Material Characterization of High Density Concrete Using Different Analytical Techniques to Support Licencing Requirements for a Class II Radiation Facility

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Abstract

As a part of the commissioning process for a class II irradiation facility at the University of Ontario Institute of Technology (UOIT), it is required to provide the elemental composition of the construction materials (high density concrete) used for the purpose to shield ionizing radiation to the Canadian Nuclear Safety Commission (CNSC) with reference to the RD/GD-289 regulatory document. This paper explains the analytical techniques and the results of the elemental composition of the high density concrete used as the shielding material.

Keywords: RD/GD-289, radiation shielding, high density concrete, inductively coupled plasma, x-ray fluorescence, scanning electron microscopy, thermogravimetric analysis

1. Introduction

A new research facility located in the basement of the Energy Research Center (ERC) at UOIT is designed to accommodate a Model G-10 gamma irradiator, an accelerator-based high intensity neutron generator with an output of 10^{10} neutrons per second, a high output x-ray machine, and isotropic neutron sources. The construction materials of the ERC building utilized three main types of concrete. Regular concrete with a density of 2.4 g/cm^3 was used to construct the foundation, footings, and the floor of the research facility, while high density (HD) poured concrete and high density interlocking chevron type (HD-ICT) concrete bricks with a density of 4.0 g/cm3 and 3.8 g/cm3 respectively were used for the inner walls as shown in Figure 1.

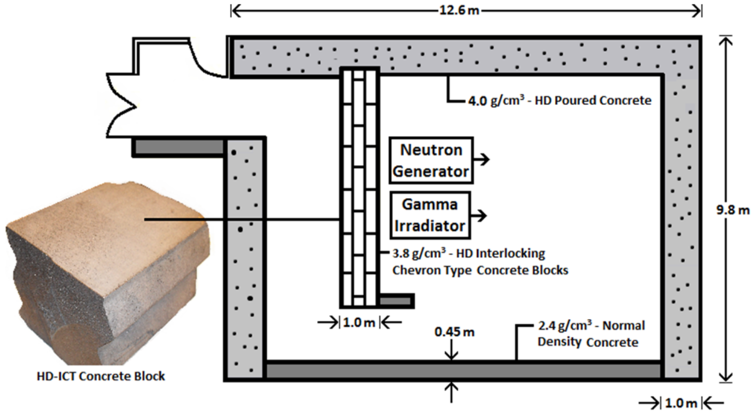

Figure 1 Plan view of the UOIT class II neutron and gamma irradiation facility within the Energy Research Center (ERC)

The removable wall inside the irradiation facility was built from HD-ICT concrete bricks to bring oversized equipment to the facility while adequately providing biological shielding against ionizing radiation. The main ingredient in the HD-ICT concrete bricks are the hematite (Fe2O3), ilmenite (FeO TiO2), magnetite (Fe3O4), and steel aggregates [1].

As per the RD/GD-289 regulation document provided by the CNSC, class II nuclear facilities are required to provide compositional information pertaining to shielding materials for the purposes of modelling radiation doses using software codes such as the Monte Carlo N-Particle (MCNP) radiation transport code. The physical and material properties of the HD poured concrete and HD-ICT concrete bricks were investigated using scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), x-ray fluorescence (XRF) spectroscopy, and thermogravimetric analysis (TGA) techniques. Several advantages and disadvantages of these analytical techniques have been discussed within the scope of this paper.

2. Methodology

2.1 XRF Sample Preparation and Analysis

A calibrated portable Innov-X Systems α-2000 AS XRF spectrometer was used for elemental characterization of HD concrete. Small chunk samples of HD poured concrete, HD-ICT concrete bricks, and aggregates were ground using a mortar and pestle manually. The grinding time for each sample was approximately 10 minutes to achieve consistency with sample particle size. A count time of 120 seconds was kept consistent between analyses to avoid any statistical discrepancies between elemental results for different samples. Figure 2 shows the superimposed XRF spectra obtained from all three samples. It is clear from the spectra that elements such as titanium (Ti), iron (Fe), rubidium (Rb) and selenium (Se) are a major portion of aggregates within the HD poured concrete. Since the HD poured concrete consists of Portland cement and mineral aggregates, the spectral difference between the

HD poured concrete and the aggregates can be deduced to be the Portland cement mixture (mainly calcium and strontium oxides).

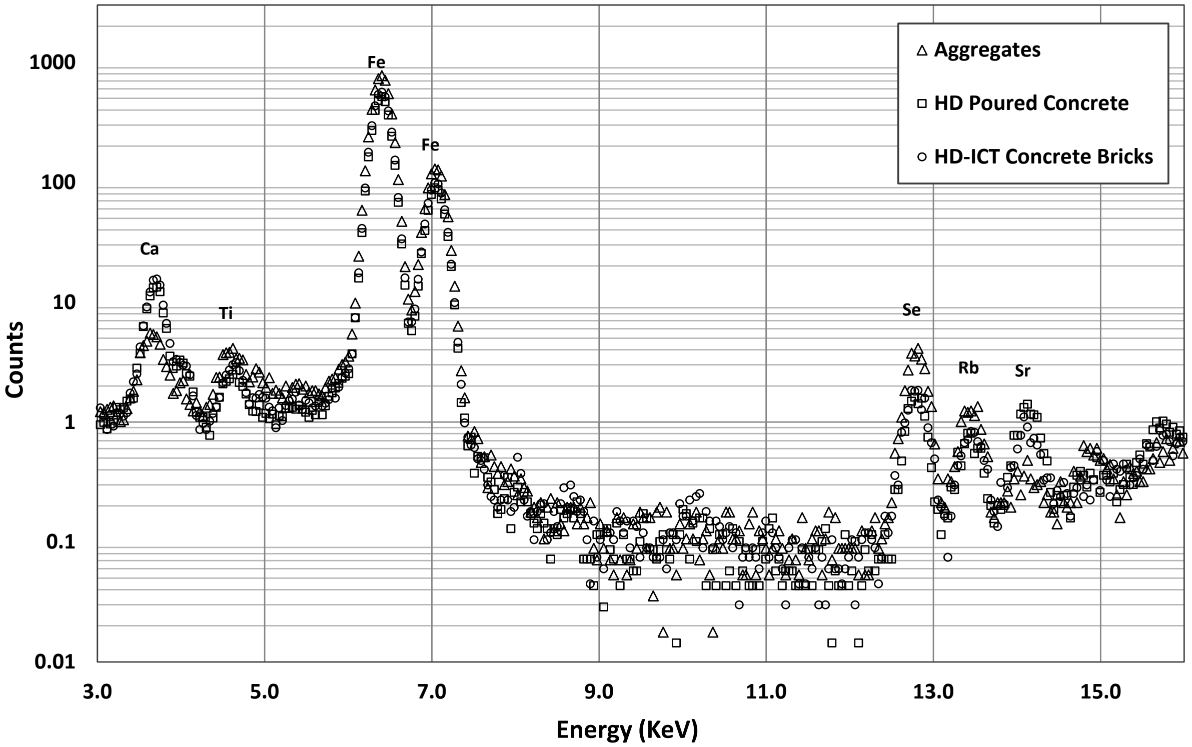

Figure 2 Superimposed x-ray fluorescence spectra of concrete aggregates, HD poured concrete and HD-ICT concrete bricks

An XRF spectrometer consists of an x-ray tube enclosing a cathode emitter and an anode target usually made of materials such as rhodium (Rh), tungsten (W), chromium (Cr), molybdenum (Mo), etc. Electrons generated from thermionic emission from the cathode emitter are accelerated by an electric field induced by a voltage potential and are bombarded at the anode target. The resulting x-rays are allowed to impinge on the sample through the XRF aperture with minimal Bremsstrahlung contamination (via filters). The x-rays transfer their kinetic energy to the atoms of the sample material through Photoelectric and Compton effects. The vacancy created by an electron ejection or excitation is then filled by a higher orbital electron or by the excited electron itself as it returns to ground state to stabilize to a lower potential energy. The electron releases energy in the form of characteristic x-rays that are specific to the elements within the sample. Since this is specific for each element, the detection of these characteristic x-rays via XRF spectrometry makes it a method for element identification when compared against a library of calibrated energies. Table 1 shows a list of elements that are common to concrete and their respective $K_{\alpha 1}$ and $K_{\beta 1}$ energies.

Element	$K_{\alpha 1}$ Peak Energy (keV)	$K_{\beta 1}$ Peak Energy (keV)
Hydrogen (H)	---	---
Oxygen (O)	0.530	---
Sodium (Na)	1.040	1.070
Magnesium (Mg)	1.250	1.300
Aluminum (Al)	1.490	1.550
Silicon (Si)	1.740	1.830
Phosphorus (P)	2.020	2.140
Sulphur (S)	2.310	2.460
Potassium (K)	3.310	3.590
Calcium (Ca)	3.690	4.010
Titanium (Ti)	4.510	4.930
Manganese (Mn)	5.900	6.490
Iron (Fe)	6.400	7.060
Zinc (Zn)	8.640	9.570
Rubidium (Rb)	13.390	14.960
Lead (Pb)	74.960	84.920

Table 1 $K_{\alpha 1}$ and $K_{\beta 1}$ peak energies of common elements found in concrete

Calibration of the XRF instrument requires several factors to be considered: detector resolution, sample matrix effects, accuracy of calibration standards and its suitability to sample matrix, sample homogeneity, and particle size. The standards used to calibrate must display similar traits to the sample matrix to produce reliable XRF results [2].

2.2 SEM-EDS Sample Preparation and Analysis

A Jeol JSM 6400 scanning electron microscope was used for high resolution imaging of sample surfaces of the HD poured concrete and the HD-ICT concrete bricks while obtaining compositional information through energy dispersive spectroscopy (EDS) using an incident electron beam to produce characteristic x-rays which are detected and compared against a library of calibrated energies. Preparation for SEM-EDS involves pressing an aluminium stub (diameter = 1 cm) with adhesive carbon tape on one side onto fine ground samples of HD concrete. The adhesive carbon tape is used as a means to hold the finely ground HD concrete samples while maintaining electrical conductivity. The SEM analysed the samples in a 20 kV accelerated voltage. The spot frames that were chosen for analysis were selected based upon visual judgement and image contrast. The different intensities of brightness and contrast generated from secondary radiation emitted from each of the different spot frames explained a considerable amount about the composition of that relative frame when compared to the percentage composition gained from EDS. With reference to the HD poured concrete sample, the lighter portions of each spot frame refer to elements such as Mg, Al, Si, P, S, K, Ca, Ti and Rb while the darker frames refer mostly to Fe (See Figure 3). Due to oxidization from exposure to air, oxygen was present in all frames in almost equal proportions. Observations through SEM showed sample matrix heterogeneity i.e. elements are localized at micro-scale and are unevenly distributed. It can be assumed that these spatial locations refer to the whole sample. Thus, averaging the compositions of these different spot frames would determine the relative composition of HD poured concrete as shown in Figure 4.

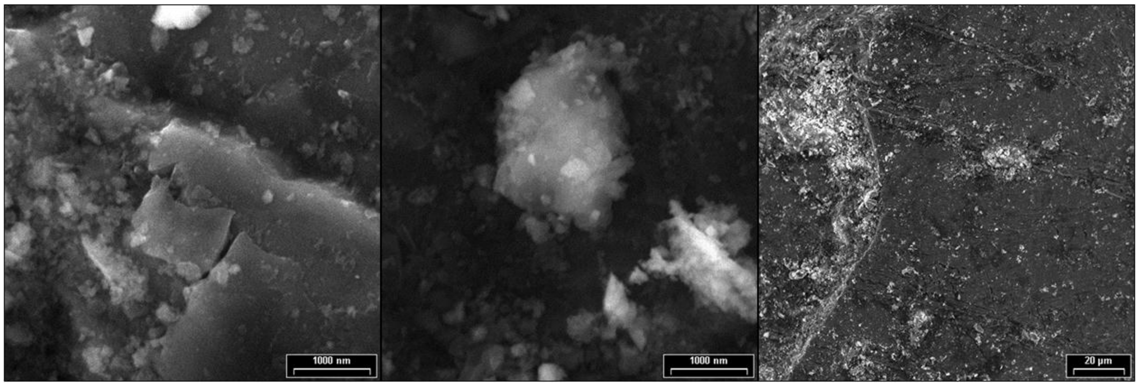

Figure 3 SEM imaging of the HD poured concrete sample (low-contrast SEM spot frame magnified at x10000 (left), a high-contrast SEM spot frame magnified at x10000 (middle), and an overlay SEM spot frame magnified at x300 (right)

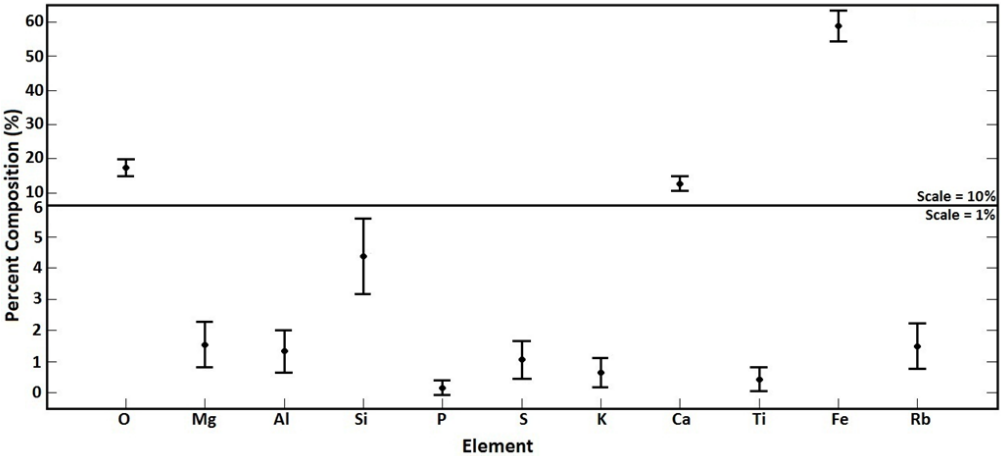

Figure 4 Measured percentage composition of HD poured concrete using SEM-EDS

With reference to the HD-ICT concrete brick sample analysed using SEM-EDS, Figure 5 shows a low-contrast SEM spot frame magnified at x10000, a high-contrast SEM spot frame magnified at x10000, and an overlay SEM spot frame magnified at x300. In this case, the high-contrast spot frame refers to the same elements as in HD poured concrete except Rb, and the low-contrast spot frame refers mostly to Fe. Again, the oxygen content can be seen in high ratios in all three frames which can be assumed as a bonding partner for many complementary elements to create mineral oxides and unbound H_2O. Figure

6 shows a graphical representation of the composition of the HD-ICT concrete brick sample using the SEM-EDS technique.

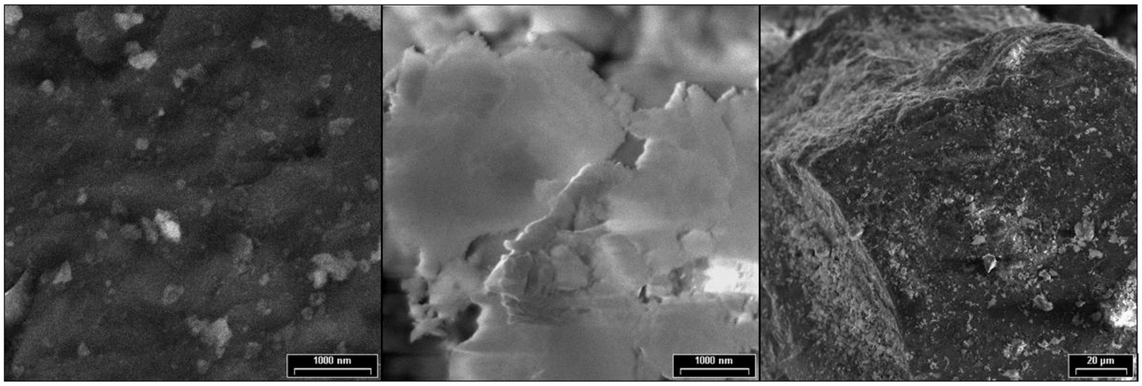

Figure 5 SEM imaging of the HD-ICT concrete brick sample (low-contrast SEM spot frame magnified at x10000 (left), a high-contrast SEM spot frame magnified at x10000 (middle), and an overlay SEM spot frame magnified at x300 (right)

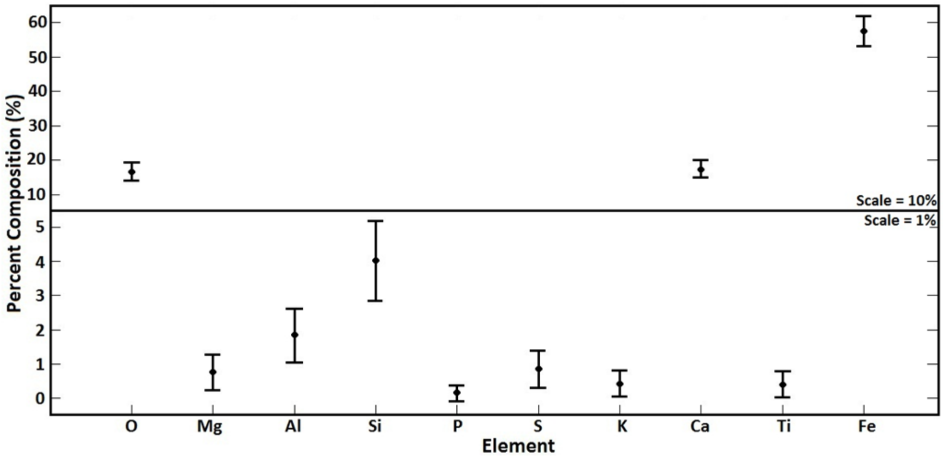

Figure 6 Measured percentage composition of HD-ICT concrete bricks using SEM-EDS

SEM-EDS uses a collimated beam of high-energy electrons which are bombarded and slowed-down within the target sample. Collected secondary and backscattered electrons along with characteristic x-rays are used to provide spatial and compositional information [3]. The received secondary electron signals from the deceleration process directly produces SEM images while characteristic x-rays determine the chemical composition via energy dispersive spectroscopy. However, the clarity of the image depends on the noise of the received signal, developed from the statistical nature of signal construction and collection process [4]. Ferraris, Hackley and Aviles [3] refer to four factors that can account for noise: poor particle size distribution, poor differentiation between primary particulates and compounded particulates, 3D/2D spatial effects, and contaminants produced during sample preparation. Evans and Tokar [5] also experienced difficulties due to poor size distribution and other non-uniform characteristics when recognizing elements embedded within sand particulates from sediment sources.

2.3 ICP-AES Sample Preparation and Analysis

The most critical, sensitive, and time consuming part of ICP-AES analysis is the sample preparation which aims to achieve total digestion of sample material into an acidic solution; the better the digestion of the sample within a known acid, the greater the accuracy of the measured concentration of elements within the sample. Powdered samples of the HD-ICT concrete brick and HD poured concrete were initially digested using nitric acid (also known as aqua fortis). The prepared solution was fed into a Vista MPX ICP spectrometer for analysis. Iron was barely digested by aqua fortis and was observed at low concentrations (4.81-6.45%). A more rigorous digestion procedure was conducted next which involved aqua regia (3:1 mixture of HCl and HNO3 respectively). This digestion procedure provided iron concentrations of 26.94-36.33%. However, this is still lower in comparison to the manufacturer's chemical composition of the HD-ICT concrete bricks which consists of approximately 58.44% iron.

	Iron %	**Calcium %**
Manufacturer Data	58.440	4.185
Digestion with Aqua Fortis	4.810	5.210
Digestion with Aqua Regia	26.940	4.420

Table 2 Measured iron and calcium yield using ICP-AES in HD poured concrete samples

	Iron %	**Calcium %**
Manufacturer Data	58.440	4.185
Digestion with Aqua Fortis	6.450	5.060
Digestion with Aqua Regia	36.330	4.000

Table 3 Measured iron and calcium yield using ICP-AES in HD-ICT concrete brick samples

Table 2 and Table 3 compares the digestion efficiency of both acids and presents the resulting concentrations of iron and calcium for the HD poured concrete sample and the HD-ICT concrete brick sample. The measured approximated composition of both the HD poured concrete and the HD-ICT concrete bricks is represented in Figure 7 and Figure 8.

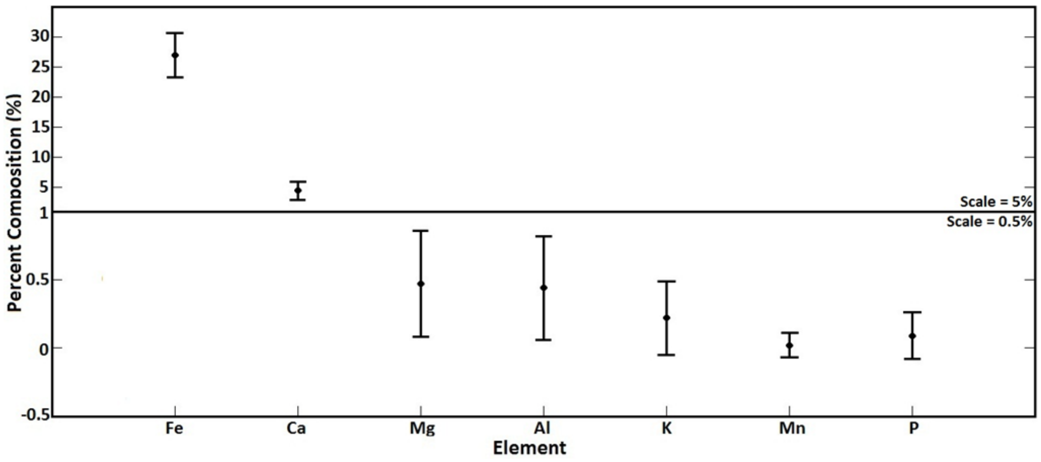

Figure 7 Measured percentage composition of HD poured concrete using ICP-AES

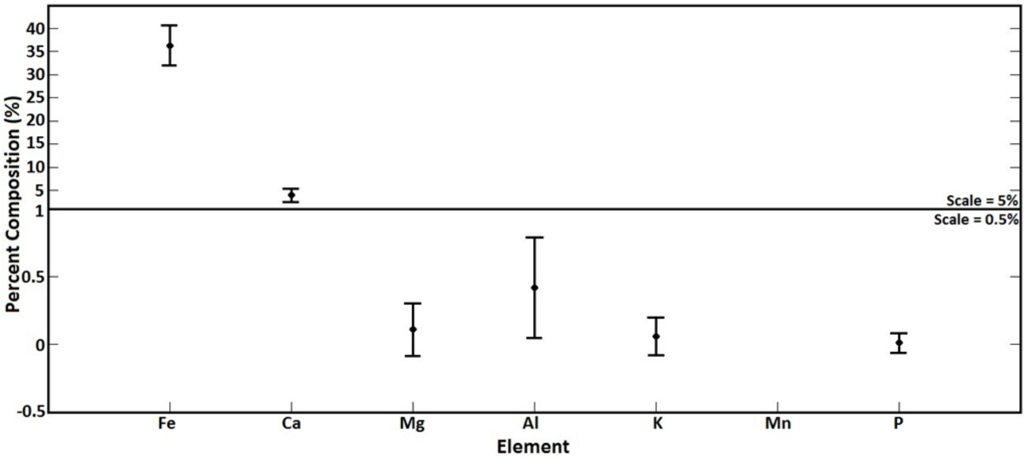

Figure 8 Measured percentage composition of HD-ICT concrete bricks using ICP-AES

ICP initially involves treating finely ground samples with acid and heat. The acid is specific to the element that is being digested; however for most elements nitric acid is sufficient. The digested samples are filtered of solid particulates with filter paper. The water within the sample is driven off as the nebulized solution goes through a 6,000 ºC to 10,000 ºC argon plasma in a process known as volatization. The aerosol is atomized, ionized, and excited within the argon plasma which consists of free electrons and argon ions (Ar+). The induced plasma has a 40 MHz radiofrequency and passes through an induction coil to produce a magnetic field [6]. The outer shell electrons are ejected from the argon atoms as they are thermally excited and are repeatedly accelerated by the magnetic field and collide with the argon ions. Due to the tremendous amounts of heat generated, the outer shell electrons of the nebulized sample solution are thermally excited. The resulting light emissions as the electrons return to their ground state are directed toward a slit and grating to disperse wavelengths. As each element will emit a characteristic light with a specific wavelength, cross-referencing of these wavelengths with a library of calibrated wavelengths identifies the elemental composition of the sample [6]. The intensity of the specific wavelength of light emitted from these interactions is directly proportional to the concentration of that respective element within the sample. However, 100% digestion cannot be fully ensured of a specified element due to the resistivity of that element to the digestion acid. Another major drawback lies in detecting elements with various oxidation states. ICP-AES does not identify different oxidation states of the same element, and will categorize the combined result with an oxidation state of 0 or +1 [6]. Experimental data suggests that aqua regia digests far better than aqua fortis (nitric acid). Aqua regia performs better with refractory metals; metals resistant to high amounts of heat, corrosion and wear [7]. Since the digestion properties of this acid is sufficient for most of the elements in HD concrete, it can be used effectively during sample preparation for ICP-AES analysis to characterize the material composition of HD concrete [8].

2.4 Thermogravimetric Analysis

Thermogravimetric analysis is useful for determining the stability of a material based on various temperature and atmospheric conditions. A sample is placed in an alumina sample pan and the temperature is increased to a desired final temperature while changes in the mass of the sample are simultaneously monitored. Changes in mass at characteristic temperatures, such as melting and boiling points, can give insight into the composition of material. Inert atmospheres such as nitrogen or argon will show a profile of volatile components and decomposition products while analysis under air can indicate combustion or formation of oxides. Since certain components of a respective sample change by the means of combusting or vapourizing at characteristic temperatures, a suggestion of material composition can be established.

Thermogravimetric analyses were performed for ground samples of HD concrete using a TA Instruments Q600 SDT thermal analyzer. Samples of 5-10 mg were heated from room temperature to 1000 ºC at a rate of 20 ºC per minute under flowing argon (50 mL per minute) to determine decomposition profiles. One of the main goals in employing the TGA technique was to determine the composition of “free” (not embedded) H2O in the HD concrete sample. Residual free water from the formation process, or from atmospheric adsorption, should evolve from the TGA spectra at 100 ºC under argon. Additionally, chemically-bound water should evolve up to 400 ºC [9,10,11]. The mass loss associated with free water for the HD concrete sample was 0.046 ± 0.021% of the total composition, while the total water loss from either free or chemically-bound water was 0.131 ± 0.055%. The TGA profiles also showed decomposition around 600 ºC, which is likely due to the dehydration of Ca(OH)2 [9,11,12]. The concentrations of calcium and oxygen found through EDS analysis suggests the presence of Ca(OH)2, as it is a common component of cement materials. This mass loss associated with the decomposition of Ca(OH)2 accounts for 0.311 ± 0.111% of the composition. The remaining mass loss up to 1000 ºC is 0.036 ± 0.064%.

3. Conclusions

Since approximately 30-40% of the material composition of concrete (normal or high density) consists of elements below the atomic number of 15 (phosphorus), XRF spectroscopy was not useful in quantifying the percentage composition as these elements were not spectrally resolvable due to the lack of x-ray interaction with the low density of electrons of those elements. However, the XRF spectra of the HD poured concrete sample, the HD-ICT concrete brick sample, and mineral aggregates presented valuable information with regards to elemental make-up and relative quantity of the Portland cement mixture. SEM-EDS was very useful and efficient for identifying and quantifying elements such as Fe, O, Si, S, Ti and Rb. An advantage of SEM-EDS over ICP-AES and XRF is the detection of oxides which can be manipulated to calculate the oxygen content within the sample. Iron concentrations were accurately measured with SEM-EDS with a percentage difference of 0.79% for HD poured concrete and 1.61% for HD-ICT concrete bricks with respect to the manufacturer’s data. For other elements present in trace amounts, accuracy was not achieved; however, ICP-AES proved to be very accurate for trace elements being analysed. When measuring iron concentrations using ICP-AES, a lower iron concentration was obtained which can be attributed to the mixture of iron oxides with silica particulates. It can be assumed that iron oxides mixed with silica in concrete allows for the iron to embed itself within the silica particulates. Since silica particulates cannot be digested effectively with aqua regia or aqua fortis, the embedded Fe will not be completely detected using ICP-AES as the solid particulates would have been filtered from the sample solution before being fed into the ICP spectrometer for volatization. The percentage composition results from both SEM-EDS and ICP-AES analyses are shown in Table 4 and Table 5.

Element	**Manufacturer**	**SEM-EDS**	**ICP-AES**
Fe	58.440	58.9	26.940
Ca	4.185	12.7	4.420
Mg	0.215	1.5	0.468
Mn	0.090	---	0.022
Na	0.010	---	---
O	33.285	17.3	---
Al	0.555	1.4	0.442
Si	2.015	4.4	---
H	0.385	---	---
P	0.010	0.2	0.087
S	0.110	1.1	---
K	0.020	0.6	0.215
Ti	0.535	0.4	---
Rb	---	1.5	---

Table 4 Measured composition of HD poured concrete using both SEM-EDS and ICP-AES in comparison to the manufacturer data

Element	**Manufacturer**	**SEM-EDS**	**ICP-AES**
Fe	58.440	57.5	36.330
Ca	4.185	17.4	4.000
Mg	0.215	0.8	0.108
Mn	0.090	---	---
Na	0.010	---	---
O	33.285	16.7	---
Al	0.555	1.8	0.421
Si	2.015	4.0	---
H	0.385	---	---
P	0.010	0.1	0.013
S	0.110	0.9	---
K	0.020	0.4	0.062
Ti	0.535	0.4	---

Table 5 Measured composition of HD-ICT concrete bricks using both SEM-EDS and ICP-AES in comparison to the manufacturer data

A disadvantage of ICP-AES was the amount of time taken to perform ICP with respect to SEM-EDS or XRF. SEM-EDS analysis took about 4 man-hours in total which includes the sample preparation while ICP-AES took about 12 man-hours in total. Also, the samples were required to be filtered of solid particulates for ICP which in total takes about a day of delay time to completely pass through the filter paper(s). Allocation of sample preparation and instrument time for sample analysis is a very important factor in the industry and for business as it is affects the efficiency and economic value of the analysis. Furthermore, a complex preparation of standards and calibration solutions are required for ICP-AES which allow calibration of the spectrometer for photon wavelength identification, while SEM-EDS analysis does not require much preparation other than preparing the carbon-coated aluminium stub. Thus, for concrete composition analysis, SEM-EDS provided efficient results for non-trace elements while ICP-AES provided accurate but time-consuming results for trace elements within HD concrete. TGA analysis was able to determine the amount of water present in both free and chemically-bound forms. It can also provide a suggestion of components in the concrete samples, when used in conjunction with elemental analysis techniques. The final composition of HD poured concrete and HD-ICT concrete bricks is represented in Table 6.

Analytical Technique	**Element**	**Manufacturer (%)**	**Calculated**	
			HD Poured Concrete (%)	**HD-ICT Concrete Brick (%)**
SEM-EDS	Fe	58.44	58.9	57.5
	Si	2.015	4.4	4
	Ti	0.535	0.4	0.4
ICP-AES	Ca	4.185	4.42	4
	Mg	0.215	0.468	0.108
	Al	0.555	0.442	0.421
	K	0.02	0.215	0.062
	Mn	0.09	0.022	0
	P	0.01	0.087	0.013
	O, H	33.285	30.646	33.496

Table 6 Final composition of HD poured concrete and HD-ICT concrete bricks using combined results obtained from SEM-EDS and ICP-AES

4. References

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