, resulting in a large negatively-charged species or “oxyanion.”
2. **Hydroxyl-metal complexes (Pb, Co, Ni and Cu).** These elements have lower field strengths and do not hydrolyse to the same extent as elements in Group 1. Consequently, they are usually present in solution dominantly as cations at low to neutral pH, but can form neutral or anionic hydroxyl complexes at higher pH.
3. **Large metal cations (Sr, Ba and Cs).** These large-radii elements have low field strength and therefore do not hydrolyse to any significant extent in solution. Consequently, they are present as cations at all pHs.

1.3.2 Mechanisms of Waste Leaching From Cement Wasteforms

Before interpreting the results of leach tests (see Section 3.1, page 21 and APPENDIX B, page 65), it is important to review the possible processes controlling the flux of elemental constituents

from the wastefrom and into the solution during the test. When a wastefrom undergoes its first rinse and is then suspended in the middle of a quantity of de-ionised water ten times its volume, elemental flux from the sample to the solution may occur in three ways:

1. Ion diffusion from the wastefrom's macropore porewater network in contact with the leachwater
2. Ion diffusion from the intraparticle micropore porewater network in contact with the leachwater, such as through the gel water of C-S-H
3. Dissolution of cementitious mineral grains whose surfaces are in direct contact with the leachwater.

It is likely that mechanism #1 is the dominant mechanism of elemental transport to the leachwater during the test, especially at early time. For example, because ion diffusivities are much greater through macropores than through intraparticle micropores, mechanism #1 is decidedly more important than mechanism #2. Furthermore, mechanism #1 is reasonably more important than mechanism #3 if macroporewaters are saturated with respect to minerals they are in contact with. Diffusive loss of dissolved mineral constituents from the macropore network to the leachwater could actually lead to dissolution of mineral grain surfaces not directly in contact with the leachwater as minerals re-establish saturation through mineral dissolution. An exception to this would be if the solubility of the solid phase controlling the elemental constituent's concentration is much lower in the porewater than that in the leachwater. An example of this would occur in the case of Ca leachability from an OPC wastefrom in de-ionised water. Because the pH of OPC wastefrom is very high (> 13), porewater Ca concentration is very low (controlled by equilibrium with portlandite). When an OPC wastefrom is placed in de-ionised water with an initial pH of 7, however, portlandite solubility is very high. Thus in this situation, Ca leachability should be dominated by mechanism #3.

Some elemental constituents may heavily partition into the porewater. In such cases, concentration versus time^{1/2} curves in the leachate should be linear at early time or be represented by classic cylindrical diffusion equations over the course of the leaching.

1.3.3 Standard Leach Tests and Their Interpretational Limitations

There are two standard leach tests commonly used for evaluating cementitious wasteforms: The Toxicity Characteristic Leaching Procedure (TCLP) (U.S. Environmental Protection Agency, 1992) and ANSI/ANS 16.1. The latter is used more often when the immobilisation of radioactive waste, rather than other hazardous wastes is being studied and was therefore used in this study. It involves the immersion of each wasteform in a volume of de-ionised water about ten times its volume for 2160 hours. The water is replaced after intervals of static leaching, and is analysed for the waste elements initially present in the wasteform.

Simple leach tests such as the TCLP and ANSI/ANS 16.1 cannot adequately represent the long-term leach behaviour and impact of stabilised/solidified waste on the environment because of the short time span of the tests and the simplification of the physicochemical conditions. In an attempt to scale up in time, rather than using leachwaters of typical groundwater compositions, standardised leach tests often use aggressive solutions, such as deionised water or acidic solutions as leachwaters (Hills and Pollard, 1997). Some elements may show differences in their leach behaviour over different time scales. For example, Hanna et al. (2001) using magic angle spinning nuclear magnetic resonance (MAS NMR) found that after 10 days of curing, Cs only occurred in the aqueous phase in blended cements. After 1 year of curing Cs had begun to inhabit semi-crystalline or amorphous solid sites, resulting in what the authors claimed to be a substantial reduction in Cs leaching. Unfortunately, a reduction in leaching implied on a one-year scale may still be insufficient to demonstrate the effectiveness of a wasteform. Kienzler et al. (2000) found that Cs release from OPC wasteforms was linearly time-dependant during 19-year leach tests. They concluded that cement has no retention capacity for Cs (also noted in Glasser (2001)). This is the only reference found for leach tests lasting longer than ANSI/ANS 16.1 test (2160 hours). Despite their drawbacks, simple leach tests do offer a benchmark by which a decidedly inappropriate wasteform development procedure or treatment can be differentiated from a potentially promising one.

2. EXPERIMENTAL METHODS

2.1 Wasteform Preparation

Three sets of cement-based wasteforms were produced. Their properties are shown in Table 1 (page 42), Table 2 (page 43) and Table 3 (page 44). All wasteforms were made with a water to solid ratio of about 0.6 by mass (37.5% water, 62.5% solid). Although this is a higher ratio than the industry standard for construction applications of 0.4 to 0.45 (28.6% water, 71.4% solid to 31.0% water, 68.9% solid), its use for wasteform production allows for greater aqueous waste incorporation. Because waste ion leachability is likely higher at higher water/solid ratios, this possibly demonstrates a “worst case scenario” for the effectiveness of the carbonation process for waste immobilisation.

The first set (Table 1), produced for leach testing, consisted of 18 wasteforms produced with a multi-element (Cl^- , NO_3^- and SO_4^{2-} salts of Se^{6+} , Th^{4+} , Pb^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Sr^{2+} , Ba^{2+} and Cs^+) mix water prepared by Kinectrics. Of the 18 wasteforms, two were made with straight OPC to serve as standard reference controls, eight were made with a blend of OPC and fly ash, and eight were made with a blend of OPC and reagent-grade silica fume. Within each set of eight pozzolan-added wasteforms, two served as composition controls, two were produced for vacuum carbonation, and four were produced using the one-step carbonation technique (discussed below). The amount of fly ash and silica fume added to the cement blends was 30% and 5% of the total dry mass of solids, respectively. Attempts to add silica fume in quantities that would simulate the silica addition to cement due to fly ash addition (~13%) proved difficult. Specifically, silica fume has a very large bulk volume and was cumbersome to work with.

The second set of wasteforms (Table 2) was prepared and carbonated in a similar manner to those above except that de-ionised water was used as mix water. These were produced for compressive strength testing and extent of carbonation determinations. De-ionised water, rather than the Kinectrics' waste solution, was used for these wasteforms to isolate the effects of wasteform composition and carbonation technique from those that may arise from entrained waste.

The mix water of the first set was to include ^{13}C as a contaminant. It was determined that dissolution of ^{13}C as a carbonate ($^{13}\text{CO}_3^{2-}$) with the other contaminants would cause volatilisation of much of the ^{13}C (as CO_2) because of the very low pH (~ 2) of the solution. Instead, ^{13}C was studied in a separate set of wasteforms. Ten wasteforms were produced with mix water containing ^{13}C (Table 3). ^{13}C was used as a surrogate for ^{14}C because of the licensing required to use ^{14}C . ^{14}C is considered a health risk, because it can readily exchange for $^{12/13}\text{C}$ in CO_2 and thus be inhaled into the lungs and eventually incorporated into tissue. ^{13}C is expected to behave similarly to ^{14}C in wasteform environments. The mix water was prepared by dissolving solid $\text{Na}_2^{13}\text{CO}_3$ in de-ionised water to produce a CO_3^{2-} concentration of 1000 ppm. The wasteforms were prepared in a manner similar to the first two sets. After preliminary performance data from the first set did not reveal substantial benefits with the use of silica fume, it was decided to use fly ash only for this set. These wasteforms were produced for leach testing only.

The cement used in all wasteform preparation was St. Mary's CSA CAN3-A5 Type 10 OPC. The fly ash was obtained from Ontario Power Generation's Nanticoke thermal generating station during August 2001. The silica fume, obtained from Sigma Chemical Co., was reagent-grade and had a measured surface area of $390 \pm 40 \text{ m}^2\text{g}^{-1}$. The OPC, fly ash and silica fume were acid-digested and analysed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Activation Laboratories, ACTlabs, Ancaster, ON) for major constituents ("whole rock analysis") and for the elements that comprised the multi-element mix water (except Cl, N and S). To determine the Cl, N and S content of the OPC and fly ash, one gram samples of each were dissolved at a water:solid ratio of 100:1. The solutions were sealed in HDPE bottles and were gently spun on a wheel immersed in a 25°C water bath for 24 h. The supernatant was sampled, filtered and analysed by Ion Chromatography (IC) (Solutions Analytical Laboratory (SAL), University of Waterloo, Waterloo, Ontario). The cement and fly ash used to produce the third set of wasteforms was analysed for ^{13}C by Continuous Flow Stable Isotope Mass Spectrometry (CF-SIMS; Environmental Isotope Laboratory (EIL), University of Waterloo, Waterloo, Ontario). The results of these analyses are shown in Table 4 (page 45) and Table 5 (page 46). The multi-element mix water solution was analysed by ICP-MS and IC to ensure the concentration of waste constituents conformed to the original recipe used in its preparation. The concentration of ^{13}C in

the mix water could not be confirmed by analysis, as it was beyond the operating range of any available analytical technique. The multi-element mix water analysis results and the calculated concentration of ^{13}C are shown in Table 6 (page 47).

The initial mass of each contaminant element in each wasteform was determined by performing a mass balance using data from Table 4, Table 5 and Table 6.

$$m_i = C_{i(\text{OPC})} \times m_{\text{OPC}} + C_{i(\text{pozzolan})} \times m_{\text{pozzolan}} + C_{i(\text{mix water})} \times m_{\text{mix water}} \quad (1)$$

Where:

- m_i = mass of element i in wasteform
- $C_{i(\text{OPC})}$ = concentration of element i in the OPC
- $C_{i(\text{pozzolan})}$ = concentration of element i in the pozzolan used
- $C_{i(\text{mix water})}$ = concentration of element i in the mix water
- m_{OPC} = mass of OPC used
- m_{pozzolan} = mass of pozzolan used
- $m_{\text{mix water}}$ = mass of mix water used

The results of these calculations are shown in Table 7 (page 48) and Table 8 (page49).

2.1.1 Paste Mixing and One-step Carbonation

The cement mixing method was based on *ASTM Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency* (ASTM, 1999a). This standard procedure stipulates that after the cement is added to the mixing water, 30 second should be allowed for absorption of the water. Next the paste is mixed slowly for 30 second, followed by a 15 second pause. Finally, the paste is mixed at moderate speed for 1 minute. Sometimes, modifications were made to the standard practice, where necessary, to accommodate the addition of pozzolan. Although fly ash was added to the cement prior to the addition of water, attempts to add silica fume in this manner proved difficult. The extremely high surface area of the silica fume enabled it to hydrate at a much faster rate than OPC. As a result there was not enough water to adequately hydrate the OPC and the resulting paste was dry and friable. To allow enough time for the cement paste to absorb more of the mix water and begin hydrating, silica fume was added after the first mixing period. In addition, the second mixing period was doubled to ensure adequate mixing of the final product.

After the control and vacuum carbonation wastefoms were cast, the remaining paste was mixed for another two minutes in the presence of a stream of pure CO₂ gas. Simultaneously, the paste was chilled by an ice bath to increase the solubility of CO₂ gas in paste water, while at the same time counteracting the heating effect due to the exothermic CO₂ dissolution reaction.

After pouring wastefoms from this carbonated paste, the remaining slurry was mixed, chilled and carbonated for two more minutes in an attempt to achieve a higher level of carbonation. This paste was then cast and these wastefoms were also stored at ~23°C and 100% Relative Humidity (RH) to prevent drying.

Steps were taken to prevent contamination by atmospheric CO₂ during mixing of the wastefoms. The mixing apparatus was placed in a sealed plexiglass box that had hand-sized holes cut into the left- and right- hand sides to allow for manipulation of the mixer, and a port for gas injection. Before adding the waste solution to the cement blend intended for the uncarbonated and vacuum-carbonated wastefoms, N₂ gas was allowed to flow through the apparatus for several minutes to displace atmospheric air. During the mixing a slight over-pressurisation of N₂ gas was maintained to prevent back-diffusion of atmospheric CO₂. Carbon dioxide gas was allowed to flow through the apparatus before and during the final mixing stages of the one-step treatments to enrich the CO₂ content of the mixing atmosphere.

Because there was concern whether significant isotopic exchange would occur between the ¹³C-rich CO₃ in the cement paste and the ¹³C-depleted mixing atmosphere, duplicate 1-gram paste samples were taken before and after exposure to the dynamic CO₂ atmosphere and were analysed for ¹³C (Environmental Isotope Laboratory). From these analyses, it was calculated that only 0.0448% of the ¹³C initially present in the paste was lost during mixing.

2.1.2 Wasteform Moulding

Cubic stainless-steel moulds were used to cast wastefoms produced for compressive strength tests. The moulds and procedures followed are as described in *ASTM Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (using 2-in. or [50-mm] Cube Specimens)*

(ASTM, 1999b). Cylindrical polypropylene moulds were used to cast wastefoms approximately 40 mm in diameter and 55 mm in length for chemical leach testing. These moulds conformed to the requirements of ANSI/ANS 16.1. After casting, and prior to compressive strength or leach tests, wastefoms were stored at ~23°C and 100% RH conditions to prevent drying.

2.1.3 Vacuum Carbonation

After two weeks of curing, the wastefoms produced for vacuum carbonation treatment were demoulded. The specimens were weighed before being suspended above a saturated KCl solution (solid KCl present) in a 5 L gas-tight stainless steel cell (Figure 3, page 40). The cell was evacuated until near-vacuum conditions were attained (approximately 1 kPa total pressure). The vacuum was shut off and the system was allowed to equilibrate (indicated by constant pressure). As a saturated KCl solution at 25°C has a vapour pressure that is 85% of that of pure water, the relative humidity in the cell - at equilibrium - was close to this value. Under these conditions, liquid water of moderate ion concentration cannot exist in the pores of the wastefoms. Cement porewater has a water vapour partial pressure higher than that of the saturated KCl solution (~100% that of pure water). As porewater evaporated to attain equilibrium, it diffused out of the wasteform where water vapour concentrations were lower. Equilibrium in the cell was re-established by condensation of water vapour into the KCl solution. The wastefoms were left under these conditions for 6 days to allow a gradual drying, i.e. removal of the free liquid porewater from the samples. After this drying period, small quantities of CO₂ were periodically added to the cell, causing an initial increase of pressure to about 8 kPa, followed by a progressive decrease as the CO₂ reacted with the cement. Once the pressure dropped below 6 kPa, a pair of solenoid valves would open in sequence, allowing the next controlled quantity of CO₂ to enter the cell. The solenoid valves were computer-controlled using a 16-bit data acquisition system. The data acquisition system also allowed for periodic logging of gas pressure within the reaction cell and the total number of injections. The CO₂ injection process was continued for 5 days, at which time the cell was again evacuated to remove air that may have leaked into the cell, which would decrease the efficiency of CO₂ transport from the source to the specimens. The injection process was continued for another 5 days, at which time CO₂ was gradually allowed into the cell until ambient pressure was attained. The carbonated wastefoms were then removed and re-weighed.

2.2 Chemical Leach Tests

Chemical leach tests on wasteforms were performed as specified in the ANSI/ANS 16.1 procedure. The wasteforms were immersed in a volume of de-ionised water about ten times its volume for a prescribed period of time. The water was replaced after intervals of static leaching and analysed for the waste elements that were added to the original cement mix water. Ten leachate samples were collected from each wasteform specimen at various times over 2160 h. In this study only the samples from the first 9 leaching intervals (1128 h) were analysed. The leachate samples collected from duplicate wasteforms were combined in a 1:1 (mass) proportion before analysis to give a cost-effective average of sample composition. Leachate solutions were analysed by ICP-MS at ACTlabs for the trace element constituents comprising the simulated wastewater solution, except for Cl, N and S, which were performed by IC at SAL.

Dissolved inorganic carbon (DIC) concentration in the leachate samples from the wasteforms containing ^{13}C was determined by alkalinity titration (Stumm and Morgan, 1981). In this method, 0.0026 M H_2SO_4 (concentration of $\text{H}^+ = 0.0052$ M) was added in small amounts to a 1 mL leachate sample. At pH 8.3, DIC is in the form HCO_3^- . However by pH 4.3, all DIC has converted to H_2CO_3 by reaction with H^+ . Because there are no other sources of alkalinity in cement leachwater in this pH range (caustic alkalinity from portlandite and C-S-H dissolution and from alkalis is neutralised above pH 10), the concentration of DIC can be calculated by dividing the moles of H^+ added to reduce the sample pH from 8.3 to 4.3 (calculated from the mass of H_2SO_4) by the mass of sample. The leach samples were also analysed by Stable Isotope Ratio Mass Spectrometry (S-IRMS) for the fraction of C atoms that were ^{13}C (Environmental Isotope Laboratory). From these two values the mass of ^{13}C was determined

To make comparisons between leach tests easier, ANSI/ANS 16.1 defines a Leachability Index (L_i). A L_i is related to the leaching characteristics of the wasteform and has a specific meaning for each wasteform. The higher a L_i for a leached element, the lower its leachability. The L_i represents leaching data in terms of mass-transport theory but without implying that long-term leaching mechanisms are known. The latter can only be determined from longer-term leaching.

In cases where the cumulative fraction leached (defined in APPENDIX A, page 61) was greater than 0.20, a graphical determination of L_i is presented in ANSI/ANS 16.1. Otherwise, L_i is defined as:

$$L_i = \left(\frac{1}{n} \right) \sum_{a=1}^n \left[\log \left(\frac{\beta}{D_i} \right) \right]_n \quad (2)$$

where n = number of leach intervals (10 is standard, 9 used here)

β = 1.0 cm²/s (defined constant)

D_i = effective diffusivity of element i (cm²/s)

The effective diffusivity of element i is defined as:

$$D_i = \pi T \left[\frac{a_n/A_o}{\Delta t_n} \right]^2 \left[\frac{V}{S} \right]^2 \quad (3)$$

where a_n = amount of element leached during leaching interval n (mg)

A_o = initial mass of a given element in wasteform at start of leaching (mg)

V = volume of wasteform (cm³)

S = geometric surface area of wasteform (cm²)

T = mean time of leaching interval (s); $[0.5(t_n^{1/2} + t_{n-1}^{1/2})]^2$

Δt_n = duration of leaching interval n (s).

2.3 Compressive Strength Testing

After 60 days of curing, compressive strength measurements were performed on the cubic wasteforms by Joe Aloisio (Kinectrics, Concrete Assessment and Repair) at Kinectrics, Toronto. A standard test method was followed (ASTM, 1999b). In this test a hydraulic press was used to exert increasing uniaxial pressure on the wasteform. The maximum pressure reached prior to wasteform failure is taken as the compressive strength.

2.4 Determination of Extent of Carbonation

The wasteforms tested for compressive strength were subsequently analysed for extent of carbonation. Vacuum treatment resulted in a lighter-coloured outer selvage of carbonated material. This selvage was measured on wasteform fragments that had a surface face perpendicular to the outside surface of the former wasteform (i.e. a partial cross-section). Eighty (80) grit sandpaper was used to produce a smooth surface for measurement.

One-step treatment resulted in homogeneous carbonation, so an alternative method was required to determine the extent of carbonation. Two one-gram samples of a wastefrom from each wastefrom-type duplicate pair were digested with approximately 10 g of 5 M HCl in Erlenmeyer flasks fitted with septum stoppers. The acid was syringe-injected through the septum. Complete digestion occurred in about 1 hour. During this time the flasks were occasionally swirled gently to ensure mixing. A syringe needle pierced the stopper to allow venting of gases produced during digestion. Water-saturated CO₂ is the only gas released in significant quantities during digestion, as it is the only wastefrom constituent that is volatile under low-pH conditions. The mass of CO₂ evolved was gravimetrically determined by subtracting the mass of the flasks after digestion from that before. From this value, a correction was made to account for the mass of water leaving the container with the CO₂.

3. RESULTS AND DISCUSSION

3.1 Chemical Leach Tests

Table 9 (page 50) shows the cumulative mass fraction released for each mix water element over the 1128 h of the leach tests, i.e. total accumulated mass in the leachates/initial mass in the wasteform. Note that values have been presented in scientific notation to improve readability. Plots of cumulative mass fraction released against time for each element can be found in APPENDIX B (page 65).

The Leachability Indices in Table 10 (page 51) were derived from the cumulative mass fractions released. All Leachability Indices were above the U.S. Nuclear Regulatory Commission requirement for wasteforms containing radioactive waste ($L_i = 6$; U.S. NRC, 2002). Also, it should be noted that the wasteforms in this study were produced at a w/s (water/solid ratio) of 0.6. Cement for construction purposes is usually prepared at w/s values near 0.45. High-performance concretes that are being developed to house solid forms of radioactive wastes are produced at w/s values as low as 0.3. Thus direct comparison of leach test performance in this study to that of other studies is not straightforward. For example, if the same *fraction* of a waste element leached from two wasteforms of different w/s ratios made from the same mix water, the higher w/s wasteform would have retained more mass of waste constituent per unit of binder than the lower, because it has more waste initially present.

The results of the leach tests are best discussed under the three speciation groupings established above. For brevity in this discussion, the following acronyms will be used: “OPC” – OPC-containing; “FA” – OPC and fly ash-containing; and SF – OPC and silica fume containing. Leachate pHs during the leach tests are given in Section 3.1.4.

3.1.1 Cl and Oxyanions (Cl, N, S, Se, ^{13}C and Th)

In general, the uncarbonated, OPC wasteforms were usually the most effective at retaining anionic species than the other wasteforms; the vacuum treated wasteforms were the least effective except for ^{13}C .

3.1.1.1 Leaching From Vacuum Carbonated Wasteforms

The most striking feature of the leaching of Cl and oxyanionic elements (except ^{13}C , which is discussed under Section 3.1.1.3) is generally high fraction leached from the vacuum treated wasteforms compared to both the controls and the one-step treated wasteforms. Venhuis and Reardon (2001) reported the same feature for Cl and N (NO_3). Vacuum carbonation creates an outer selvage of carbonated material accompanied by a local porewater pH reduction to between 8 and 9. Hydrated calcium aluminate phases – mostly AFm that contained anions in their interlayer regions before carbonation, would have been dissolved in this pH range (Reardon and Dewaele, 1990) releasing anions to the porewater. The systematically higher anion release from the FA wasteforms may be due to more AFm initially present in the FA wasteforms compared to the SF wasteforms because of the higher aluminium content of fly ash compared to silica fume. It is possible that leaching of anions from vacuum carbonated wasteforms would level off with time, as the outer selvages of these wasteforms are “rinsed” of anions purged from AFm. At that time anion leaching from the other wasteforms types may surpass that from vacuum carbonated wasteforms because anions contained in the core of vacuum carbonated wasteforms are protected from leaching by the outer selvage of lower-permeability carbonated material. Samples were taken at 4896 h from the leachate of wasteforms produced with multi-element mix water and were analysed for Cl, N and S. It was not clear if a cross-over in leaching was beginning to occur at that time. Longer-term leach tests may determine if and when a cross-over will happen, which is required before a decision can be made about the usability of vacuum carbonation for immobilising anionic wastes.

The leaching behaviour of N (in the form NO_3^- in solution) did not follow that of other anions for the vacuum carbonated SF wasteforms. Unlike other anions, N in solution has the same size and geometry as C (a trigonal planar arrangement of oxygens around the central atom, i.e. NO_3^- and CO_3^{2-}). Unlike other anions, this structural similarity may allow some N to be incorporated into the precipitating calcium carbonates, proxying for C in the crystal structure. However, the reason why this did not occur to the same extent in FA wasteforms is not clear. Possibly, a greater proportion of N in SF wasteforms was partitioned into porewater, available for precipitation, rather than in the limited AFm (relative to the FA wasteforms) prior to vacuum carbonation.

The cumulative fraction of N leached from the vacuum carbonated FA wasteforms appeared to be greater than one. This is may be due to a problem with the experimental method used to determine the initial concentration of N in the wasteforms and/or a compounding of analytical errors during calculation.

3.1.1.2 Can Increased Wasteform Al Content Decrease Anion Leaching?

Two questions that arose from the behaviour of anion leaching from vacuum carbonated wasteforms are:

1. If AFm is a major storehouse for anions, would wasteforms with a greater amount of this phase perform better because a smaller fraction would be destroyed upon vacuum carbonation?
2. Can AFm formation be encouraged by simply increasing the Al content in the wasteforms prior to production?

To answer these questions two wasteforms were produced from high-alumina cement (OPC blended with 37% alumina (Al_2O_3)) along with two produced with OPC. A 14440 ppm solution of CsCl was used as mix water. Preparation, curing and vacuum carbonation of all four wasteforms were as described above. After vacuum carbonation ANSI/ANS 16.1 leach tests were performed. Leachwater was changed at 2, 7, 24, 48 and 120 h. Samples of leachwater from the same leach interval and wasteform type were combined in a 1:1 ratio before being analysed by ICP-MS (ACTlabs) and IC (Analytical Chemical Services, University of Waterloo).

After 120 h of leaching, 0.69% of the Cl initially present in the OPC wasteforms was leached whereas 11% of that in the high alumina cement wasteforms was leached. More striking was the 20% of S leached from the high alumina cement wasteforms compared to only 0.92% from the OPC-only wasteforms. Enhanced leaching of Cs was also seen from Al-enhanced wasteforms (13% vs. 7.0%).

One possible explanation for these results is that C-S-H is a significant storehouse for anions in cement. Although anions are retained in AFm in great densities, they can also be retained by C-S-H, which is substantially more abundant than AFm. Thus, it is possible that C-S-H is the

dominant immobilising phase for anions - indeed, it is the main source of sorption potential in cement wastefrom systems (Glasser, 1997). In this experiment, the added Al acted to tie-up Ca in AFm rather than in C-S-H, reducing the amount of C-S-H. As a result, rather than anions being better immobilised by increasing their amount in AFm throughout the wastefrom, they became more susceptible to displacement and dissolution upon vacuum carbonation as C-S-H is stable to a lower pH (<9) than Ca-aluminates (<11) (Reardon and Dewaele, 1990).

3.1.1.3 ^{13}C : A Special Case of Anion Leaching

^{13}C showed lower leachability from vacuum carbonated compared to other wastefroms. According to the model for other anions, large quantities of ^{13}C -carbonate ($^{13}\text{CO}_3^{2-}$) should be released to the porewater during vacuum carbonation by exchange and dissolution of the initially-present AFm. At the same time, however, portlandite, C-S-H and other Ca phases dissolve and convert to calcium carbonate minerals. These reactions occur in the outer regions of the wastefroms, where the porewater is in contact with several kPa of CO_2 gas. The ^{13}C -carbonate released from the AFm thus may then become reprecipitated or sequestered in a hail of calcium carbonate precipitates. These precipitates are relegated to regions at and below the surfaces of the wastefroms, but the reactions progress inwards over time. Once these carbonated wastefroms are placed in contact with a leaching solution, the originally-added ^{13}C -carbonate is present only as a small fraction of the total carbonate present (mainly ^{12}C -containing) in the porewater and secondary precipitates. This effective dilution of the original ^{13}C in the phases that are in contact with the leachate accounts for the low fraction of ^{13}C released as compared to the control and one-step wastefrom samples.

It is noted that the measured ^{13}C release fractions (and therefore L_i values) cannot be reliably corrected for the ^{13}C contributed from the CO_2 gas that was used for carbonation.

Approximately 1% of the C atoms in the gas are ^{13}C (analysed by EIL). So, for every gram of carbon added to a wastefrom through carbonation, 10 mg of ^{13}C are added. Only the ^{13}C added via the mix water is reflected in the cumulative fraction leached because the extent that the wastefroms were carbonated was not determined. This means the ^{13}C release fractions are maximum values and thus the effectiveness of the vacuum carbonation technique in reducing the leachability of ^{13}C may be considerably higher than indicated.

3.1.1.4 Anion Leaching From Non-Vacuum Carbonated Wasteforms

Anion release from wasteforms that were not vacuum carbonated was typically lower than that from vacuum-carbonated samples. Among the anions, the leaching of Th was very low (all $L_i > 19$). Despite close correspondence in these low values, three general features can be discerned:

1. Anions were leached to a greater extent from wasteforms containing pozzolans than those that did not contain pozzolans.
2. Anions were generally leached more from the non-carbonated SF wasteforms than non-carbonated FA wasteforms.
3. The change in leachability of anions from both FA and SF wasteforms due to one-step carbonation was variable, depending on the element, but generally minor.

3.1.2 Hydroxyl-metal Complexes (Pb, Co, Ni and Cu)

The leachabilities of the hydroxyl-metal elements (Pb, Co, Ni, and Cu) were generally the lowest compared to other elements (except Th) in this study. In general, the leachability of these elements is the highest in SF wasteforms, followed by FA wasteforms and is the lowest in OPC wasteforms. The exception is the lower leachability for Co and Ni in FA wasteforms compared to OPC wasteforms. Vacuum and one-step carbonation generally had little influence on the leaching of Co, Ni, and Cu from FA wasteforms. One-step carbonation had little effect on the leaching of Co, Ni and Cu from SF wasteforms. However, vacuum carbonation reduced the leaching of Pb, Co, Ni and Cu from SF wasteforms compared to uncarbonated SF wasteforms.

Concentrations of many metals, such as Pb, Co, Ni and Cu, in high pH, low-CO₂ waters are often controlled by hydroxide mineral solubility (Baes and Mesmer, 1976). Hydroxide mineral solubility generally decreases with increasing pH but can flatten out even or increase again at very high pH if neutral or anionic hydrolysis products become dominant species. The actual solubility behaviour, however, is complex and depends on the number and valence of hydrolysis products, their equilibrium constants and the composition of the water they are in. If metal hydroxide solubility is assumed to be decreased with increased pH, most of the hydroxy-metal leaching results seen here could be explained. The addition of pozzolans to cement reduces the pH of cement porewater. pH reduction to below pH of 12.5 is difficult - but not impossible -

because the portlandite stability boundary is encountered at this pH. Silica fume always reduces pH further and more quickly than fly ash for two reasons: silica fume has a smaller particle size and thus reacts faster, and fly ash contains alkalis, whereas silica fume does not. The reason why Co and Ni showed lower leachability from FA wastefoms compared to OPC wastefoms is not known. Reduced leaching of all four metals from vacuum carbonated SF wastefoms was probably due to reduced wastefom permeability that accompanies vacuum carbonation, but it is unclear why the same phenomenon did not occur in FA wastefoms to the same extent.

Although Pb hydrolyses similarly to Co, Ni and Cu, its leachability was anomalous within this group as it was significantly lower from both SF *and* FA vacuum carbonated wastefoms compared to that from uncarbonated SF and FA wastefoms. Traditionally, geochemists normally classified Pb along with Ca, Sr, Ba and Cs as “large ion lithophile” elements, which have ionic radii greater than 0.1 nm. The ionic forms of Co, Ni and Cu in water, on the other hand, have radii around 0.07nm. The term “Lithophile” refers to these elements’ tendency to partition into silicate minerals during the cooling of magma (Goldschmidt, 1937), but the classification is also useful for distinguishing other chemical properties and behaviours. For example, Pb readily forms a straight carbonate mineral (PbCO₃) as will Sr, Ba and Cs, while Co, Ni and Cu form hydroxyl carbonates, or none at all. For this reason, Pb will also be discussed in Section 3.1.3 on the behaviour of large metal cations.

3.1.3 Large Metal Cations (Sr, Ba, Cs (and Pb))

Venhuis and Reardon (2001) found less leaching of Sr and Cs from vacuum carbonated wastefoms compared to uncarbonated wastefoms. This effect of vacuum carbonation on large metal cation leaching was also seen in this study as the cumulative fraction of Sr, Ba, Cs and Pb leached from vacuum carbonated wastefoms was generally much less than that from one-step carbonated and uncarbonated wastefoms. Lowest levels of Cs leaching from the non-carbonated OPC wastefoms was the only exception and the results are anomalous. Inspection of the data and re-analysis of the leachwater confirmed this anomaly. The highest Leachability Index for Cs found in the literature was 11.9, when the zeolite clinoptiolite (Ca_{0.5}, Na, K)₆[Al₆Si₃₀O₇₂]•20H₂O) was used as an additive to high performance slag cement (Kikuchi et al., 1999). It is possible that another zeolite, such as gismondine (Ca[Al₂Si₂O₈]•4.5H₂O), formed *in*

situ in this study. Gismondine is known to have high Cs binding potential in cementitious environments (Bagosi and Csetenyi, 1998). Another duplicate set of uncarbonated OPC wasteforms was produced later to specifically address this anomaly. This wasteform set was also subject to ANSI/ANS 16.1 leach tests for 120 h and the anomaly was not repeated. An average of 12.3% of the initially present Cs leached from the second set of wasteforms compared with 0.0861% from the original set. Further work should be done to determine the cause of the original Cs anomaly.

Vacuum carbonation partially transforms soluble Ca-bearing cement minerals into relatively insoluble calcium carbonate. During this transformation Sr, Ba, Cs and Pb housed in the original cement minerals or in the porewater could substitute for Ca in the lattices of calcium carbonate minerals due to their like charge and similar size - thus forming solid-solutions. They may also form pure-phase carbonate minerals (Klein and Hurlbut, 1993). In addition vacuum carbonation reduces porosity and pore-size distribution in the carbonated selvage around the wasteform (Dewaele et al., 1991) providing a lower diffusivity barrier in the region. So, there is a physical as well as chemical mechanism for the reduced leaching of these elements from vacuum carbonated wasteforms. Venhuis and Reardon (2001) also found that Sr and Cs leachability was reduced in vacuum carbonated wasteforms relative to uncarbonated wasteforms.

The carbonation reaction can also create another solid sink for large metal cations – sulphate mineral precipitation. Carbonation, whether performed externally or by adding CO₂ at the time of the mix, generates high SO₄²⁻ concentrations in the porewater because of the exchange of SO₄²⁻ for CO₃²⁻ in AFm (Glasser et al., 1999). Some metal sulphates, such as barite (BaSO₄) and cerussite (PbSO₄), are very insoluble minerals and may precipitate from the porewater as a result of an increase in SO₄²⁻ concentration. X-ray diffraction performed on samples of similar wasteforms (Venhuis, 2000) have not identified any sulphate mineral phases, but total SO₄²⁻ concentrations are low enough that they may have eluded detection by this technique.

Among the uncarbonated wasteforms, the SF wasteforms generally had the highest leaching of Sr, Ba, Cs and Pb, followed by FA wasteforms and the lowest in the OPC wasteforms. Leaching of Ba was similar from FA and SF wasteforms, but was higher from FA wasteforms. Leaching

of all four of these elements from the one-step carbonated wastefoms showed a curious trend. One-step carbonation reduced leaching slightly from SF wastefoms and increased leaching from FA wastefoms when compared to the uncarbonated SF and FA wastefoms, respectively. This perplexing opposing behaviour was consistent for all four large metal cations.

A possible clue to explain the opposing behaviour, which may also shed light on the anomalously low leachability of Cs from the uncarbonated OPC wastefoms, is found in the work of Viallis et al. (1999). These authors used solid-state nuclear magnetic resonance (NMR) to examine the structure and Cs retention properties of C-S-H. As the principal component of all OPC-based hydrated cements, even minor sorption properties of C-S-H can have an important impact on leachabilities of elemental constituents. Viallis et al. identified several interlayer sites for the exchange of cations in C-S-H and concluded that Cs retention by C-S-H varies inversely with its Ca/Si ratio. The explanation they give is that Ca^{2+} increasingly occupies these interlayer sites as the Ca/Si ratio of C-S-H increases.

So what controls the Ca/Si ratio of C-S-H? Most studies on this subject have dealt with the pure $\text{CaO-SiO}_2\text{-H}_2\text{O}$ water system, rather than real cements, where obtaining confident measurements on this gel-like phase in the midst of other crystalline material has proved elusive. The published solubility and compositional data of C-S-H in pure systems have been reviewed and modelled by Reardon (1992). The modelling shows how the predicted Ca/Si ratio of C-S-H varies with the pH of the equilibrating water over the stability range of C-S-H ($\text{pH} > 10$). It is seen that the Ca/Si ratio undergoes a maximum at a porewater pH of 12.5. Thus, C-S-H's ability to retain Cs and other cations must be at a minimum at this pH, i.e. their leachabilities should be highest. Hydrated OPC cement, without addition of pozzolans, typically have pHs above 13. How high above 13 depends on the alkali content ($\text{Na}_2\text{O} + \text{K}_2\text{O}$). The addition of pozzolans to cement reduces the pH of cement porewater. A reduction to below the pH of the Ca/Si maximum is difficult because it coincides with the portlandite stability boundary, but it is not impossible. Silica fume always reduces pH further and more quickly than fly ash for two reasons: silica fume has a smaller particle size and thus reacts faster, and fly ash contains alkalis whereas silica fume does not. In the present study, if the porewater pH of the uncarbonated FA wastefoms was reduced to above the Ca/Si maximum, and the pH of the uncarbonated SF wastefoms was

reduced below the maximum during one-step carbonation, as illustrated in Figure 4 (page 41), the fundamental findings of Cs and the other large metal cations' leachability data would be explained as in the following:

1. Uncarbonated OPC wasteforms had lower Ca/Si ratios than uncarbonated FA wasteforms and thus lower large metal cation leachability.
2. Uncarbonated FA wasteforms had lower Ca/Si than uncarbonated SF wasteforms and thus lower large metal cation leachability.
3. One-step carbonation, which added carbonic acid to the hydrating cements in the form of dissolved CO₂, compounds the pH reduction effect. In the case of FA wasteforms, CO₂ addition would drive the pH closer to the maximum and thus increase large metal cation leachability. In the case of SF wasteforms, CO₂ addition would drive the pH away from the maximum and thus decrease large metal cation leachability.

More credence could be given to this explanation if it was supported by actual porewater pH data. Porewater expression techniques are available to obtain these data and should be applied.

3.1.3.1 Interchange-ability of Large Metal Cation Retention Models

Two separate models have been proposed for the mechanism of large metal cation retention in vacuum carbonated and one-step carbonated wasteforms. Although CO₂ is added to the wasteforms in both cases, the models are carbonation-method specific. During one-step carbonation CO₂ is pervasively but sparsely added to the hydrating paste. Carbonates of Ca and/or other large metal cations may not form under these conditions as CO₂ may be readily and extensively accommodated in AFm or form its own pure-phase mineral, calcium carboaluminate (Ca₃Al₂O₆CaCO₃•11H₂O). Under vacuum carbonation, CO₂ is more densely added to the hydrated wasteform in a thin outer selvage. In this situation, the pH drops in the porewater such that AFm and C-S-H are mostly dissolved and calcium carbonate takes their place.

3.1.4 pH During Leach Tests

The pH of leachwater from wasteforms produced with the multi-element mix water during the first 456 hours of leaching is shown in Table 11 (page 52). Leachate pH of non-vacuum carbonated wasteforms was generally close to 11. This high pH is imparted by diffusion of high

concentration OH^- from the wasteform's porewater, which is maintained by equilibrium with portlandite, C-S-H and calcium aluminate minerals in the cement matrix.

Although pozzolans are added to OPC to reduce porewater pH (in addition to increasing the amount of C-S-H), a difference in pH was not seen in leachwaters from OPC and FA/SF wasteforms. However, it is possible that the leachwaters did not accurately reflect porewater pHs. Because pozzolans increase the amount of C-S-H in cement, they increase the volume of the micropore network (Section 1.3.2) and thus permit greater ion transport in and out of the cement and more rapid attainment of equilibrium between porewater and leachwater. The OPC wasteforms may have had a higher porewater pH than the FA or SF wasteforms that was not reflected in the leachwaters because the leachwaters did come to equilibrium with the wasteform porewater.

In the case of vacuum carbonated wasteforms, portlandite, C-S-H and calcium aluminate minerals have been converted to calcium carbonate, silica gel and aluminium oxyhydroxide in the outer selvages of the wasteforms. The pH should then be controlled by the dissolution of calcium carbonate – the most soluble of the three phases at the ambient partial pressure of CO_2 in the leachwater. This pressure is initially at atmospheric equilibrium (0.03 kPa). Equilibrium calculations show that the pH should be close to 9.8, assuming the leachwater attains saturation with respect to calcium carbonate under closed-system conditions (no atmospheric CO_2 ingress) and 8.3, under open system conditions (complete CO_2 ingress). In the event of partial equilibrium of the leachwater with respect to calcium carbonate, somewhat lower pHs would result. An inspection of the pH values for the vacuum carbonated wasteforms shows values generally consistent with $\text{CaCO}_3/\text{CO}_2$ equilibrium. However, leachwaters of vacuum carbonated silica fume wasteforms generally have higher pHs than that of vacuum carbonated fly ash wasteforms. This may be due to the larger amount of silica gel produced in the carbonation of the silica fume wasteforms. Silica gel, similarly to C-S-H above, may act as a diffusive pathway to the high OH^- porewater in the interior of the specimens.

3.2 Compressive Strength

The results of the compressive strength tests are shown in Table 12 (page 53). All wasteforms were above the U.S. Nuclear Regulatory Commission's minimum compressive strength requirements for wasteforms containing radioactive waste (0.689 MPa; U.S. NRC, 2002). Because pozzolans increase the proportion of C-S-H relative to portlandite, and C-S-H is responsible for most of the strength exhibited by cement, it is not surprising that wasteforms containing fly ash or silica fume had higher compressive strength values than the straight OPC wasteforms. Because silica fume is more reactive than fly ash, it was probably more effective at increasing the C-S-H content, which would explain why the silica fume wasteforms showed higher strength values than the fly ash wasteforms. Carbonation did not have a substantial influence on wasteform strength except that vacuum carbonated SF wasteforms were stronger than the uncarbonated SF wasteforms. Sweeny et al. (1998) suggested that cement strength improvements might occur upon formation of calcium carbonate and carbonate metal double salts (i.e. carbonates containing two different cations) in pore spaces of the carbonated wasteforms. It is not clear, however, why the FA wasteforms, which showed even greater carbonation, did not show this improvement in strength with carbonation.

3.3 Extent of Carbonation

3.3.1 Uncarbonated and One-step Carbonated Wasteforms

The results of acid-digestion (see Section 2.4, page 19) of the uncarbonated and one-step carbonated wasteforms are shown in Table 13 (page 54). Among the uncarbonated wasteforms the FA and SF wasteforms contained less CO₂ than the OPC wasteforms. One-step carbonation increased the amount of CO₂ in the treated wasteforms, with the longer-exposure treatment having a greater effect than the shorter-exposure treatment.

The total amount of CO₂ in the uncarbonated and one-step carbonated wasteforms appears to be dependent on both CO₂ concentration in the mixing atmosphere *and* pozzolan addition. Pozzolans reduce paste porewater pH and in turn reduce CO₂ solubility while the one-step treatment increases CO₂ solubility by increasing the CO₂ partial pressure above the paste. The one-step treatments work to counteract the solubility reducing effect of pozzolans.

3.3.2 Vacuum Carbonated Wasteforms

A selvage of carbonated material 0.5 cm and 1.0 cm thick was measured visually on the vacuum carbonated wasteforms containing silica fume and fly ash, respectively. The exact amount of CO₂ uptake by individual wasteforms could not be quantified by simply recording mass changes before and after the carbonation treatment. This is because water was removed while CO₂ was added to the wasteforms. However, the total mass of water removed to the desiccant during vacuum carbonation of all the wasteforms produced with the multi-element solution was recorded. Because there is an approximate 1:1 molar relationship between water removed from cement and CO₂ added during carbonation (Reardon and Dewaele, 1990) the total mass CO₂ % of the wasteforms after carbonation can be calculated using the following equation:

$$\% \text{CO}_2 = \frac{\left[\left(m_w \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g}} \right) \times \left(\frac{44.0 \text{ g}}{1 \text{ mol CO}_2} \right) \right]}{(m_i - m_w) + \left[\left(m_w \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g}} \right) \times \left(\frac{44.0 \text{ g}}{1 \text{ mol CO}_2} \right) \right]} \times 100\% \quad (4)$$

where: m_w = mass of water removed to desiccant = 126.82 g

m_i = initial mass of wasteforms (i.e. before carbonation) = 1350.07 g.

The % CO₂ of all the vacuum carbonated wasteforms was 20.2% (present mostly in the outer carbonated selvages). Therefore, on average, vacuum carbonation adds more CO₂ to wasteforms than either of the one-step treatments.

4. SUMMARY OF CONCLUSIONS

Compressive strength performance and the leachability of thirteen waste elements from a variety of OPC-based wasteforms were studied. The wasteforms were made from OPC, OPC and fly ash, or OPC and silica fume. Some of the fly ash- or silica fume-containing wasteforms were also carbonated by vacuum or one-step carbonation.

The extent of carbonation was found to be about 20% for vacuum carbonation method - substantially higher than that for one-step treatment (up to about 10%). For vacuum carbonated wasteforms, carbonation occurred at the outer selvages of the wasteforms, whereas one-step treatment resulted in homogenous carbonation.

During the first few hundred hours of leach tests, the leachate pH of uncarbonated and one-step treated wasteforms was found to be close to 11, whereas the leachate pH of vacuum carbonated waste was much lower, around 8-9.

Based on their hydrolysis characteristics, the waste elements studied were placed in one of three groups: Cl and oxyanions (Cl, N, S, Se, ^{13}C and Th); hydroxyl-metal complexes (Pb, Co, Ni and Cu); and large metal cations (Sr, Ba and Cs). The leaching behaviour of elemental waste constituents was often consistent within these groups.

In general, Cl and oxyanion (N, S, Se, ^{13}C , Th) were most effectively retained in uncarbonated OPC wasteforms than carbonated wasteforms or OPC wasteforms with pozzolan. Among carbonation techniques, leachability of these elements was not significantly affected by one-step carbonation, but was increased by vacuum carbonation. By lowering porewater pH, vacuum carbonation likely dissolves AFm - which contains anions in its interlayer sites - displacing anions to the porewater. Although ^{13}C -carbonate ions probably behaved like other anions and were displaced from AFm during vacuum carbonation, they likely re-precipitated in the large quantity of secondary carbonate minerals produced during vacuum carbonation. ^{13}C leachability was thus the lowest from vacuum carbonated wasteforms.

The leachabilities of the hydroxyl-metal elements (Pb, Co, Ni, and Cu) were the lowest compared to other elements (except Th) in this study. In general, the leachability of these elements was the highest in silica fume-containing wastefoms, followed by fly ash-containing wastefoms and was the lowest in OPC wastefoms. The exception is the lower leachability for Co and Ni in fly ash-containing wastefoms compared to OPC wastefoms. Metal hydroxide solubility is the usual control on the concentration of these elements in cement porewater and is generally inversely dependent on pH. It is believed that pozzolans, particularly silica fume, could lower the pH. In general, carbonation techniques did not affect the leaching behaviour of these elements. One exception to this was the lower leaching from vacuum carbonated SF wastefoms.

Among the uncarbonated wastefoms, the silica fume-containing wastefoms had the highest leaching of large metal cations (Sr, Ba, Cs and Pb), followed by fly ash-containing wastefoms and the lowest in the OPC wastefoms. Vacuum carbonation significantly reduced large metal cation leachability when compared to uncarbonated and one-step carbonated wastefoms. When cement phases convert to carbonate minerals during carbonation, these elements substitute for Ca to form solid solutions with calcium carbonate or form their own pure-phase carbonates. In either case, the elements became housed in relatively insoluble phases. One-step carbonation did not result in substantial reductions in the leachability of large metal cations compared to uncarbonated OPC wastefoms. However, it had an interesting inverse effect on the leachability of large metal cations from fly ash- and silica fume-containing wastefoms. A model is presented that proposes that this inverse behaviour occurs because:

1. The degree of ion sorption on C-S-H is inversely dependent on the C-S-H Ca/Si ratio (Viallis et al. 1999) and
2. The C-S-H Ca/Si ratio is dependent on the equilibrating porewater pH and goes through a maximum at pH 12.5 (Reardon, 1992).

OPC paste has a porewater pH above 13 and it is believed that fly ash and silica fume reduced porewater pH to above 12.5 and below 12.5 respectively. Upon one-step carbonation, the pH

was reduced further, pushing the Ca/Si ratio towards its maximum in the case of fly ash (reducing sorption), and away from its maximum in the case of silica fume (increasing sorption).

The following summary comments can be made about the wasteform treatments in terms of leaching:

1. Comparing just the controls, FA wasteforms usually outperformed SF wasteforms, but because of the differing effects that carbonation had, neither wasteform composition was superior when averaged across carbonation treatments.
2. Generally, one-step carbonation did not result in substantial reductions in leachability and occasionally increased leachability. In addition, there was little difference between shorter and longer exposure one-step carbonation with respect to leaching.
3. The greatest leaching of anionic elements (except for ^{13}C) was always from vacuum carbonated wasteforms, whereas the least leaching of large metal cations (including Pb) was usually seen from vacuum carbonated wasteforms. Vacuum carbonation had little effect on the leaching of hydroxyl-complex forming metals, except in the case of Pb where the leaching reduction was pronounced.
4. The uncarbonated OPC wasteforms showed least leaching for six of the 13 elements studied – more than any other treatment.

All wasteforms were of acceptable compressive strength. Fly ash, and, to a greater degree, silica fume, improved wasteform compressive strength when compared to OPC wasteforms.

Carbonation treatments had little effect on wasteform compressive strength.

This study has provided much information about the leaching characteristics of a representative set of waste elements from several cement-based wasteform treatments. Although it has not indicated a wasteform design that is ideal for the elements examined, the study suggests that some treatments may be effective for certain groups of elements. Most notably, vacuum carbonation shows promise in improving the immobilisation of isotopes of large metal cations such as Sr, Ba, Cs and Pb, as well as ^{14}C (as suggested by ^{13}C here) in cement-based wasteforms.

Areas for Future Research

There are many areas where research is required to develop useable OPC-based wasteform technologies. Several areas where further work would be valuable were identified in this study:

- The high fraction of anions leached from vacuum-carbonated wasteforms relative to uncarbonated wasteforms is undesirable. Although a method of enriching wasteform Al content in order to encourage the formation of anion-retaining phases (mostly AFm) was tested and was found to be unsatisfactory, follow-up research is still warranted. In future experiments, Al content could be enriched by adding aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$) to the paste rather than alumina (Al_2O_3) as was done here. This may reduce competition for Ca between C-S-H and AFm as aluminate would contribute Ca.
- The addition of anhydrite or gypsum to OPC to control setting rates has an undesirable side effect in wasteforms: Sulphate from these minerals competes with waste anions for limited immobilisation sites. This sulphate could be reduced or removed completely provided it can be replaced with waste sulphate or possibly other waste anions that are able to form ettringite-like phases.
- The poor performance of vacuum carbonation for the retention of anions in wasteforms revealed in this study may be an artefact of the short-term duration of the leach tests. Once the anions, which were mobilised in the exterior carbonated selvages of the wasteforms, have been lost to diffusion, the leachability of the remaining anions from the vacuum carbonated samples may in fact outperform the controls and one-step treatments. A lower physical permeability of the outer carbonated zone could contribute to this. Longer-term leaching tests – at least one to two years - would be required to evaluate this possibility.
- The cause of the anomalously high Cs retention behaviour seen in the first set of uncarbonated OPC wasteforms should be re-investigated as Cs is normally a difficult waste element to immobilise. Solid-state analyses should be performed on both sets of the uncarbonated OPC wasteforms to determine how the mineralogical fate of Cs differs between them.

- In this study a model to explain the inverse effect one-step carbonation had on the leachability of some elements from fly ash-containing wastefoms compared to silica fume-containing wastefoms was developed. This model proposes that porewater pH changes can have an effect on waste element leachability because the C-S-H Ca/Si ratio, on which the degree of ion sorption on C-S-H is dependent, is affected by the equilibrating porewater pH. This model should be tested experimentally as it has important implications on wastefom design. Among the experiments should be included a chemical characterisation of expressed cement porewater with special attention paid to pH. Quantification of the sorptivity-change dependence of C-S-H with respect to pH may be possible, which would allow accurate modeling of the immobilising potential of C-S-H, and ultimately OPC-based wastefoms.
- Although the waste elements studied here were all stable isotopes, actual nuclear waste would also contain radioactive isotopes. Transmutation and related heat production can have a destructive effect on the crystallographic properties of immobilising phases. Also, radiogenic daughter elements can have very different solubility controls and sorption characteristics than their parent elements. Both of these aspects become more important in the long-term and need to be considered.

Figures

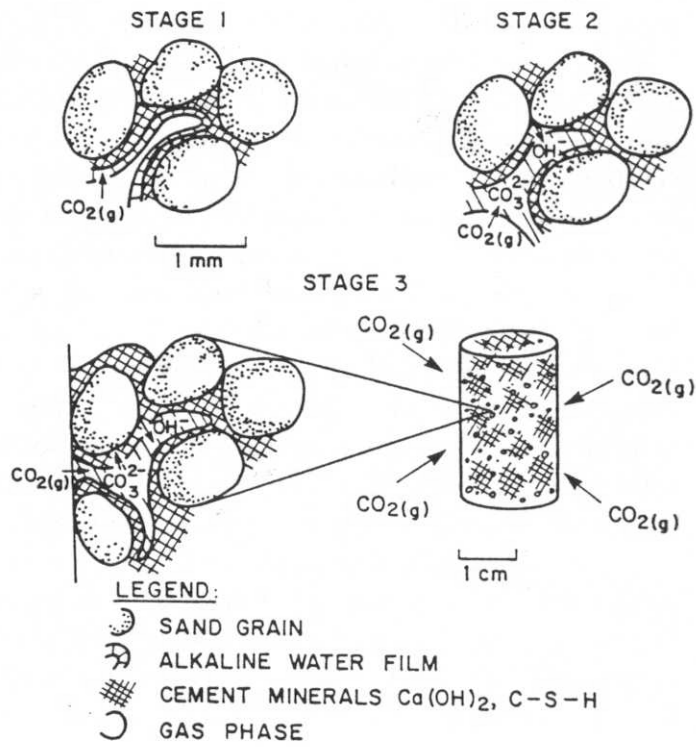


Figure 1: Schematic Illustrating the Model Proposed by Reardon et al. (1989) to describe the Three Stages of Diffusion Control on CO_2 gas reacting with an initially unsaturated cementitious material

Element	Hydrolysis Species	
	pH 8 - 9 (Vacuum Carbonated Cement Porewater)	pH 10 - 13 (Hydrating/Hydrated Cement Porewater)
Cl		Cl⁻
N		NO₃⁻
S		SO₄²⁻
Se		SeO₄²⁻
C	HCO₃⁻	CO₃²⁻
Th		ThO₃²⁻
Pb	Pb ²⁺ , PbOH ⁺	Pb(OH) _{2(aq)} , Pb(OH)₃⁻
Co	Co ²⁺	Co(OH) _{2(aq)} , Co(OH)₃⁻
Ni	Ni ²⁺	Ni(OH) _{2(aq)} , Ni(OH)₃⁻
Cu	Cu ²⁺ , Cu ₂ (OH) ₂ ²⁺ , Cu(OH) ⁺	Cu(OH) _{2(aq)} , Cu(OH)₃⁻ , Cu(OH)₄²⁻
Sr		Sr ²⁺
Ba		Ba ²⁺
Cs		Cs ⁺

Figure 2: Dominant Hydrolysis Species of the Waste Elements Selected For Study In Cementitious Environments (Anionic Species are Shown in Boldface)

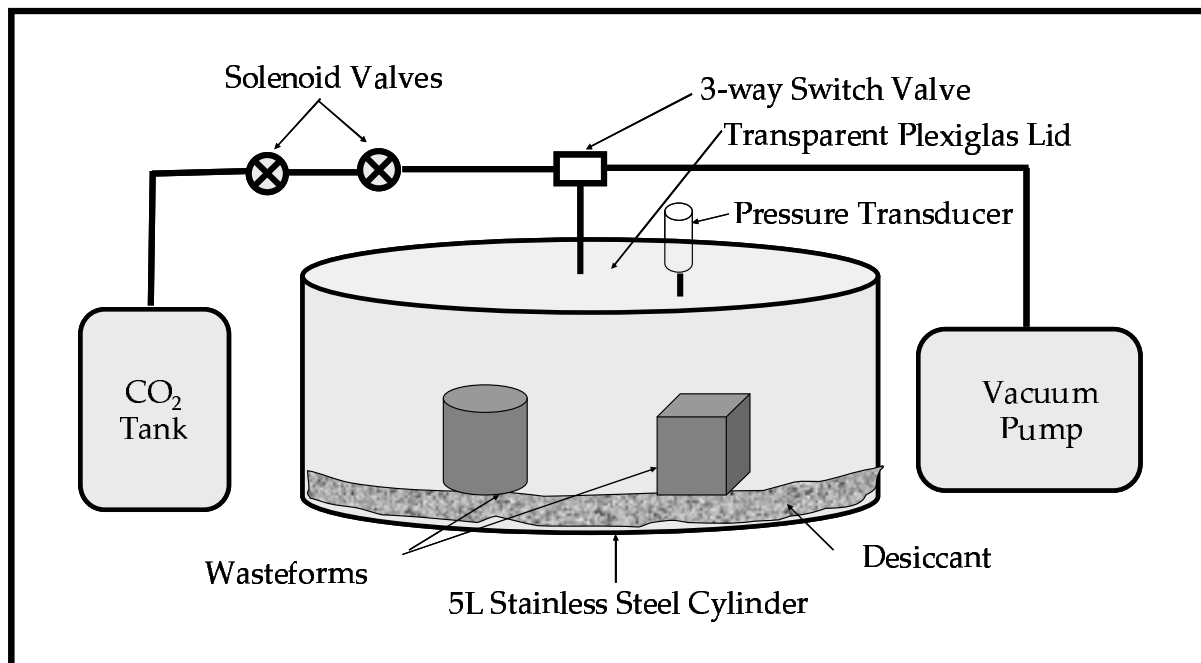


Figure 3: Vacuum Carbonation Apparatus

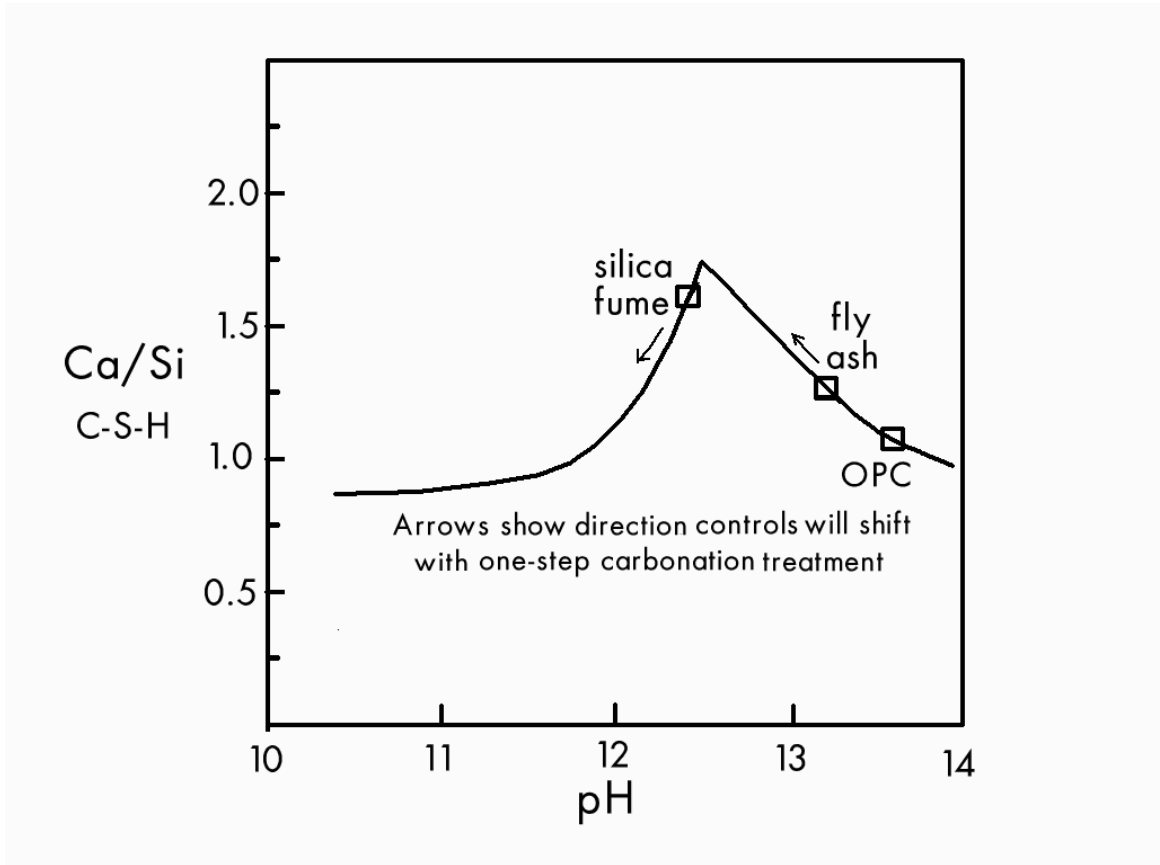


Figure 4: Ca/Si Ratio of C-S-H as a Function of pH and Conjectured Positions of Wasteform Porewater for OPC, Fly Ash and Silica Fume Controls at Time of Leaching (Adapted from Reardon, 1992)

Tables

Table 1: Characteristics of Wasteforms Produced With Multi-element Mix Water

Wasteform Name	Carbonation Method	Composition				Mass (g)	Average mass of duplicates (g)	Length (cm)	Diameter (cm)	Volume (cm ³)	Surface Area (cm ²)	Surface area/volume ratio (cm ⁻¹)
		Solids (% by mass)										
		OPC	Fly ash	Silica Fume	Water/solid ratio (by mass)							
L-OPC-CTRL-1	None (control)	100.00	0.00	0.00	0.61	126.21	126.73	6.1	4.1	80.5	105.0	1.3
L-OPC-CTRL-2		100.00	0.00	0.00	0.61	127.25		6.1	4.1	80.5	105.0	1.3
L-FA-CTRL-1	None (control)	70.00	30.00	0.00	0.60	123.85	123.99	6.1	4.1	80.5	105.0	1.3
L-FA-CTRL-2		70.00	30.00	0.00	0.60	124.12		6.1	4.1	80.5	105.0	1.3
L-FA-COA-1	One-step, shorter exposure	70.03	29.97	0.00	0.62	123.6	123.88	6.4	4.1	84.5	108.8	1.3
L-FA-COA-2		70.03	29.97	0.00	0.62	124.16		6.45	4.1	85.2	109.5	1.3
L-FA-COB-1	One-step, longer exposure	70.03	29.97	0.00	0.62	124.76	124.71	6.5	4.1	85.8	110.1	1.3
L-FA-COB-2		70.03	29.97	0.00	0.62	124.66		6.6	4.1	87.1	111.4	1.3
L-FA-V-1	Vacuum	70.00	30.00	0.00	0.60	123.12	122.67	6.1	4.1	80.5	105.0	1.3
L-FA-V-2		70.00	30.00	0.00	0.60	122.22		6.1	4.1	80.5	105.0	1.3
L-SF-CTRL-1	None (control)	94.88	0.00	5.12	0.61	130.58	129.15	6.6	4.1	87.1	111.4	1.3
L-SF-CTRL-2		94.88	0.00	5.12	0.61	127.72		6.65	4.1	87.8	112.1	1.3
L-SF-COA-1	One-step, shorter exposure	95.00	0.00	5.00	0.61	130.12	129.98	6.7	4.1	88.5	112.7	1.3
L-SF-COA-2		95.00	0.00	5.00	0.61	129.83		6.7	4.1	88.5	112.7	1.3
L-SF-COB-1	One-step, longer exposure	95.00	0.00	5.00	0.61	131.21	131.28	6.7	4.1	88.5	112.7	1.3
L-SF-COB-2		95.00	0.00	5.00	0.61	131.34		6.7	4.1	88.5	112.7	1.3
L-SF-V-1	Vacuum	94.88	0.00	5.12	0.61	129.71	130.14	6.8	4.1	89.8	114.0	1.3
L-SF-V-2		94.88	0.00	5.12	0.61	130.56		6.7	4.1	88.5	112.7	1.3

Table 2: Characteristics of Wasteforms Produced for Compressive Strength Tests and Extent of Carbonation Determinations

Wasteform Name	Carbonation Method	Composition				Length (cm)	Width (cm)	Volume (cm ³)	Surface Area (cm ²)	Surface area/volume ratio (cm ⁻¹)
		Solids (% by mass)			Water/solid ratio (by mass)					
		OPC	Fly ash	Silica Fume						
CS-OPC-CTRL-1	None (control)	100.00	0.00	0.00	0.61	5.08	5.08	103.0	121.6	1.2
CS-OPC-CTRL-2		100.00	0.00	0.00	0.61	5.08	5.08	103.0	121.6	1.2
CS-FA-CTRL-1	None (control)	69.85	30.15	0.00	0.61	5.08	5.08	103.0	121.6	1.2
CS-FA-CTRL-2		69.85	30.15	0.00	0.61	5.08	5.08	103.0	121.6	1.2
CS-FA-COA-1	One-step, shorter exposure	69.85	30.15	0.00	0.61	5.08	5.08	103.0	121.6	1.2
CS-FA-COA-2		69.85	30.15	0.00	0.61	5.08	5.08	103.0	121.6	1.2
CS-FA-COB-1	One-step, longer exposure	69.85	30.15	0.00	0.61	5.08	5.08	103.0	121.6	1.2
CS-FA-COB-2		69.85	30.15	0.00	0.61	5.08	5.08	103.0	121.6	1.2
CS-FA-V-1	Vacuum	69.85	30.15	0.00	0.61	5.08	5.08	103.0	121.6	1.2
CS-FA-V-2		69.85	30.15	0.00	0.61	5.08	5.08	103.0	121.6	1.2
CS-SF-CTRL-1	None (control)	94.87	0.00	5.13	0.59	5.08	5.08	103.0	121.6	1.2
CS-SF-CTRL-2		94.87	0.00	5.13	0.59	5.08	5.08	103.0	121.6	1.2
CS-SF-COA-1	One-step, shorter exposure	94.87	0.00	5.13	0.59	5.08	5.08	103.0	121.6	1.2
CS-SF-COA-2		94.87	0.00	5.13	0.59	5.08	5.08	103.0	121.6	1.2
CS-SF-COB-1	One-step, longer exposure	94.87	0.00	5.13	0.59	5.08	5.08	103.0	121.6	1.2
CS-SF-COB-2		94.87	0.00	5.13	0.59	5.08	5.08	103.0	121.6	1.2
CS-SF-V-1	Vacuum	94.87	0.00	5.13	0.59	5.08	5.08	103.0	121.6	1.2
CS-SF-V-2		94.87	0.00	5.13	0.59	5.08	5.08	103.0	121.6	1.2

Table 3: Characteristics of Wasteforms Produced with ¹³C Solution for Leach Tests

Wasteform Name	Carbonation Method	Composition				Mass (g)	Length (cm)	Diameter (cm)	Volume (cm ³)	Surface Area (cm ²)	Surface area/volume ratio (cm ⁻¹)
		Solids (% by mass)			Water/solid ratio (by mass)						
		OPC	Fly ash	Silica Fume							
L(C-13)-OPC-CTRL-1	None (control)	100.00	0.00	0.00	0.65	123.78	5.3	4.1	69.3	94.0	1.4
L(C-13)-OPC-CTRL-2		100.00	0.00	0.00	0.65	124.84	5.2	4.1	68.7	93.4	1.4
L(C-13)-FA-CTRL-1	None (control)	69.97	30.03	0.00	0.59	123.08	5.3	4.1	69.3	94.0	1.4
L(C-13)-FA-CTRL-2		69.97	30.03	0.00	0.59	124.8	5.2	4.1	68.7	93.4	1.4
L(C-13)-FA-COA-1	One-step, shorter exposure	69.79	30.21	0.00	0.57	126.65	5.6	4.1	73.3	97.9	1.3
L(C-13)-FA-COA-2		69.79	30.21	0.00	0.57	126.74	5.6	4.1	73.3	97.9	1.3
L(C-13)-FA-COB-1	One-step, longer exposure	69.79	30.21	0.00	0.57	126.66	5.2	4.1	68.7	93.4	1.4
L(C-13)-FA-COB-2		69.79	30.21	0.00	0.57	126.84	5.3	4.1	69.3	94.0	1.4
L(C-13)-FA-V-1	Vacuum	69.97	30.03	0.00	0.59	118.22	5.3	4.1	69.3	94.0	1.4
L(C-13)-FA-V-2		69.97	30.03	0.00	0.59	117.81	5.3	4.1	69.3	94.0	1.4

Table 4: Whole Rock Analysis of Solids Used in Wasteform Preparation

Oxide	Concentration (mass %)		
	OPC	Fly ash	Silica Fume
SiO ₂	19.57	43.6	93.9
Al ₂ O ₃	5.46	23.51	0.03
Fe ₂ O ₃	2.33	4.72	0.06
MnO	0.055	0.0225	<0.003
MgO	2.28	2.195	0.12
CaO	62.53	8.22	0.12
Na ₂ O	0.2	0.825	0.12
K ₂ O	1.11	1.54	0.09
TiO ₂	0.299	1.3665	0.006
P ₂ O ₅	0.12	0.41	<0.03
LOI	1.36	9.92	5.34
Total	95.3	96.3	99.8

Table 5: Concentration of Elements Comprising Mix Waters in Solids Used to Prepare Wasteforms

Species	Concentration (ppm)		
	OPC	Fly ash	Silica Fume
Cl	383	32	N/A
N	3.52	13.13	N/A
S	5300	4967	N/A
Se	1.9	16.6	<0.1
¹³ C	398.0		N/A
Th	3.5	14.5	<0.1
Pb	28.7	45.1	<0.01
Co	7.5	39.3	<0.1
Ni	28.1	66.3	0.6
Cu	17.6	124	0.3
Sr	288	1220	0.5
Ba	140	477	2.6
Cs	0.9	1.6	<0.1

Table 6: Concentration of Elements in Mix Waters

Element	Concentration (ppm)	
	Multi-element solution	Na ₂ ¹³ CO ₃ solution
Cl	2.25	
N	248	
S	142	
Se	332	
¹³ C		200.3
Th	1,104	
Pb	258	
Co	253	
Ni	225	
Cu	510	
Sr	498	
Cs	1,039	
Ba	515	
Na		767

Table 7: Initial Mass of Waste Elements in Wasteforms Produced With Multi-element Mix Water

Wasteform Name	Initial mass (mg)											
	Cl	N	S	Co	Ni	Cu	Se	Sr	Cs	Ba	Pb	Th
L-OPC-CTRL-1	30.06	12.20	421.24	12.71	12.99	26.01	16.03	80.37	50.03	38.96	15.98	53.40
L-OPC-CTRL-2	30.30	12.30	424.71	12.82	13.10	26.23	16.16	81.03	50.44	39.28	16.11	53.84
L-FA-CTRL-1	21.63	11.78	409.64	13.03	13.49	27.57	15.83	90.62	48.28	44.83	15.49	51.76
L-FA-CTRL-2	21.68	11.80	410.54	13.06	13.52	27.63	15.86	90.82	48.38	44.93	15.53	51.87
L-FA-COA-1	21.24	12.07	402.38	13.30	13.69	28.10	16.21	89.95	49.50	45.04	15.73	53.05
L-FA-COA-2	21.34	12.12	404.20	13.36	13.76	28.23	16.29	90.36	49.72	45.25	15.80	53.29
L-FA-COB-1	21.44	12.18	406.16	13.43	13.82	28.36	16.36	90.79	49.97	45.47	15.88	53.55
L-FA-COB-2	21.43	12.17	405.83	13.42	13.81	28.34	16.35	90.72	49.92	45.43	15.87	53.51
L-FA-V-1	21.50	11.71	407.23	12.95	13.41	27.41	15.74	90.09	47.99	44.57	15.40	51.46
L-FA-V-2	21.34	11.62	404.25	12.86	13.31	27.21	15.62	89.43	47.64	44.24	15.29	51.08
L-SF-CTRL-1	29.55	12.58	414.45	13.09	13.58	27.29	16.61	85.24	51.64	41.49	16.50	55.16
L-SF-CTRL-2	28.91	12.31	405.37	12.81	13.28	26.69	16.24	83.37	50.51	40.58	16.14	53.95
L-SF-COA-1	29.53	12.51	414.11	13.02	13.50	27.12	16.51	84.93	51.32	41.28	16.42	54.82
L-SF-COA-2	29.47	12.48	413.19	12.99	13.47	27.06	16.47	84.74	51.21	41.19	16.38	54.70
L-SF-COB-1	29.78	12.61	417.58	13.12	13.62	27.35	16.64	85.64	51.75	41.62	16.55	55.28
L-SF-COB-2	29.81	12.62	417.99	13.14	13.63	27.38	16.66	85.72	51.81	41.67	16.57	55.34
L-SF-V-1	29.36	12.50	411.69	13.01	13.49	27.11	16.50	84.67	51.30	41.22	16.39	54.79
L-SF-V-2	29.55	12.58	414.39	13.09	13.58	27.29	16.61	85.23	51.63	41.49	16.50	55.15

Table 8: Initial Mass of ¹³C in Wasteforms

Wasteform Name	Initial mass of ¹³C (mg)
L(C-13)-OPC-CTRL-1	39.64
L(C-13)-OPC-CTRL-2	39.98
L(C-13)-FA-CTRL-1	39.98
L(C-13)-FA-CTRL-2	40.54
L(C-13)-FA-COA-1	41.43
L(C-13)-FA-COA-2	41.46
L(C-13)-FA-COB-1	41.44
L(C-13)-FA-COB-2	41.49
L(C-13)-FA-V-1	38.40
L(C-13)-FA-V-2	38.27

Table 9: Cumulative Fraction of Contaminants Leached

Pozzolan	Carbonation	Cumulative Fraction Leached												
		Cl	N	S	Se	¹³ C	Th	Pb	Co	Ni	Cu	Sr	Ba	Cs
		(x 10 ¹)	(x 10 ²)	(x 10 ³)	(x 10 ⁴)	(x 10 ²)	(x 10 ⁷)	(x 10 ⁵)	(x 10 ⁵)	(x 10 ⁴)	(x 10 ⁴)	(x 10 ³)	(x 10 ³)	(x 10 ⁴)
None	None	0.87	3.17	6.31	1.18	2.23	3.67	10.50	8.14	9.23	1.13	28.49	7.26	8.61
Fly ash	None	0.55	24.58	8.05	24.77	4.09	3.93	22.64	6.24	4.81	1.38	31.74	36.51	2611.44
	One-step (shorter exposure)	0.97	30.53	7.21	30.28	4.21	6.86	27.51	6.52	4.58	2.91	41.77	54.05	3244.00
	One-step (longer exposure)	0.83	31.23	7.40	38.83	3.86	3.97	30.71	7.14	4.96	2.06	54.10	65.67	3578.58
	Vacuum	4.61	126.76	347.10	1449.25	1.77	10.08	10.33	7.02	6.69	1.40	2.90	1.28	1010.18
Silica fume	None	1.23	46.11	6.17	30.30		5.01	34.93	51.96	15.52	3.87	65.21	40.95	5941.93
	One-step (shorter exposure)	1.08	42.10	5.99	28.99		3.87	26.44	53.10	16.33	2.61	65.50	41.53	5688.19
	One-step (longer exposure)	1.05	41.27	6.22	54.49		9.89	31.30	51.94	17.48	3.04	60.47	40.53	5329.31
	Vacuum	3.36	32.38	77.26	164.35		4.65	9.41	25.64	7.75	2.53	8.25	3.05	2931.12

Table 10: Leachability Indices

Pozzolan	Carbonation	Leachability Indices												
		Cl	N	S	Se	¹³ C	Th	Pb	Co	Ni	Cu	Sr	Ba	Cs
None	None	9.1	9.9	11.3	14.6	10.2	19.8	14.7	15.3	13.6	14.8	10.1	11.2	13.2
Fly ash	None	9.5	8.3	11.3	12.1	10.2	19.8	14.4	15.3	13.7	14.7	9.9	9.8	8.0
	One-step (shorter exposure)	9.1	8.2	11.3	11.9	10.1	19.3	14.0	15.4	13.8	14.4	9.7	9.5	7.8
	One-step (longer exposure)	9.1	8.1	11.1	11.7	10.1	19.7	13.9	15.3	13.8	14.6	9.5	9.3	7.7
	Vacuum	7.8	6.5	7.0	8.5	10.6	19.1	14.8	15.2	13.7	14.6	12.1	12.9	9.1
Silica fume	None	9.0	7.8	11.3	12.0		19.6	13.9	13.4	13.5	14.0	9.5	9.9	7.3
	One-step (shorter exposure)	9.0	7.8	11.3	12.0		19.7	14.1	13.4	13.4	14.3	9.4	9.8	7.2
	One-step (longer exposure)	9.1	7.9	11.2	11.5		19.2	14.0	13.4	13.4	14.0	10.0	10.2	7.3
	Vacuum	7.7	8.1	9.0	10.5		19.6	14.8	14.1	13.6	14.3	12.0	13.2	7.9

Table 11: pH of Leachwater During First 456 Hours of Leach Testing

Pozzolan	Carbonation	pH							
		2 hours	7 hours	24 hours	48 hours	72 hours	96 hours	120 hours	456 hours
None	None	11.86	11.03	11.43	11.41	11.03	11.39	8.53	8.94
Fly ash	None	11.68	10.65	8.43	11.34	11.25	11.19	10.92	8.51
	One-step (shorter exposure)	11.59	10.92	11.42	11.42	11.35	11.25	10.85	8.53
	One-step (longer exposure)	11.50	10.88	11.49	11.49	11.10	11.31	9.85	8.61
	Vacuum	8.85	7.94	9.02	9.45	8.24	9.08	9.26	8.27
Silica fume	None	11.25	10.94	11.47	11.53	11.37	11.38	11.21	11.13
	One-step (shorter exposure)	11.31	10.91	11.53	11.55	11.12	11.41	8.14	11.74
	One-step (longer exposure)	11.36	10.94	11.52	11.57	10.78	11.41	11.31	11.73
	Vacuum	9.06	9.25	10.40	9.94	9.90	10.31	7.99	8.75

Table 12: Compressive Strength of Wasteforms Prepared With Multi-element Mix Water After 60 Days of Curing

Pozzolan	Carbonation Type	Compressive Strength (MPa)		
		Wasteform 1	Wasteform 2	Average
None	None	22.58	23.10	22.84
Fly ash	None	32.41	31.72	32.06
	One-step (shorter exposure)	31.20	31.20	31.20
	One-step (longer exposure)	28.44	29.82	29.13
	Vacuum	28.61	29.99	29.30
Silica fume	None	31.54	34.47	33.01
	One-step (shorter exposure)	37.23	35.34	36.28
	One-step (longer exposure)	29.48	34.82	32.15
	Vacuum	42.06	41.89	41.97

Table 13: Extent of Carbonation of Uncarbonated and One-step Carbonated Wasteforms Prepared With Multi-element Mix Water

Pozzolan	Carbonation method	Extent of carbonation (CO₂ mass % of wasteform)
None	None	5.09
Fly ash	None	4.13
	One-step (shorter exposure)	4.87
	One-step (longer exposure)	9.78
Silica Fume	None	2.02
	One-step (shorter exposure)	2.59
	One-step (longer exposure)	4.05

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APPENDIX A. CALCULATION OF CUMULATIVE FRACTION LEACHED

To illustrate the calculation of the cumulative fraction leached of an element from a wasteform during ANSI/ANS 16.1 leach tests, ^{13}C data from the uncarbonated fly ash-containing wasteforms will be used as an example.

In the preparation of the wasteforms 260.0 g OPC, 111.6 g fly ash and 220.8 g mix water was used for a total of 592.4 g of materials. The mixture was therefore 43.90% OPC, 18.8% fly ash and 37.3% mix water.

Two wasteforms were produced from this mixture. Their masses were 1) 123.8 g and 2) 124.8 g. The first wasteform was thus made from $(123.8 \text{ g} \times 0.439) = 54.4 \text{ g OPC}$, $(123.8 \text{ g} \times 0.188) = 23.3 \text{ g fly ash}$ and $(123.8 \text{ g} \times 0.373) = 46.5 \text{ g mix water}$. Doing the same calculations for the second wasteform, it was made from 54.8 g OPC, 23.5 g fly ash and 46.5 g mix water.

The OPC/fly ash blend used was 3.67% C and 1.09% of that C was ^{13}C . Therefore 0.04% of the blend is ^{13}C . The mix water was 0.02% C and 99.9% of that was ^{13}C . Therefore 0.02% of the mix water was ^{13}C . The first wasteform thus contained $((54.4 \text{ g} + 23.3 \text{ g}) \times 0.0004 + 46.5 \text{ g} \times 0.0002) = 0.041 \text{ g } ^{13}\text{C}$. The second wasteform contained 0.0405 g ^{13}C . Because leachwater from both wasteforms was combined after collection, the initial masses of ^{13}C were averaged. The average initial mass of ^{13}C was 40.3 mg.

Samples of leachwater collected at various times were analysed for C concentration and % ^{13}C . From these values the concentration of ^{13}C was calculated (i.e. C concentration \times % ^{13}C) and listed in Table A. 1.

Table A. 1: Concentration of Element in Leachwater during Leaching Intervals

Leach sampling time (hours)	mg C/kg leachwater	% ¹³C	mg ¹³C/ kg leachwater
Initial rinse (30 s)	2.88	1.10	0.0318
2	3.72	1.12	0.0415
7	3.48	1.14	0.0397
24	6.96	1.22	0.0853
48	3.12	1.18	0.0368
72	6.00	1.27	0.0760
96	5.40	1.27	0.0687
120	4.56	1.17	0.0533
456	10.7	1.75	0.187
1128	61.6	1.80	1.11

From the mass of leachwater the mass of ¹³C was calculated (i.e. ¹³C concentration in leachwater x mass of leachwater = mass of ¹³C) and listed in Table A. 2.

Table A. 2: Mass of Element Leached During Leaching Intervals

Leach sampling time (hours)	mg ¹³C/ kg leachwater	Mass of leachwater (kg)	mg ¹³C leached during leach interval
Initial rinse (30s)	0.0318	0.940	0.0298
2	0.0415	0.940	0.0389
7	0.0397	0.940	0.0371
24	0.0853	0.940	0.0799
48	0.0368	0.940	0.0345

72	0.0760	0.940	0.0711
96	0.0687	0.940	0.0643
120	0.0533	0.940	0.0499
456	0.187	0.940	0.175
1128	1.11	0.940	1.04

By dividing the mass of ^{13}C leached during each interval by the initial mass of ^{13}C present minus the mass leached during the 30 s initial wastefrom rinse the fraction leached was calculated and listed in Table A. 3.

Table A. 3: Fraction of Initial Element Mass in Leachwater During Leaching Intervals

Leach sampling time (hours)	^{13}C leached during leach interval (mg)	Fraction of initial mass of ^{13}C leached during interval
2	0.0389	0.000967
7	0.0371	0.000923
24	0.0799	0.00199
48	0.0345	0.000857
72	0.0711	0.00177
96	0.0643	0.00160
120	0.0499	0.00124
456	0.175	0.00437
1128	1.04	0.0265

To calculate the cumulative fraction leached the mass of ^{13}C leached during each interval was added to the sum of the masses leached in previous intervals (summarised in Table A. 4).

Table A. 4: Cumulative Fraction of Initial Mass of Element Leached During Leaching

Leach Time (hours)	Cumulative Fraction Leached
2	0.00171
7	0.00263
24	0.00462
48	0.00547
72	0.00724
96	0.00884
120	0.0101
456	0.0144
1128	0.0409

APPENDIX B. CUMULATIVE FRACTION LEACHED CURVES

Key to graph labels:

OPC – Wasteforms produced with only OPC

FA- Wasteforms produced with OPC and fly ash

SF – Wasteforms produced with OPC and silica fume

C – Wasteforms not carbonated

OS1 – Wasteforms one-step carbonated, shorter exposure

OS2 – Wasteforms one-step carbonated, longer exposure

V – Wasteforms vacuum carbonated

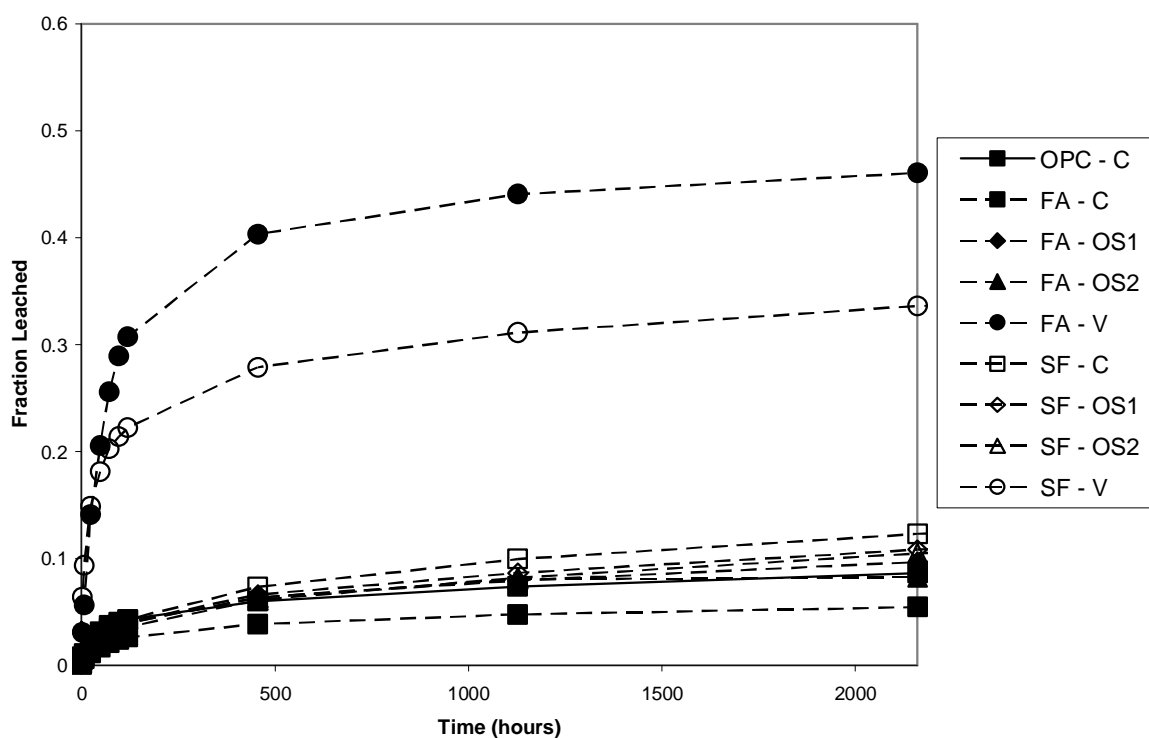


Figure B. 1: Cumulative Fraction of Cl Released

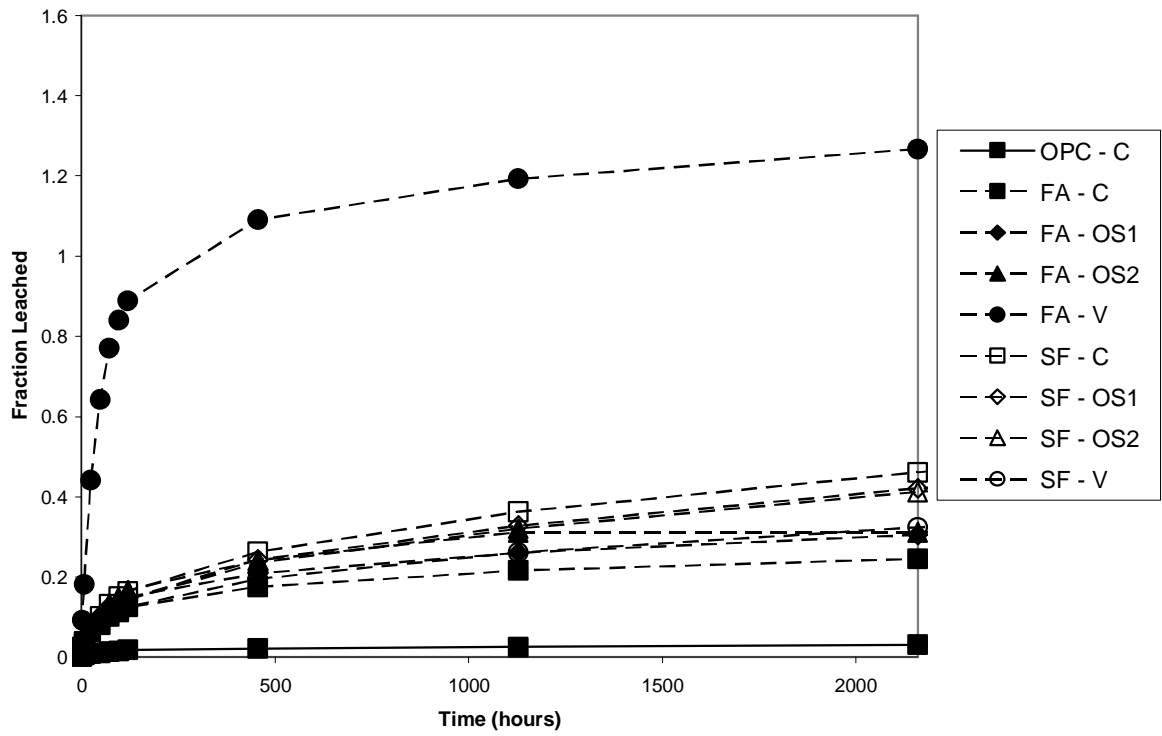


Figure B. 2: Cumulative Fraction of N Released

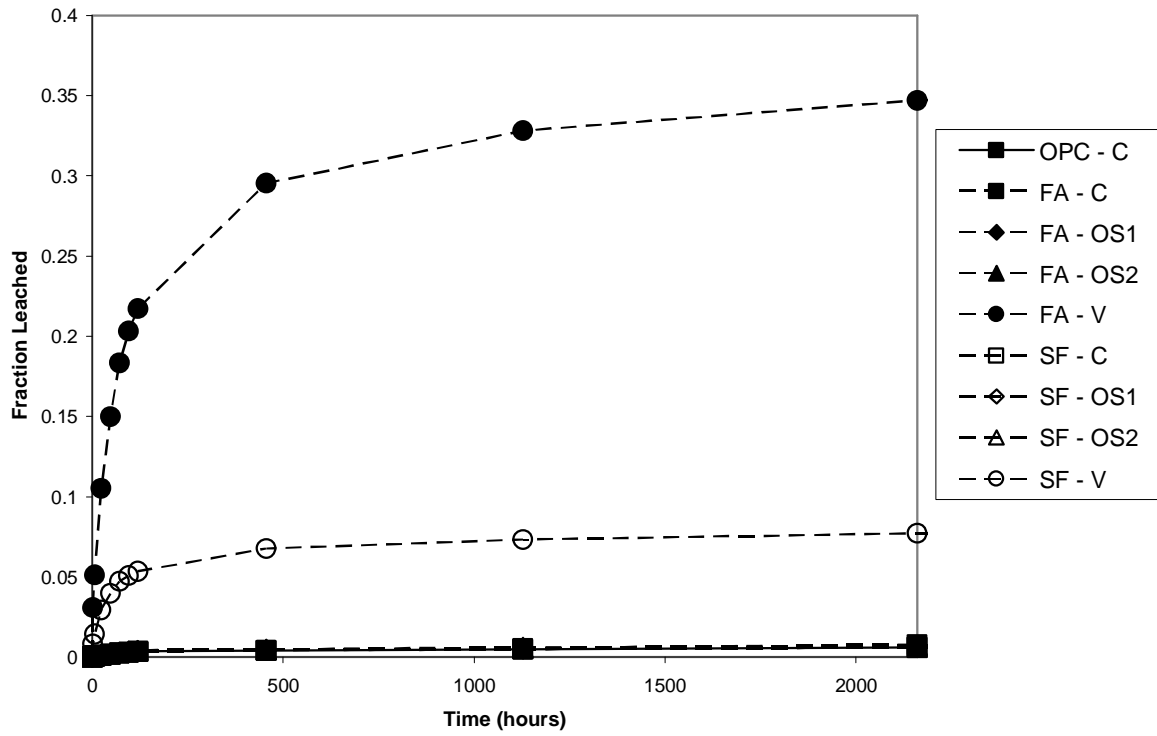


Figure B. 3: Cumulative Fraction of S Released

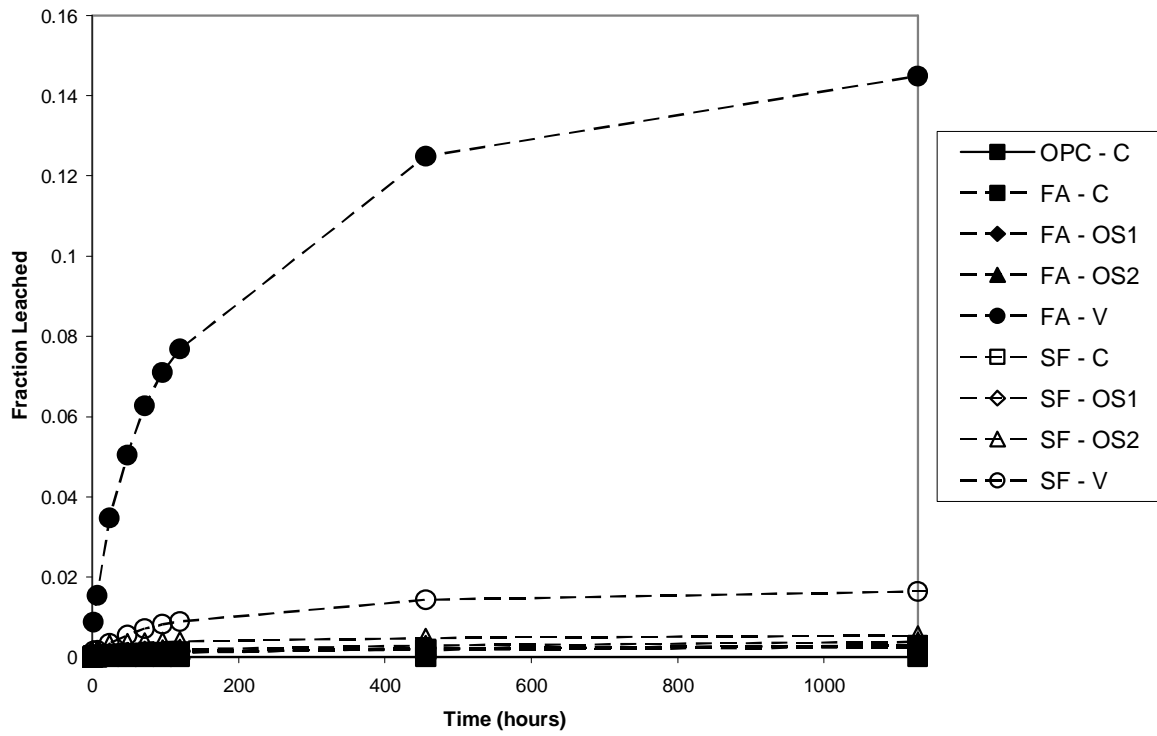


Figure B. 4: Cumulative Fraction of Se Released

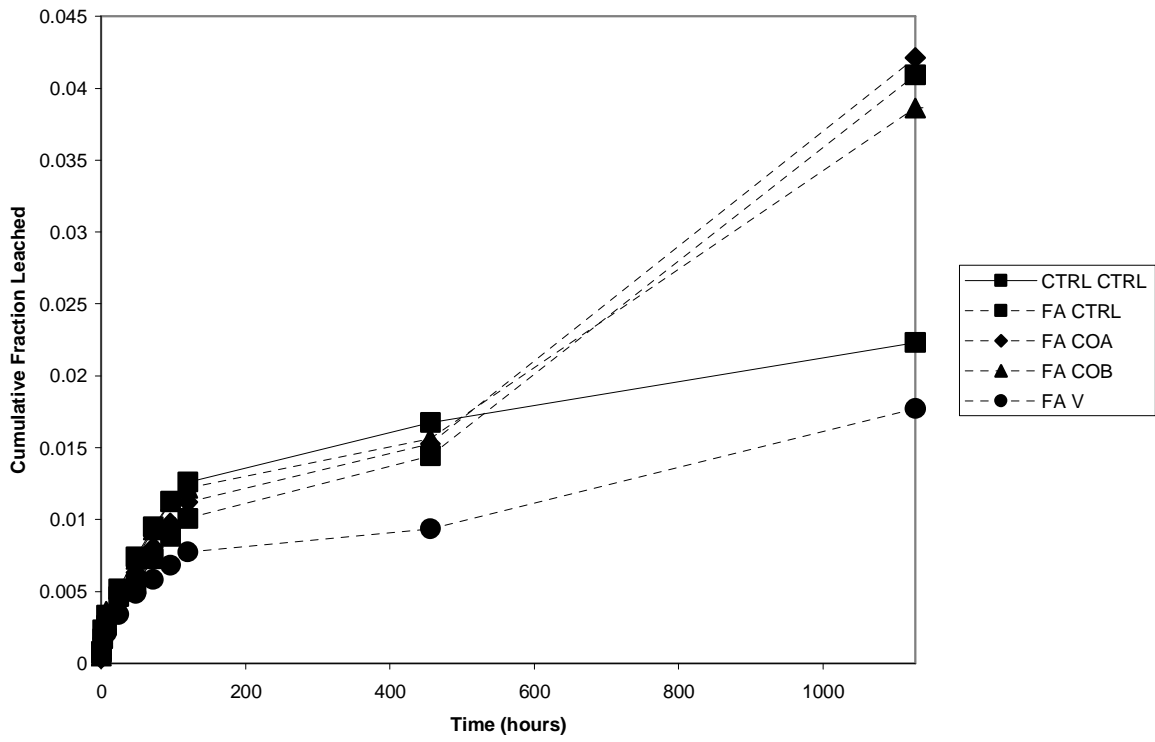


Figure B. 5: Cumulative Fraction of ¹³C Released

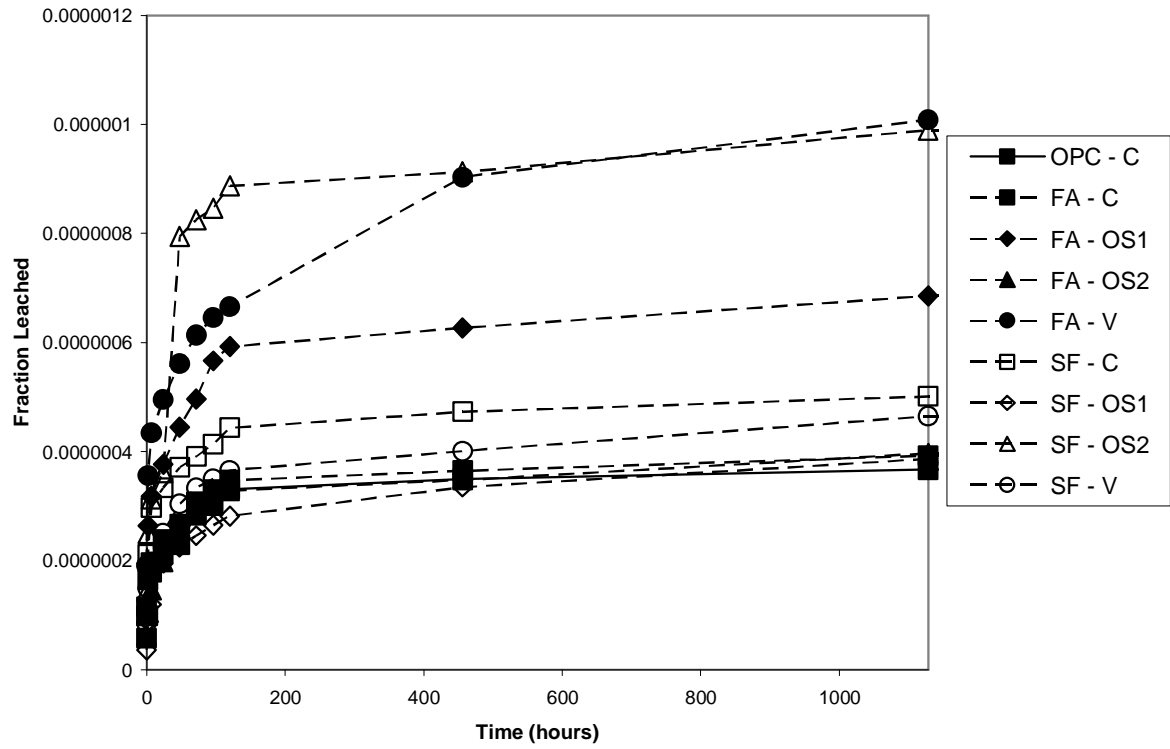


Figure B. 6: Cumulative Fraction of Th Released

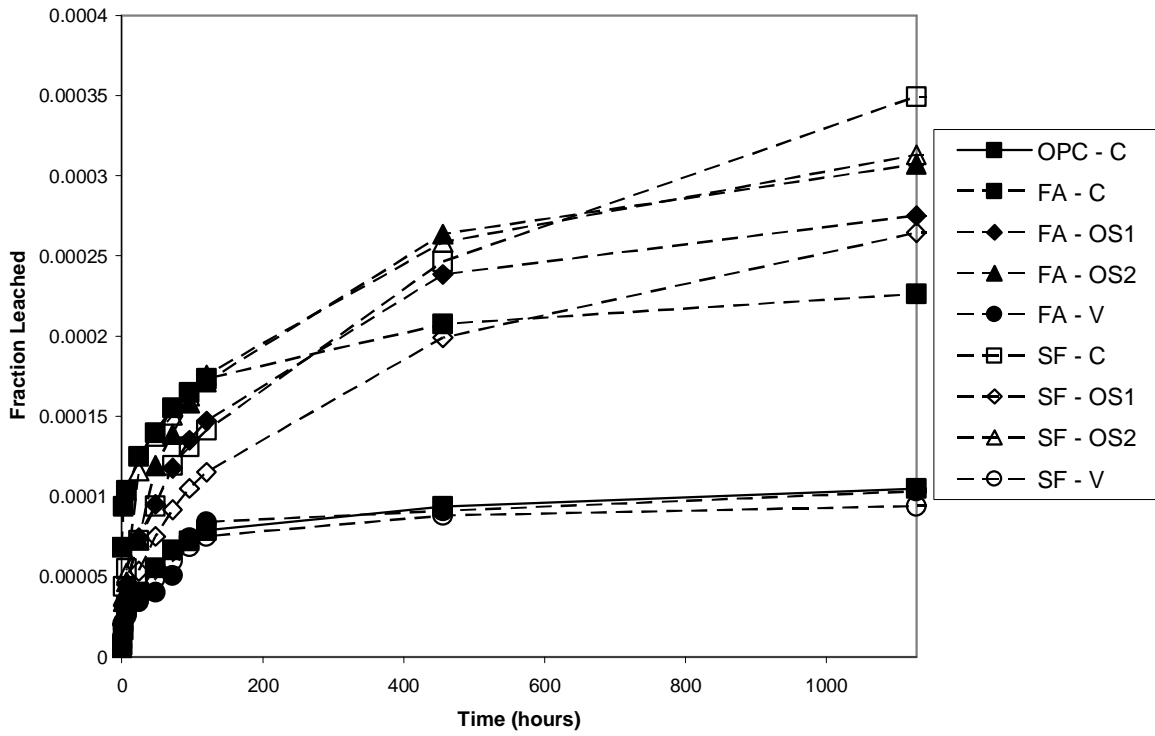


Figure B. 7: Cumulative Fraction of Pb Released

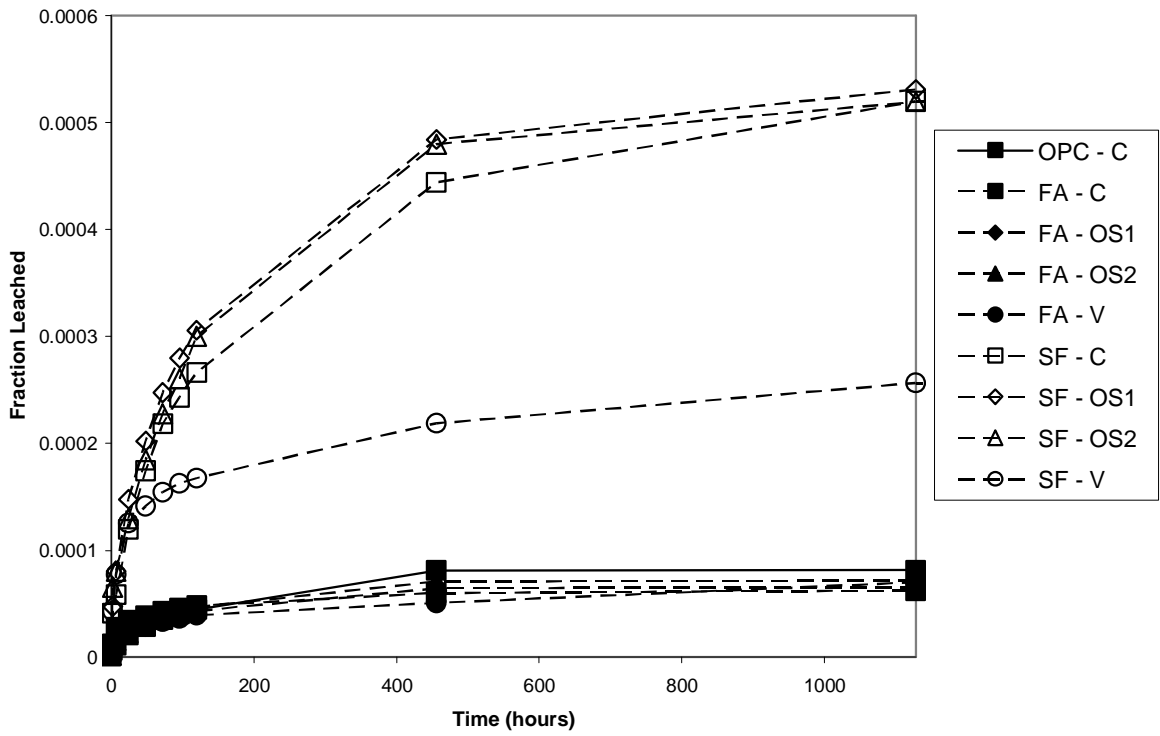


Figure B. 8: Cumulative Fraction of Co Released

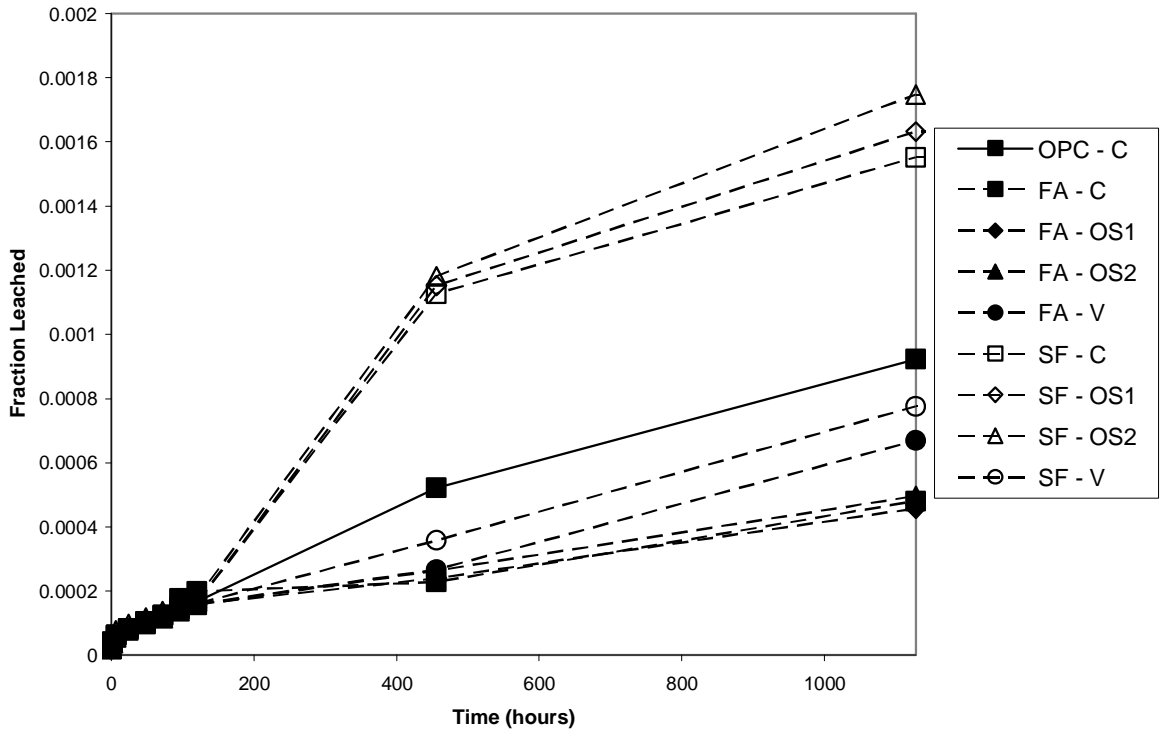


Figure B. 9: Cumulative Fraction of Ni Released

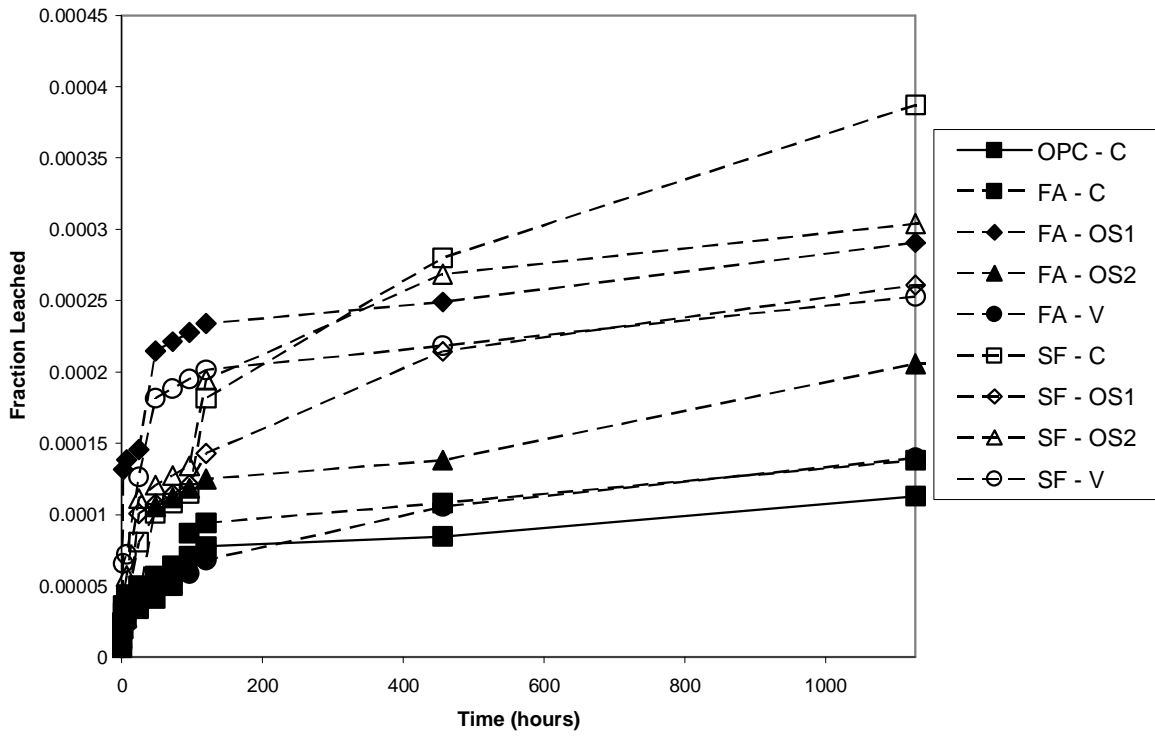


Figure B. 10: Cumulative Fraction of Cu Released

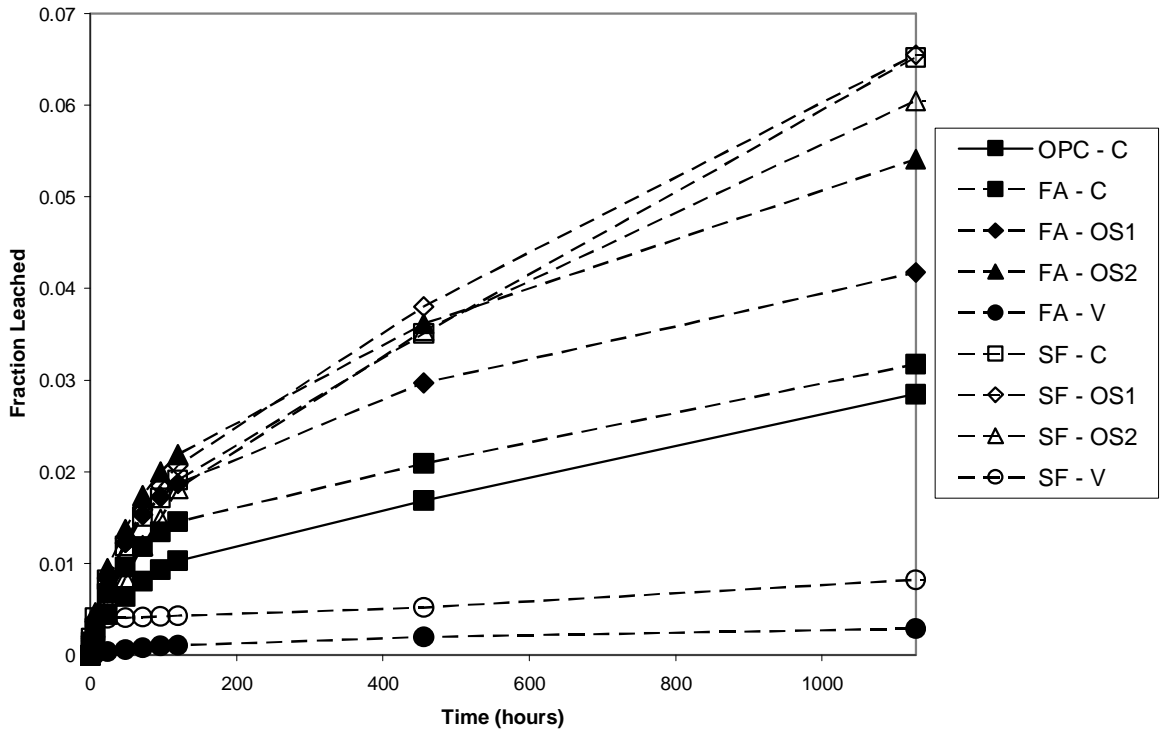


Figure B. 11: Cumulative Fraction of Sr Released

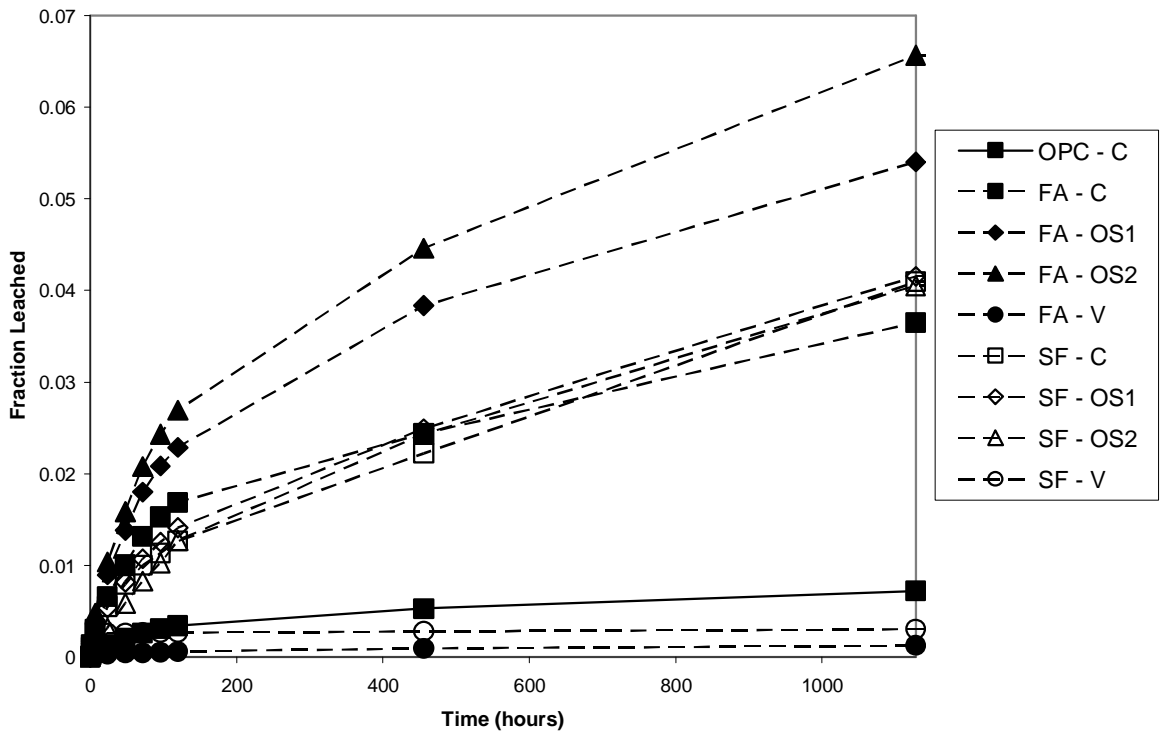


Figure B. 12: Cumulative Fraction of Ba Released

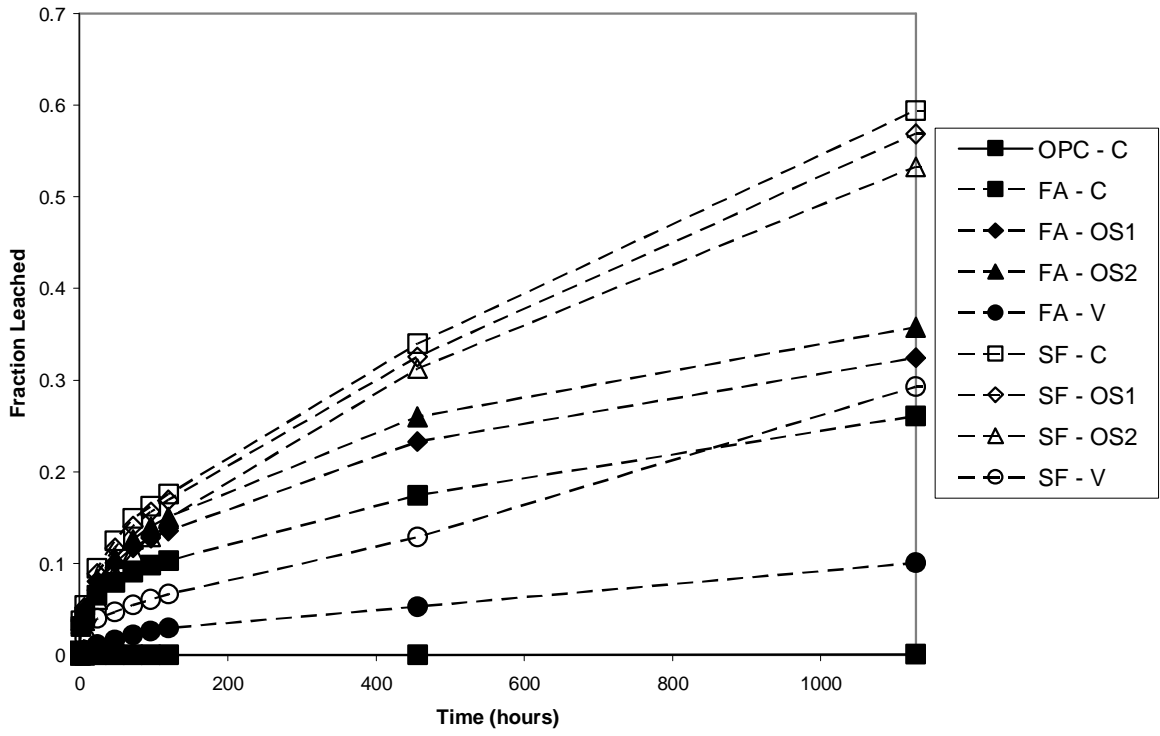


Figure B. 13: Cumulative Fraction of Cs Released