Performance of geopolymer concrete subjected to mineral acid tests in static and dynamic conditions

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Abstract

Geopolymer cements are an emerging alternative binder to Portland cements, characterised by an alumino-silicate polymer network nanostructure. These binders are purported to possess numerous beneficial properties such as acid resistance and a relatively low carbon footprint. This study sought to assess the performance of a fly ash-based geopolymer concrete developed at the CSIR, exposed to mineral acids (HCl and H_2SO_4) under static and dynamic exposure conditions. Portland cement and calcium aluminate cement concretes using calcareous aggregates (dolomite) were used as control specimens, while geopolymer cements were mixed with a range of calcareous and siliceous aggregates. The test results show that the resistance of geopolymer concretes exposed to hydrochloric acid in dynamic and static conditions is significantly higher than Portland cement and calcium aluminate cement concretes, where mass loss was used as a measure. The study also shows that the acid resistance of geopolymers can be further improved by combining them with siliceous aggregates instead of calcareous aggregates. Furthermore, a linear empirical relationship, between basicity (related to the major acidic and basic oxides established via XRF) and the rate of dissolution of concrete in acidic solutions was observed. Basicity was also related to preferential corrosion in concrete mixtures exposed to the dynamic HCl test, and it was found that the difference in the basicity of the paste and aggregate of concrete mixture was useful in determining the type and extent of preferential corrosion.

Keywords: Geopolymers, sulfuric, hydrochloric, acid, resistance.

1. BACKGROUND

The advent of alternative concrete binders such as geopolymers has resulted in the need for the benefits of these materials to be defined and quantified. Amongst the stated benefits of geopolymers is high resistance to acid attack [1] [2]. Acid resistance is a desirable property for concrete structures such as outfall sewers, which are often plagued by a severe type of degradation known as microbially-induced corrosion (MIC). While MIC is known to be more severe in warm climates, the problem has also been reported in cooler countries such as Germany, where a study of the sewer network revealed that MIC was responsible for approximately 40% of all sewer failures [3].

MIC is a highly complex problem wherein the complexity emanates from a large set of variables encountered in the sewer environment, in which the variables include, temperature, effluent flow characteristics, the sewer microbiome, concrete material properties, and concrete corrosion products.

Because MIC is a durability problem, it is useful to describe a material's resistance to MIC in relation to the definition of durability. In the context of durability, resistance to MIC relates to a concrete structure's ability to remain serviceable during its planned life [4]. Thus, in this context, a MIC resistant material need not necessarily be chemically resistant to acids. It is therefore of interest to establish which material properties contribute to MIC resistance.

It is suggested that the MIC resistance properties of a material be categorised into chemical, physical and biological properties (Figure 1-1).
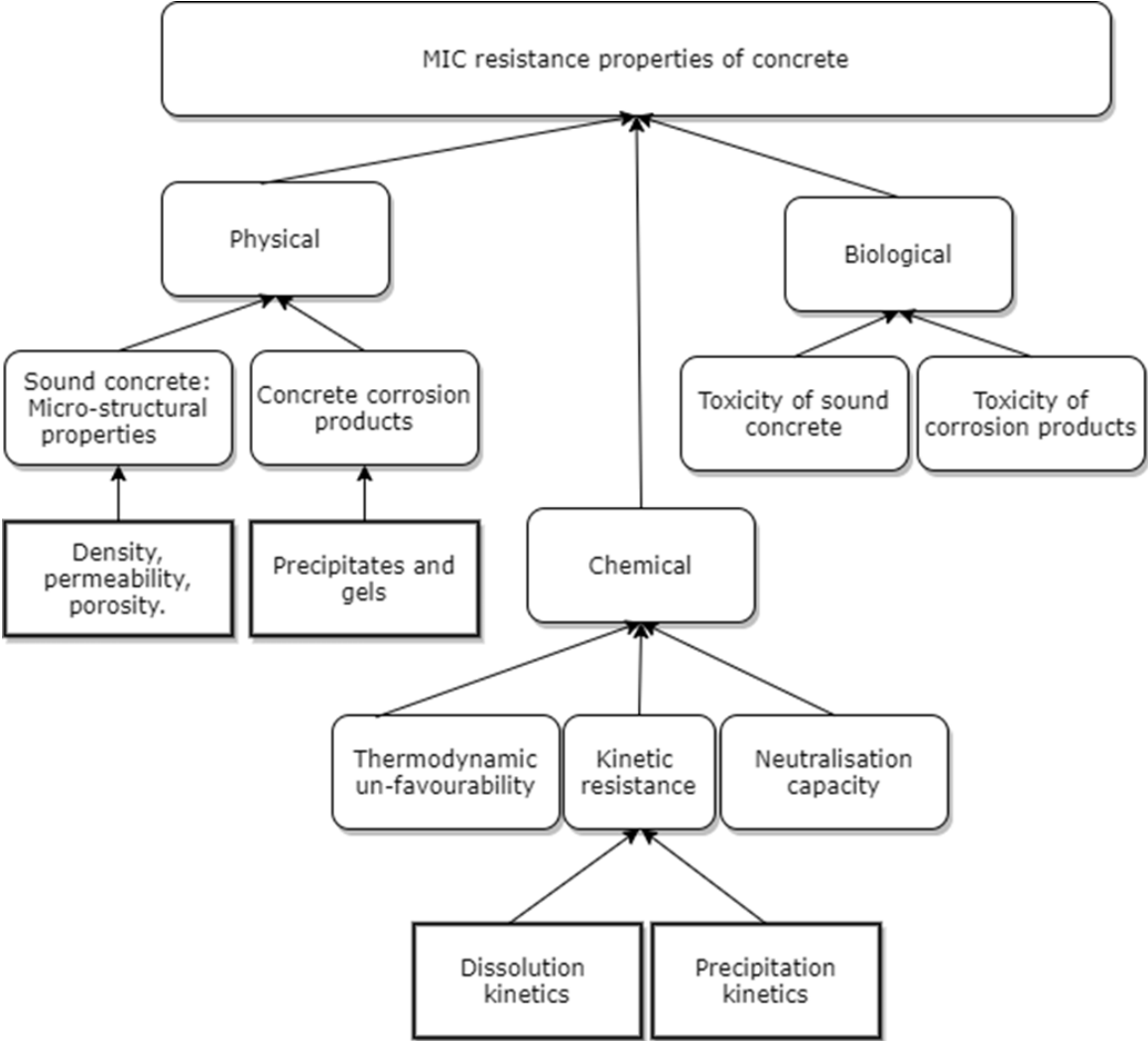
Figure 1-1: Suggested MIC resistance properties of concrete

A significant chemical property related to MIC resistance is the kinetics of the sulfuric acid corrosion reaction. Given that different materials react at different rates with sulfuric acid [5], it is suggested that materials which corrode at slower rates, possess a type of MIC resistance related to the kinetics of the corrosion reaction. At the fundamental chemical level, geopolymers are suggested by researchers to degrade via depolymerisation of aluminosilicate polymers and liberation of silicic acid, replacement of Na and K cations by hydrogen or hydronium ion and dealumination of the geopolymer structure [1].

Furthermore, the capacity of a material to neutralise a specific amount of acid is also an important chemical material property and is dependent on the stoichiometry of the corrosion reaction [5]. For instance, calcium aluminate cements (CAC) have been reported to possess a 40% higher neutralisation capacity than Portland cements [6] [7]. For the range of thermodynamic conditions present in sewers, it is also possible that some components of concrete such as compounds found siliceous aggregate are insoluble in sulfuric acid, thus making them inert due to the unfavourable thermodynamics of the corrosion reaction. Thus, the set of chemical properties of concrete important for understanding MIC performance are, on their own, highly complex.

Researchers have also advanced the notion that materials differ in their receptivity to bacteria and have suggested that some materials possess properties which enable a bacterio-static effect, which kills or stifles the growth of acid producing bacteria [6]. The bacterio-static effect is contentious because is difficult to measure. Studies attempting to measure the differences in corrosion where materials with purported biocidal properties have not yielded statistically significant results in the sewer environment. [8] [9]. Adding more complexity to the bacterio-static effect is that in some binders, the effect emanates not from the binder itself but from its corrosion products. For example, with CAC concretes, the bacterio-static effect is reported to emanate from the toxicity of aluminium ions liberated from gel (AH_3) when the surface pH of the concrete drops below 4 [6].

The physical properties of concrete also affect MIC resistance. A dense, impermeable micro-structure is suggested to improve resistance to MIC [8] [10]. Furthermore, insoluble corrosion products are also understood to provide a degree of protection to concrete subjected to MIC. For example, gypsum has been suggested to provide some degree of protection to MIC when Portland cements (PC) concretes are subjected to MIC [11]. This protection is achieved by gypsum coating the corroding surface and providing a physical barrier between the acidic solution and fresh attacks surfaces. Similarly, during the MIC of CAC concretes it has been suggested alumina gel (AH_3) provides a physical barrier to corrosion by coating the surface of the concrete [7].

With these forms of resistance identified, it is of interest to see which resistance properties can be measured in accelerated laboratory tests. It is proposed that the mineral acid tests used in this study may be used to assess two specific MIC resistance properties. The first property is related to concrete's chemical stability in acidic solutions, and measures the rate at which concrete constituents are dissolved in acid. This type of resistance to MIC is also applicable to any form of acid based corrosion. Researchers [9] suggest that corrosion process is governed by two distinct sequential steps, dissolution and precipitation, and that these steps often overlap

and occur at different rates. Furthermore, it is suggested that the rate if dissolution in acidic solutions is largely controlled by the pH of the solution and not the specific acid species [10].

In terms of the MIC of concrete, dissolution represents the first step in the damage of concrete. Given that concrete is a composite heterogeneous material, a useful rate of dissolution is likely to be an aggregated rate, wherein it accepted that the constituents that make concrete may dissolve at different rates.

A practical problem encountered in the measurement of the rate of dissolution is that the precipitation step of corrosion overlaps ongoing dissolution resulting in the deposition of precipitates at the surface of the corroding concrete specimen [9]. Furthermore, precipitation may, in cases where corrosion occurs in a closed system, cause a repression of the dissolution step by saturating the acidic solution, which in turn results in a higher concentration of dissolved ions and ultimately stalls the dissolution reaction through the common ion effect [6].

To address this problem for Portland cement concretes, Fourie [12] suggested the use of HCl which produces soluble $CaCl_2$ instead of H_2SO_4 which produces insoluble $CaSO_4$. However, not all HCl corrosion products are immediately insoluble. For instance, the corrosion reaction of HCl and CAC paste produces alumina gel (AH_3) as a corrosion product.

Therefore, to negate the stifling effects of precipitating corrosion products to the dissolution reaction, a means by which the corrosion products may be removed from fresh attack surfaces is required. It is suggested here that the dynamic HCl test developed at the University of Cape Town is a test suited to measuring the rate of dissolution for common concrete materials. The test involves immersion concrete in HCl at pH 1 and simultaneously exposes the surface of the rotating cylindrical specimen to brushing. Moreover, it suggested that brushing serves to remove corrosion products forming on the surface of a rotating cylindrical concrete specimen thereby eliminating any protection to sound concrete.

It is also useful to quantify the protective effects of precipitates forming on the surface of concrete. To this end, a static immersion test was used in which concrete specimens were immersed in HCl at pH 1. It is important to note that the primary difference between the dynamic acid test and the static acid test is the brushing, or physical removal of precipitates forming on the surface of the specimen tested in the dynamic acid test. Therefore, by measuring a parameter related to corrosion, such as mass loss over time in each test, the difference in the corrosion rates between the two tests enables a quantification of the protective effects of precipitates formed on the surface of concrete subjected to acid attack.

Thus the two, MIC resisting properties of geopolymer concrete and the control concrete mixes (Portland cement and calcium-aluminate cement concretes) assessed in this study are suggested to be the resistance to dissolution and the physical protection afforded by corrosion products precipitating on the surface of corroding concrete. These two properties were assessed using the dynamic acid test and the static acid test.

2. MATERIALS AND METHODS

2.1 Binders

A fly ash based geopolymer cement developed by the CSIR was the primary subject of testing. Portland cement and calcium aluminate cement were used as control binders because they have been used extensively in sewer concrete infrastructure. Thus, corrosion data from real sewers have been obtained for these two cement types, making them suitable for comparison with geopolymers.

Table 2-1: Binders used in concrete mixtures

Cement type and origin	Relative density	Loose bulk density (kg/m³)
CEM I, 52.5 R, Portland cement from PPC	3.1	1260 kg/m³
Cement Fondu-calcium aluminate cement (Brand: Imerys)	3.3	1370 kg/m³
Fly ash-based geopolymer cement developed by CSIR Smart Places.	2.5	1020 kg/m³

2.2 Aggregates

Two classes of aggregate were used in the experimental program, namely siliceous and calcareous aggregates. Five types of aggregate in total were collected to for use in the concrete mixes. Four siliceous aggregate types were sourced from AfriSam's quarries located in Gauteng, South Africa. Dolomite, the only calcareous aggregate used, was sourced from Lyttleton quarry in Centurion, Gauteng.

Because this study characterised aggregates and pastes separately, no blending of aggregates from different sources or types was permitted in the mix design of concrete mixtures. Therefore, for the purpose of mix design, both fine (crusher sand) and coarse fractions (stone) from were collected from each quarry.

Table 2-2: Aggregates used in concrete mixtures

Aggregate	Aggregate type	Source quarry	Relative density
Dolomite	Calcareous	Olifantsfontein	2.86
Ferro-quartz	Siliceous	Ferro (Pretoria)	2.6
Andesite	Siliceous	Eikenhof	2.94
Dolerite	Siliceous	Rooikraal	3.0
Granite	Siliceous	Roodekrans	2.67

2.3 Concrete mix designs

To enable a meaningful basis for comparison of the concretes considered in this study, the proportions of binder (cement), fine aggregate (crusher sand), and coarse aggregate (stone) were kept constant for the control mixes (PC and CAC) in the proportions provided in Table 2-3 for specimens intended for dynamic acid testing and Table 2-4 for specimens intended for static acid testing.

The mix designs shown below are adaptations of previous mixes prepared for evaluation in the VES [10] [11]. Of significance is that these mixes deliberately had relatively high binder contents (23% by mass) because binder type was a primary concern to studies in the VES.

Table 2-3 : Mix design of control specimens used in dynamic acid tests and mechanical strength testing

Concrete mix component	Proportion as a percentage of total mass	Mix Ratio (by mass)
CAC/PC	23%	1
Fine aggregate (sand)	33%	1.43
Coarse aggregate (stone)	44%	1.92
Ratio of fine to coarse aggregate by mass	43:57	
Water-cement ratio	0.35	

Specimens prepared for static tests in this study did not include coarse aggregate because the 50 mm mould size used to cast the concrete cubes was limiting. However, the same binder to aggregate ratio was maintained.

Table 2-4 : Concrete mix design of control specimens used in static acid tests

Concrete mix component	Proportion as a percentage of total mass	Mix Ratio (by mass)
CAC/PC	23%	1
Fine aggregate (sand)	77 %	3.35
Water-cement ratio	0.37	

Since corrosion occurs on an attack surface in concrete, it follows that comparing acid resistance of mix designs where the mix proportions of competing systems are equivalent by mass, is less suitable than a mix design based on volume because the generally accepted measure of corrosion in sewer pipes is dimensional (mm/yr).

Ideally, if competing concrete binder systems are to be compared, the proportions of the binder of competing systems as measured in terms of area across the attack surface should be relatively similar. It follows then, that mix proportions of the competing mix designs should be volumetrically similar. This is especially important if there is significant variation in the relative densities of the competing concrete mixes.

Since the relative density of fly ash-based geopolymer concrete is significantly (by 25%) lower than that of PC and CAC, the mass proportion of fly ash based geopolymer was reduced to ensure that the of the volume of the GP binder was approximately equal to the CAC and PC binders in the competing concrete mixes. Thus, the binder mass in the GP specimens was specified to be 75% of the mass used in CAC and PC concrete mixes. The mass proportion of GP binder thus was adjusted to 17% (vs 23%) of the total mix by mass while the coarse and fine fractions of aggregate were adjusted upwards while keeping the coarse/fine aggregate proportions constant.

Table 2-5 : Mix design of geopolymer concrete specimens used in dynamic acid tests and mechanical strength testing

Concrete mix component	Proportion as a percentage of total mass	Mass Mix Ratio (by mass)
Fly ash based geopolymer	17%	1
Fine aggregate (sand)	35.5%	2.1
Coarse aggregate (stone)	47.5%	2.79
Ratio of fine to coarse aggregate by mass	43:57	
Geopolymer liquids to geopolymer solids ratio	0.35	

As with the control (CAC and PC) mixes, GP concretes prepared for static tests did not include coarse aggregate because the 50 mm mould size was limiting.

Table 2-6: Mix design of geopolymer concrete specimens used in static acid tests

Concrete mix component	Proportion as a percentage of total mass	Mass Mix Ratio
Fly ash based geopolymer	17%	1
Fine aggregate (sand)	83 %	4.89
Geopolymer solids to geopolymer liquids ratio	0.37	

2.4 Material characterisation

Hardened cement paste and aggregate were separately analysed via X-ray fluorescence (XRF). The purpose of XRF analysis was to determine the elemental composition of the hardened cement pastes and aggregate. Furthermore, XRF analysis software was used to determine the proportions of major oxides in the aggregate and hardened cement paste. Corrosion performance and chemical composition suggested to be strongly related, and chemical elements such as calcium have been reported to influence corrosion behaviour significantly [2] [10]. Furthermore, the hardened cement pastes were assessed using SEM to observe corrosion at the micro and nano scale.

2.5 Static acid test

The process involved in producing the specimens was intended to simulate the industrial process of concrete sewer pipe manufacturing. The ordinary concrete and calcium aluminate concrete specimens were steam cured for 4 hours at 80 degrees Celsius until set, there after they were water cured for 28 days. Similarly, geopolymer specimens were cured 80 degrees Celsius in humidity sealed bags, and thereafter cured at ambient temperature in moisture sealed containers. There after the specimens were testing in both static and dynamic acid testing conditions.

Mineral acid attack under static conditions involved placing 50 mm concrete cubes in hydrochloric acid bath. The pH was maintained between 1 and 1.1 by adding concentrated acid into the PVC vessel while measuring the pH using a calibrated pH meter. Furthermore, the acidic solution was fully replaced every 24 hours.

The concrete cube specimens were first placed in water for 4 hours and their saturated surface dry mass was recorded together with their dimensions. Four cubes of the same type are placed into 5 Litres of acid (HCl) solution of pH 1.

Four concrete specimens of each mix design were placed in a container and submerged in 5 litres of pH 1 acid solution. Therefore, the total initial surface area subjected to acid attack for each specimen was 150 cm^2, and the total initial surface area of concrete specimens within a bucket containing 5 litres of pH 1 acid was 600 cm^2. The ratio of concrete specimen's initial surface area to the volume of pH 1 HCl solution is 0.12 m^2/m^3 (600cm^2/5000cm^3).
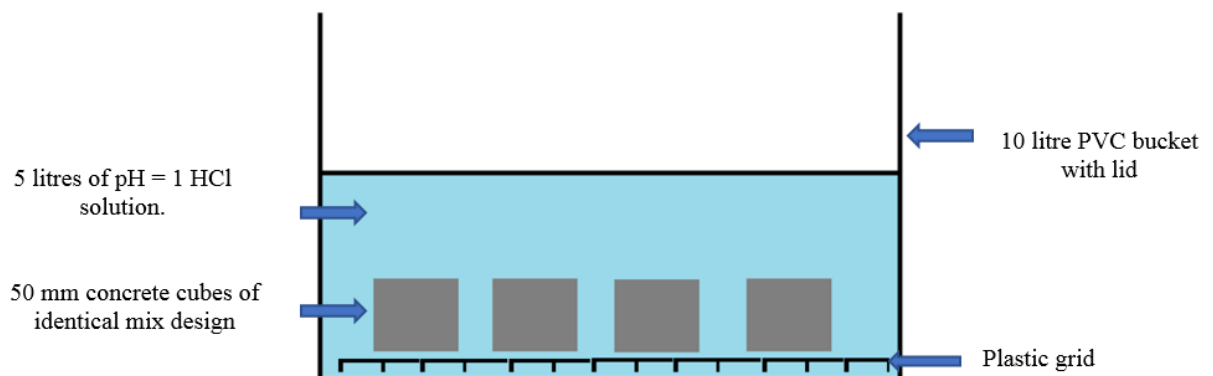
Figure 2-1 : Static test configuration

This experimental arrangement provides a relatively low surface area per unit volume of acid solution. In comparison, Xiao et al (2016) when conducting a sulfuric acid immersion test on concrete specimens, placed 12 cylindrical concrete specimens contained in a 60-litre vessel. The corroding concrete surface to acidic solution ration used in a similar study was calculated to be 0.16 m^2/m^3 [12].

Care was taken during mass measurement not to unintentionally abrade the specimens as this test was meant to measure the material removed from the specimen without disturbing any

protective precipitates or gels that formed as a result of corrosion. The mass of specimens was recorded every 6-8 hours for the duration of the experiment which ranged from 300 to 800 hours for various mixes. The mass of the specimens was monitored by measuring each specimen's mass individually and then taking the average of at least three readings as the representative reading.

2.6 Dynamic acid test

The most relevant previous work related to this test method was undertaken by Fourie [14] and Motsieloa [9]. Originally developed by Fourie [14] at the University of Cape Town, this test has was intended to simulate the corrosion condition at the effluent line. However, in this study, it is suggested that it is more suited to assessing the kinetic resistance to dissolution of concrete in acidic solutions.

This test involves subjecting concrete specimens to both acid attack and brushing simultaneously. The dynamic HCl test was conducted on all 7 concrete mixes and is typically conducted over 48 hours, however clear trends and satisfactory results were achieved for most specimens within 24 hours in this study as well as previous studies [9] [14]. In addition to HCl, three concrete mixes (GP-ferro-quartz, GP-granite and GP-andesite) with low calcium content were also subjected to H_2SO_4 in the dynamic test.

Cored cylindrical concrete specimens (78 mm diameter $\times$ 125 mm were pre-saturated with tap water for four hours and the acid tank was filled with 50 ℓ of a hydrochloric or sulfuric acid solution (pH=1).
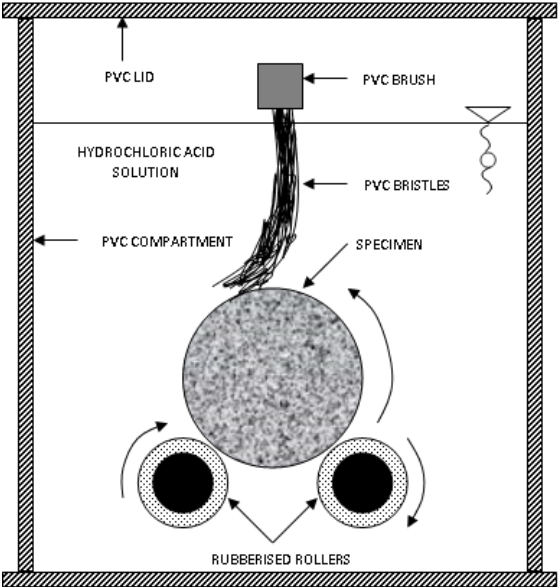

Figure 2-2 : Dynamic HCl/H₂SO₄ test

Thereafter the cores were immersed in the acid tank and rotated at approximately 16 revolutions per minute over rubberised rollers driven by pulleys connected to an electric motor. A brush with PVC bristles was lowered onto the surface of the specimen to dislodge any loose erodible material forming at the surface of the specimen (Figure 2-2).

Measurements of the mass of the specimen were measured every 2 hours and a pH of between 1.0 and 1.1 was maintained for the duration of the test. The acid solution was renewed daily for tests that were conducted for durations longer than 24 hours.

3. RESULTS

3.1 Static acid test results

Because the corrosion performances of the 7 mixes tested under the static and dynamic acid tests varied significantly, to maintain a reasonable resolution in data, the results are presented two clusters of mixes of the same order of acid resistance. Furthermore, in addition to the mass loss over time graphs, the corrosion performance is also presented in terms of the proportion (%) of mass lost over time. The rationale for providing the corrosion in these two formats is because the rate of mass loss is estimated by linear regression of the specimens mass loss over time, while the proportion (%) of original mass over time gives a better indication of the relative performance of each specimen. This is especially important because mass loss on its own may be misleading if the densities of the concrete mixes differs substantially.
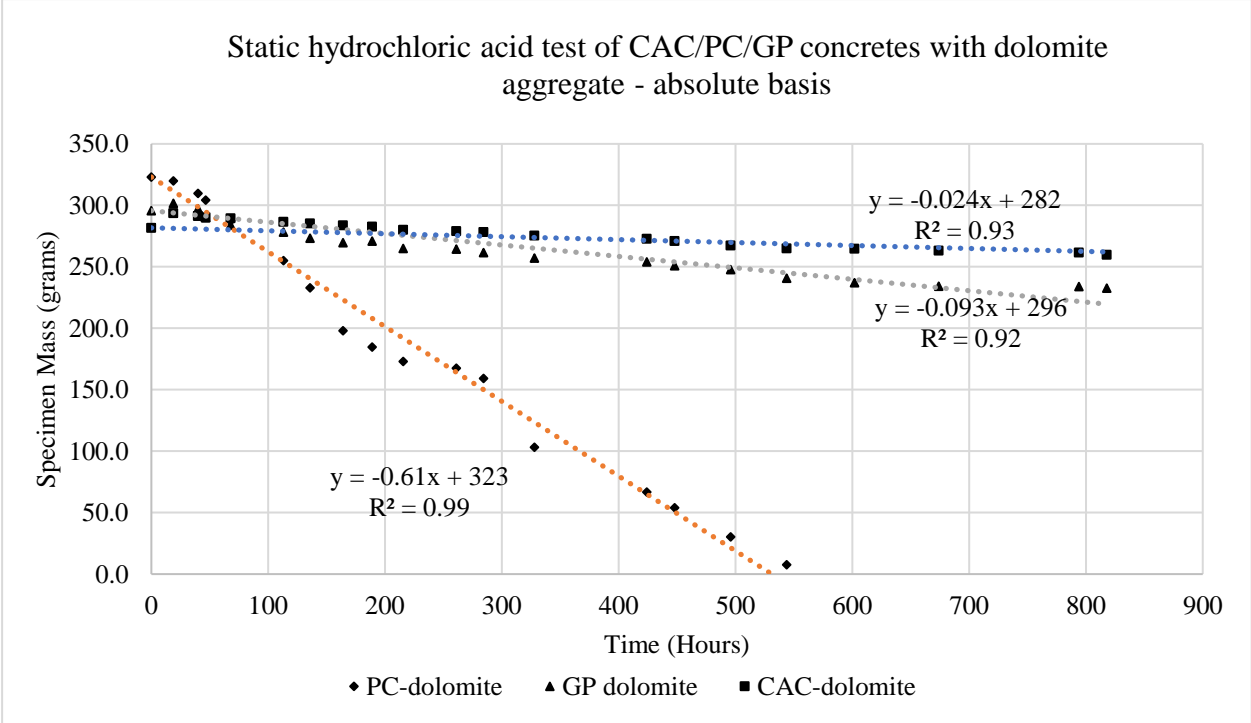

Figure 3-1: Mass loss of CAC/PC/GP concretes with dolomite aggregate in the static hydrochloric acid
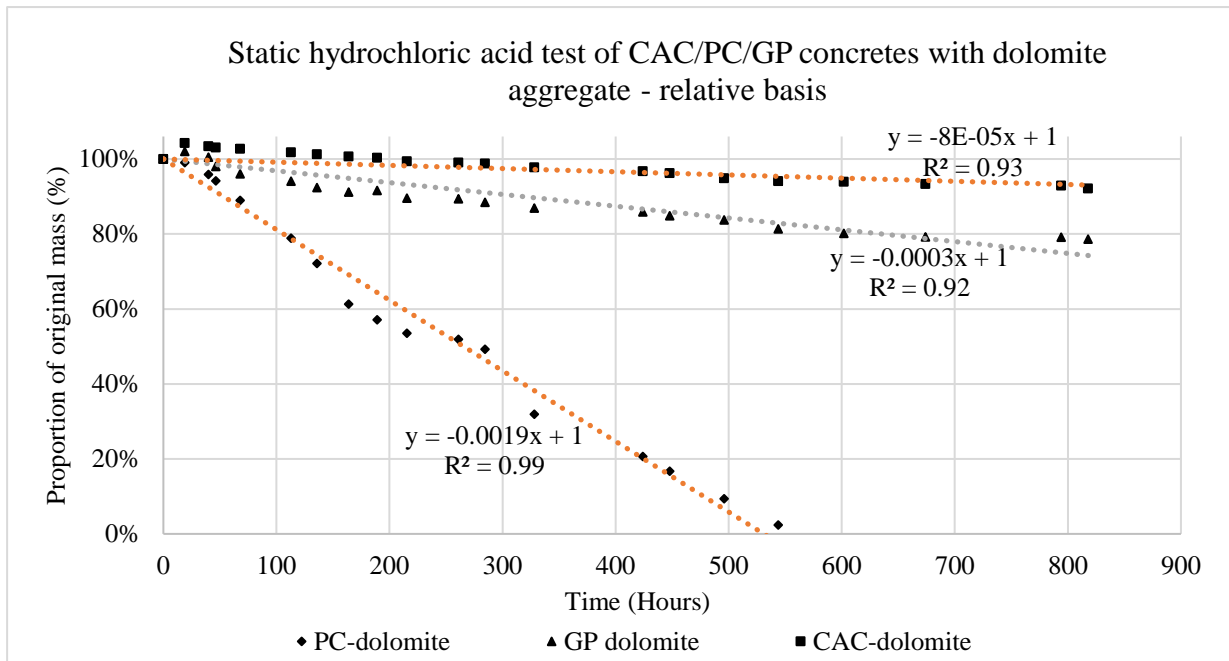
Figure 3-2: Proportion (%) of CAC/PC/GP concretes with dolomite aggregate in the static hydrochloric acid

The static test reveals that the CAC-dolomite mix is the most acid resistant mix when immersed in HCl under static conditions. By the 550th hour of immersion, PC-dolomite is completely dissolved whereas CAC-dolomite and GP-dolomite retained 92% and 79% of their original masses, respectively.

The next cluster of result is GP concrete using various siliceous aggregates. These specimens generally had a much lower rate of mass loss over the 800 hour period while immersed in pH 1 HCl, with the most resistant mix, GP-ferro-quartz, retaining more than 98% of its original mass and the least resistant mix, GP-dolerite, retaining 93% of its original mass.
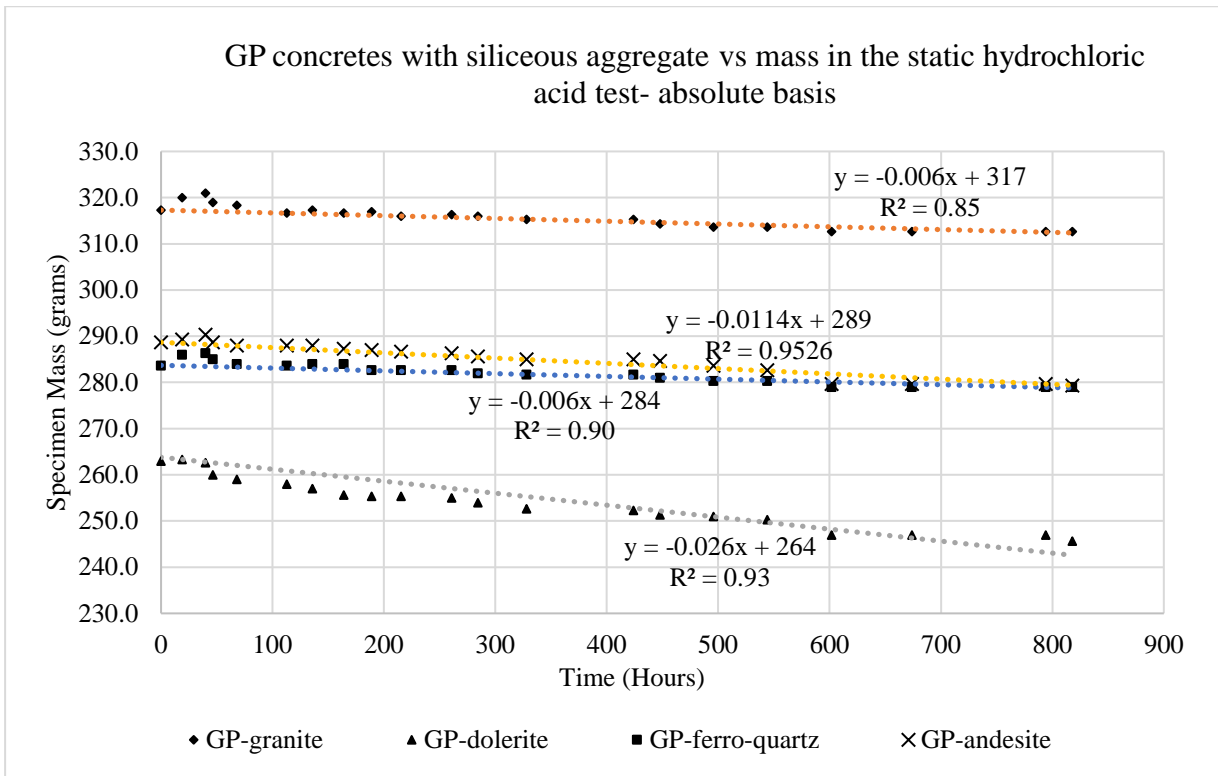
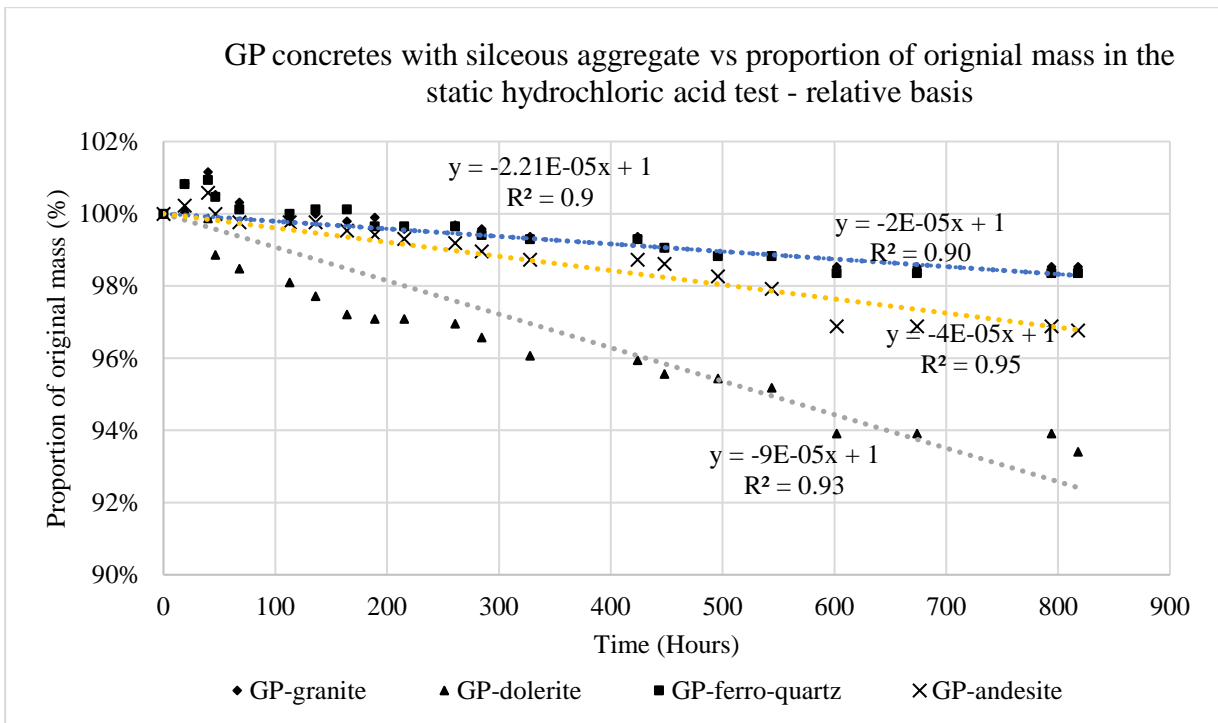*Figure 3-3 : Static hydrochloric acid test of GP concretes with siliceous aggregate*

Figure 3-4 : Proportion (%) of CAC/PC/GP concretes with dolomite aggregate in the static hydrochloric acid

3.2 Dynamic acid tests (HCl)

Results from the dynamic HCl test are also presented in the same clustered fashion as the static acid test results. Because the dynamic HCl test is much more aggressive, trends in mass loss were established over between 20 and 50 hours of testing.

The first cluster of results compares GP-dolomite, CAC-dolomite and PC-dolomite concrete mixes. Under this test CAC-dolomite is the most severely attacked mix, retaining 67% of its original mass over the 25 hour testing period whereas PC-dolomite and GP-dolomite retained 77.2% and 84.7% of their masses, respectively. A notable difference in the results between the dynamic HCl test and the static HCl test is that the order in performance between the PC-dolomite and CAC-dolomite concrete mixes is reversed.
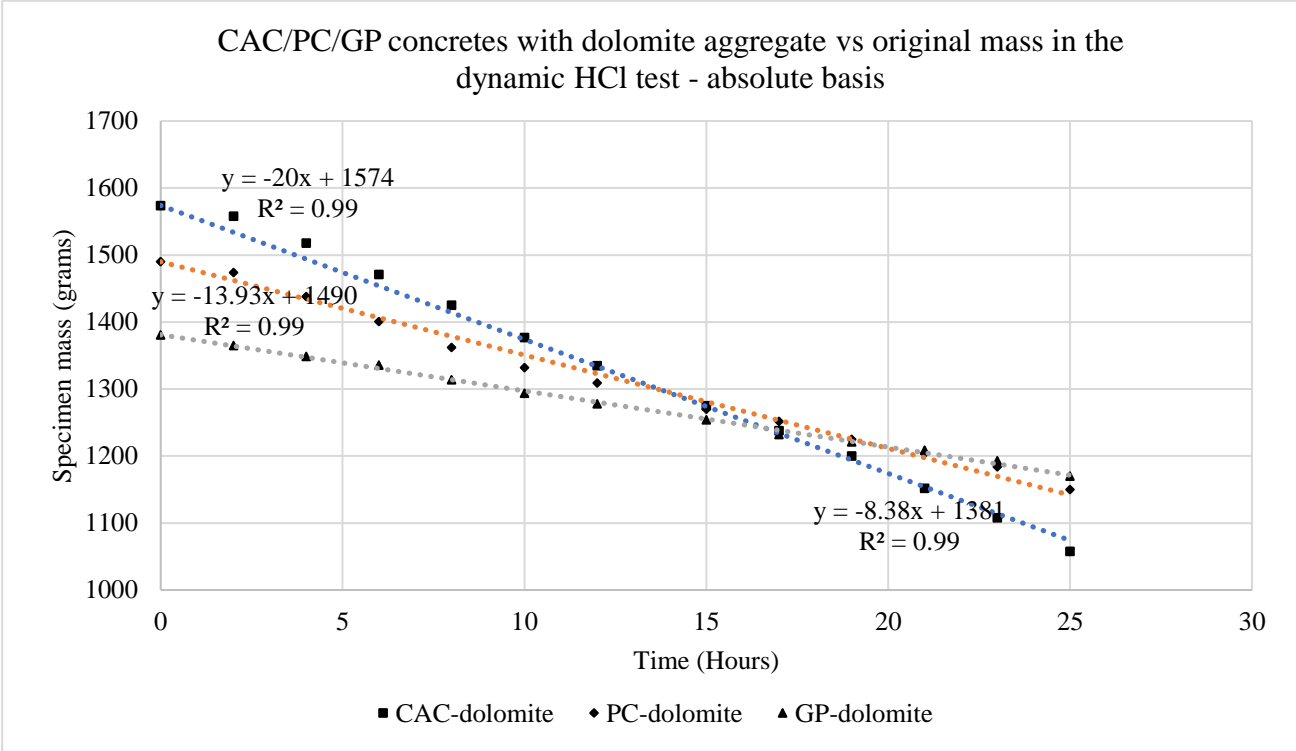

Figure 3-5: Dynamic hydrochloric acid test of CAC/PC/GP concretes with dolomite aggregate vs mass
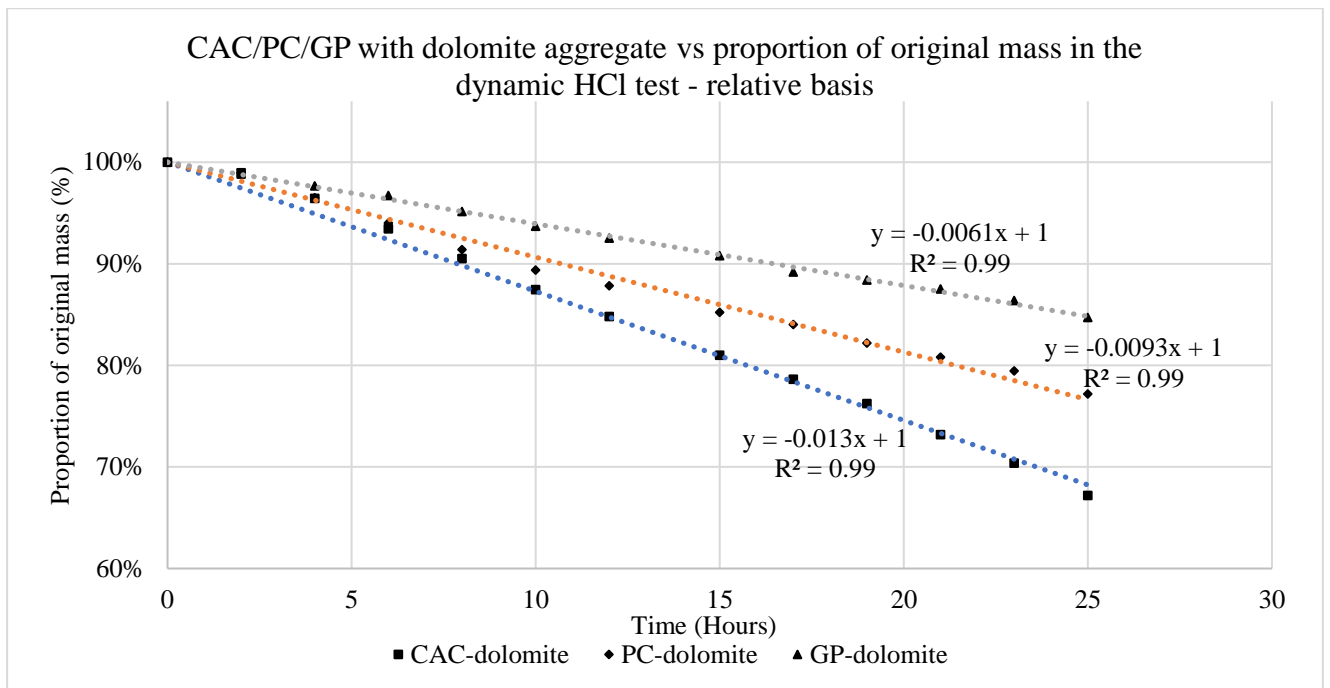
Figure 3-6: Dynamic hydrochloric acid test of CAC/PC/GP concretes with dolomite aggregate vs proportion of original mass

Geopolymer concretes tested under the dynamic HCl test display high resistance in the dynamic HCl test compared to CAC and PC mixes. GP-ferro-quartz exhibited the lowest rate of mass loss over the test duration retaining 99.72% of its original mass after 48 hours of testing .Figure 3-8 shows that of the set of GP-siliceous aggregate mixes, GP-dolerite was corroding at a substantially faster rate, which indicates a higher acid solubility of dolerite aggregate.
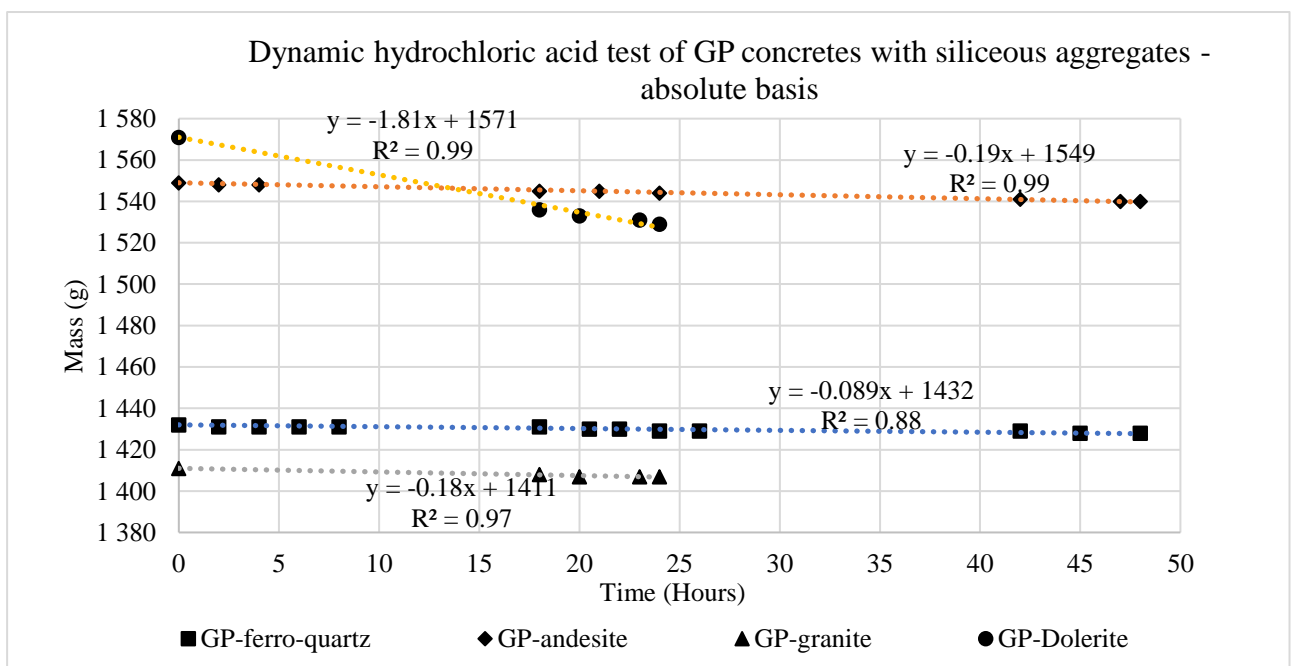
Figure 3-7: Dynamic hydrochloric acid test of GP concretes with siliceous aggregate vs mass
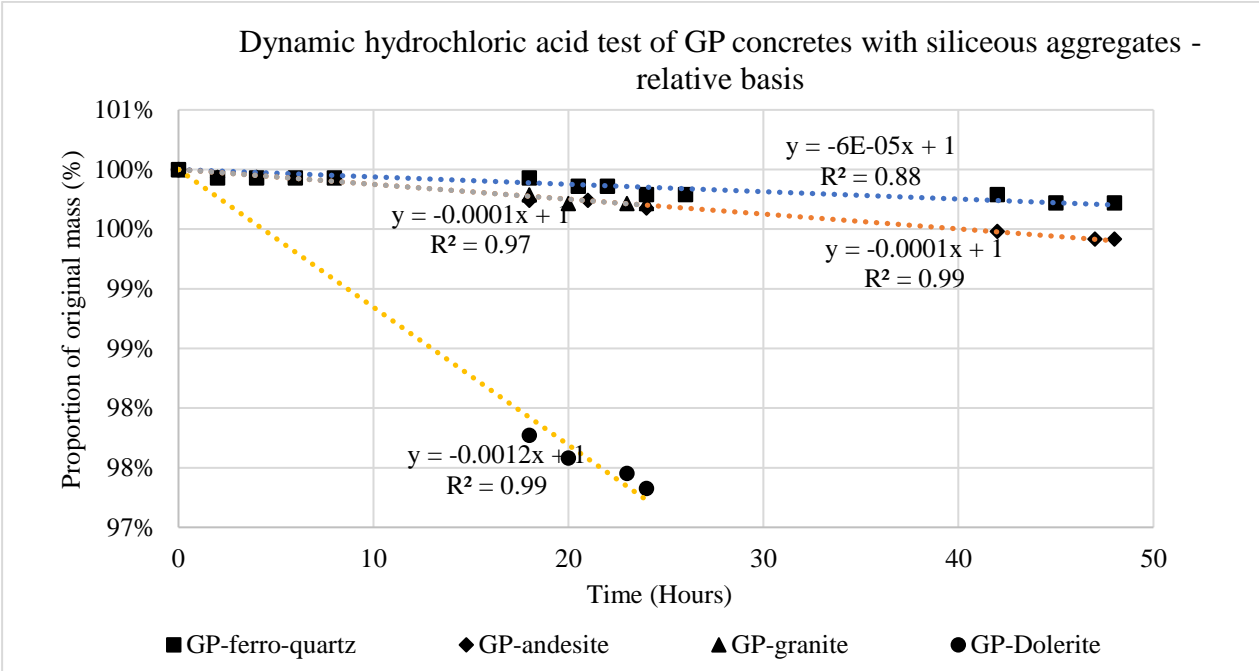

Dynamic hydrochloric acid test of GP concretes with siliceous aggregates - relative basis

$y = -6E-05x + 1$
$R^2 = 0.88$

$y = -0.0001x + 1$
$R^2 = 0.97$

$y = -0.0001x + 1$
$R^2 = 0.99$

$y = -0.0012x + 1$
$R^2 = 0.99$

■ GP-ferro-quartz ◆ GP-andesite ▲ GP-granite ● GP-Dolerite

Figure 3-8: Dynamic hydrochloric acid test of GP concretes with siliceous aggregate vs proportion of original mass

3.2 Dynamic acid tests (H_2SO_4)

The low calcium systems were useful because they enabled a comparison between the corrosion rates in HCl and H_2SO_4. This test could also be used to test the hypothesis that the dynamic test is an indicator of the rate of dissolution since work by Gay et al [12] suggests the rate of dissolution is not a function of acid type but of the pH of the solution. Thus, if both these claims are true there should be minimal difference in the corrosion rates of these mixes in HCl and H_2SO_4 when tested under dynamic conditions.
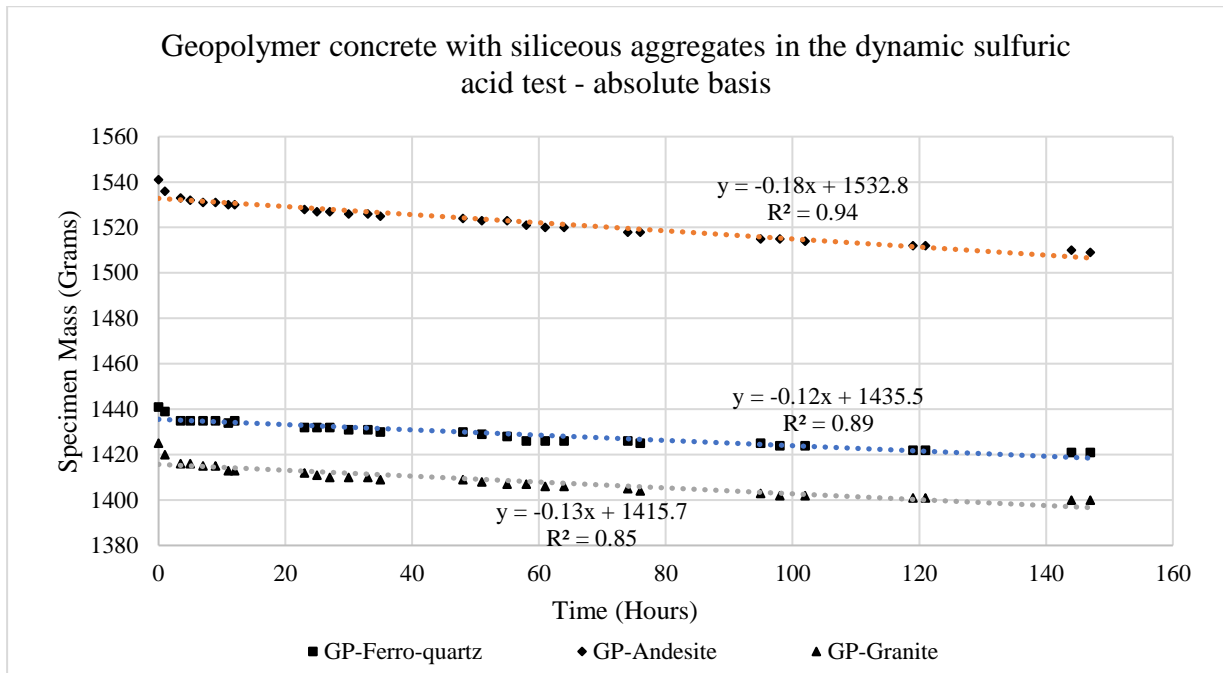
Figure 3-9: Dynamic sulfuric acid test of GP concretes with siliceous aggregate vs mass
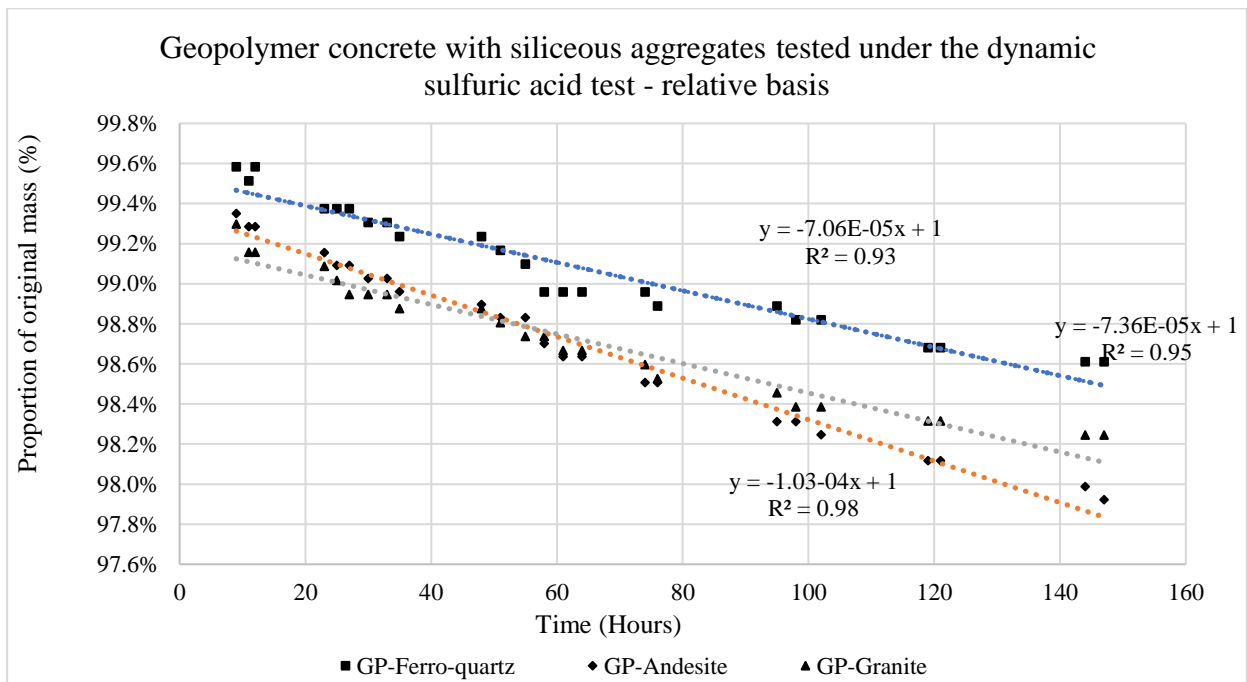

Figure 3-10: Dynamic sulfuric acid test of GP concretes with siliceous aggregate vs proportion of original mass

Figure 3-10 and Figure 3-11 show that the test was conducted over 150 hours compared to the 48 hour duration used in the dynamic HCl test. This was undertaken to establish whether the corrosion rate would begin to stall after an extended period in the test. This was the experience of Fourie [13] when he tested calcium rich concrete mixes in H_2SO_4, which resulted in the

saturation of the acidic solution with gypsum precipitate and a stalling of the corrosion reaction as a result of the common ion effect. The three GP-siliceous aggregates exhibited a relatively constant rate of corrosion over the duration.

Scanning electron microscopy results

Kriven [13] and Davidovits [14] state that the nano-structure of geopolymers consists of geopolymer micelles which range from 5 nm to 20 nm in size. A characteristic of the geopolymer matrix is that the micelles form nano-channels and pores. Figure 3-11 shows a fracture surface, where the geopolymer micelle matrix is in contact with a fly ash sphere from an un-corroded geopolymer paste specimen. Figure 3-12, Figure 3-13 and Figure 3-14 show effect of HCl on the geopolymer matrix.
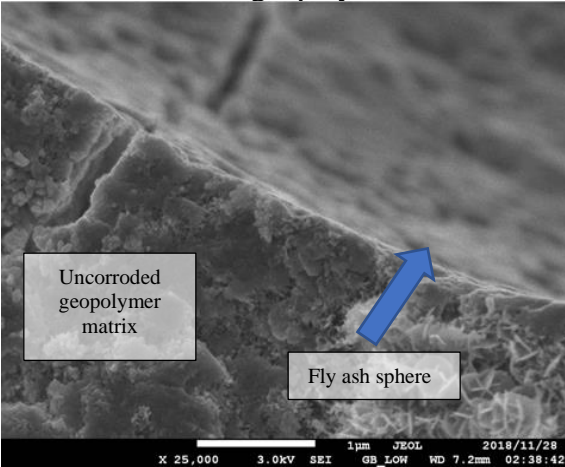

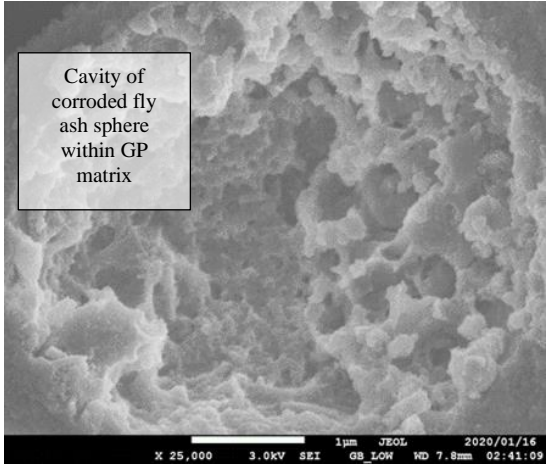*Figure 3-11: Fly ash sphere in contact with geopolymer micelle matrix*

Figure 3-12: HCl Corroded specimen: cavity where FA sphere was embedded
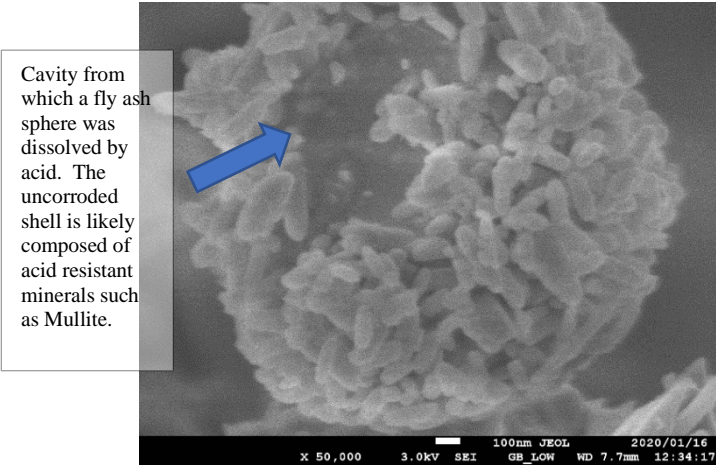

Figure 3-13: Corroded fly ash sphere enveloped by geopolymer matrix after exposure to the dynamic HCl test
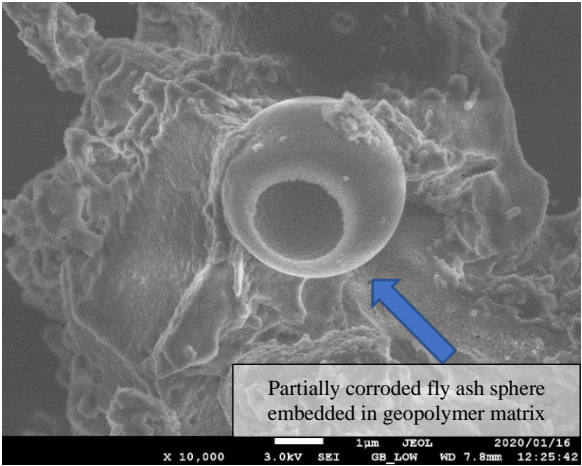

Figure 3-14: Partially corroded fly ash sphere enveloped by geopolymer matrix after exposure to the dynamic sulfuric acid test

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Figure 3-12, Figure 3-13, and Figure 3-14 indicate that fly ash spheres are preferentially corroded by hydrochloric and sulfuric acid, this is observation is in line with findings [2] which state that unreacted precursor materials such as fly ash are subject to dissolution under acid attack. Figure 3-13 shows what seems to be a geopolymer matrix shell, which, before corrosion was covering an embedded fly ash sphere. Figure 3-14 shows a partially damaged fly ash sphere, with a circular opening at one end. The damaged sphere is embedded within the geopolymer matrix. This indicates that GP matrices at the micro and nanoscale exhibit preferential corrosion of some microstructures while others are not readily dissolved in HCl.

4. DISCUSSION

4.1 Corrosion rates measured in HCl

Data from the static HCl test and the dynamic HCl test provide us with an indication of the performance of each mix relative to the other 6 mixes tested in this study. If mass loss is used as a measure for corrosion, then is clear that geopolymers present a significant increase in corrosion resistance when compared to CAC and PC binders.

By using linear regression, it was possible to estimate the rate of mass loss per unit area over time for the concrete mixes under both the static and dynamic acid test. The average corrosion rates, obtained via linear regression. for the two mineral acid tests are presented in Table 4-1 and Table 4-2 below:

Table 4-1 : Rank in resistance and corrosion rates calculated in the dynamic HCl test

Rank in resistance	Concrete mix	Corrosion rate $(mg/cm^2/hr)$
1	GP-ferro-quartz	0.19
2	GP-granite	0.44
3	GP-andesite	0.46
4	GP-dolerite	4.43
5	GP-dolomite	21.1
6	PC-dolomite	34.12
7	CAC-dolomite	52.1

Table 4-2 : Rank in resistance and corrosion rates calculated in the static HCl test

Rank in resistance	Concrete mix	Corrosion rate $(mg/cm^2/hr)$	Abrasion factor
1	GP-ferro-quartz	0.056	3.3
2	GP-granite	0.059	7.5
3	GP-andesite	0.086	5.4
4	GP-dolerite	0.14	32.9
5	CAC-dolomite	0.27	196

| 6 | GP-dolomite | 0.54 | 39.0 |
| 7 | PC-dolomite | 3.85 | 8.8 |

Table 4-2 also presents a parameter termed the "abrasion factor". The "abrasion factor", which is equal to the surface corrosion rate in the dynamic acid test divided by the surface corrosion rate in the static test for each concrete type is expressed as: [17]

$$\text{Abrasion Factor} = \frac{\text{Corrosion rate-dynamic HCl test}}{\text{Corrosion rate-static HCl test}} \qquad (1)$$

It is suggested that the "abrasion factor" provides a quantifiable measure of the effect of abrasion on concretes in acidic media. Higher values indicate that abrasion in acidic media has a severe effect while lower values indicate a minor effect. This parameter relies on the assumption that the dynamic HCl test nullifies the protective effects of precipitates and gels.

The highest abrasion factor" value was calculated for CAC-dolomite mix (196). This value supports the hypothesis of a protective precipitate or gel forming around the specimen under static conditions. However, it is not effective in the dynamic HCl test where corrosion products are removed by continuous brushing. GP-ferro-quartz displayed the lowest abrasion factor (3.3) indicating that while the conditions in the dynamic test are more severe, the reduction in resistance was much lower than all the other six concrete mixtures. The GP-ferro-quartz result also indicates that geopolymer concretes do not form corrosion products with significant protective properties while undergoing corrosion.

Table 4-3: Difference between calculated corrosion rates in the dynamic acid test (HCl vs H_2SO_4)

Concrete mix	Corrosion rate dynamic HCl test $(mg/cm^2/hr)$	Corrosion rate dynamic H_2SO_4 test $(mg/cm^2/hr)$	Difference in corrosion rate $(mg/cm^2/hr)$ between HCl and H_2SO_4
GP-ferro-quartz	0.19	0.295	0.105
GP-granite	0.44	0.328	0.112
GP-andesite	0.46	0.449	0.011

The calculated corrosion rates in both tests do not differ significantly (0.011-0.105 $g/cm^2/hr$), when considered in terms of the range in corrosion rates for the 7 concrete mixes (0.19 – 52.1 $g/cm^2/hr$) in the dynamic HCl test. This finding, though limited to only three mixes is in keeping with two claims. Firstly, that the dynamic acid test provides an indication of the combined rate of dissolution of a concrete specimen and secondly, that the rate of dissolution is primarily dependent on the pH of the acidic solution and not the acid type as suggested by Gay et al [12].

4.2 Reasons for GP corrosion resistance

It is argued that the dynamic HCl test provides an indication of the combined rate of dissolution for a specific concrete mix. The high resistance to dissolution of the geopolymer mixes can be attributed to the high Si and low Ca content of geopolymers [2]. This is in contrast to Portland and calcium aluminate cements which contain a significant proportion of Ca. It is argued here that the chemical composition of concretes is the primary factor to consider where acid resistance is concerned.

4.3 Performance of CAC and PC concretes

The performance disparity of the CAC-dolomite mix between the dynamic and static test may be explained by protection emanating from alumina gel (AH_3) forming on the surface of the corroding specimen in the static HCl test, and that the gel does not provide protection in the dynamic HCl test because the continuous brushing removes corrosion products from the surface of a corroding specimen. This explanation is in agreement with the protective mechanisms suggested in previous studies, wherein, alumina gel, the bacterio-static effect and neutralisation capacity are protective mechanisms attributed to CAC concrete [4] [6]. Given that the mineral tests used in this study did not include a bacterial component, and that the stated neutralising capacity of CAC is only 40% higher than Portland cement, it is suggested that the predominant protective mechanism emanates from alumina gel in the CAC concrete mixes.

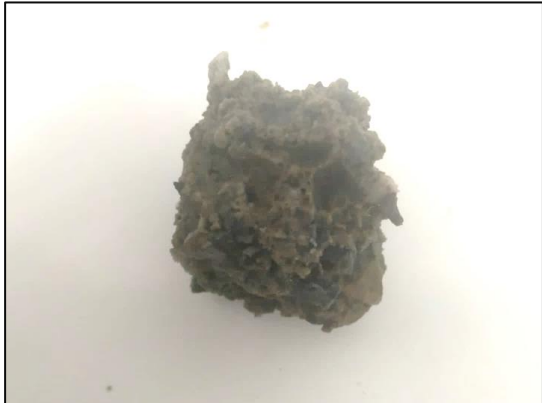Figure 4-1 : CAC-dolomite specimen taken from the static HCl test after 350 hours

Figure 4-2 : PC-dolomite specimen taken from the static HCl test after 350 hours

Figure 4-3 : CAC-dolomite specimen taken after 48 hours in the dynamic HCl test

This finding is also supported by a visual examination of CAC-dolomite specimens taken from the two acid tests. The surface of the cubic CAC-dolomite specimen from the static HCl test *Figure *4-1*) displays a relatively smooth surface, with negligible levels of preferential corrosion of the binder or the paste.

In the dynamic HCl test, the paste in the CAC-dolomite specimen(Figure *4-3*) is clearly preferentially corroded, creating a rough surface with dolomite aggregate standing proud. This observation supports the idea that the brushing in the dynamic HCl test nullifies the protective effects of the alumina gel (AH_3) layer.

Furthermore, if this specimen is compared to the PC-dolomite specimen after the same period of immersion in HCl in the static test, it can be inferred from the high levels of corrosion of the dolomite aggregate in the PC-dolomite specimen (Figure *4-2*), that there exists a protective coating on the CAC-dolomite, preventing the dolomite from being dissolved in the acidic solution.

4.4 Relating results from the dynamic HCl test to concrete chemical composition

Concrete is the combination of a cementitious binder (or hardened cement paste), binding a filler material (aggregate) to form a hardened cement paste/aggregate matrix. Therefore, by analysing the chemical properties of the aggregates and the hardened cement paste separately, it may be possible to determine the contribution of each component to acid resistance.

Since corrosion is effectively an acid-base reaction, a parameter, the basicity value, which is ordinarily used to measure the reactivity of slags in Portland cement, was selected for use measuring the ratio of major basic to acidic oxides in hardened cement pastes and aggregates.

X-ray fluorescence (XRF) analysis was used to quantify the elemental proportions of the aggregate and hardened cement paste, from which, the proportion of major oxides present in the hardened cement paste and aggregates were determined.

Thereafter the Basicity value of the hardened cement paste and aggregates were calculable using the formula below.

$$\text{Basicity} = \frac{CaO\ (\%) + MgO\ (\%)}{SiO_2\ (\%)} \tag{2}$$

Furthermore, the combined basicity value of a concrete mix was also calculable by multiplying the concrete mix proportions of the HCP and aggregate with their associated basicity values and taking the sum of the two, as expressed by formula (3) below.

$$\text{Basicity}_{\text{concrete specimen}} = (\text{Basicity}_{\text{HCP}} \times \text{binder }\%) + (\text{Basicity}_{\text{Aggregate}} \times \text{aggregate}\%) \tag{3}$$

Table 4-4:: Basicity values of hardened cement pastes

HCP type	CaO (%)	MgO (%)	SiO2 (%)	Basicity
PC	53.7%	2.01%	17.77%	3.138
CAC	32.9%	2.40%	4.06%	8.686
GP	11.6%	0.53%	44.06%	0.276

Table 4-5: Basicity values of aggregates used in the study

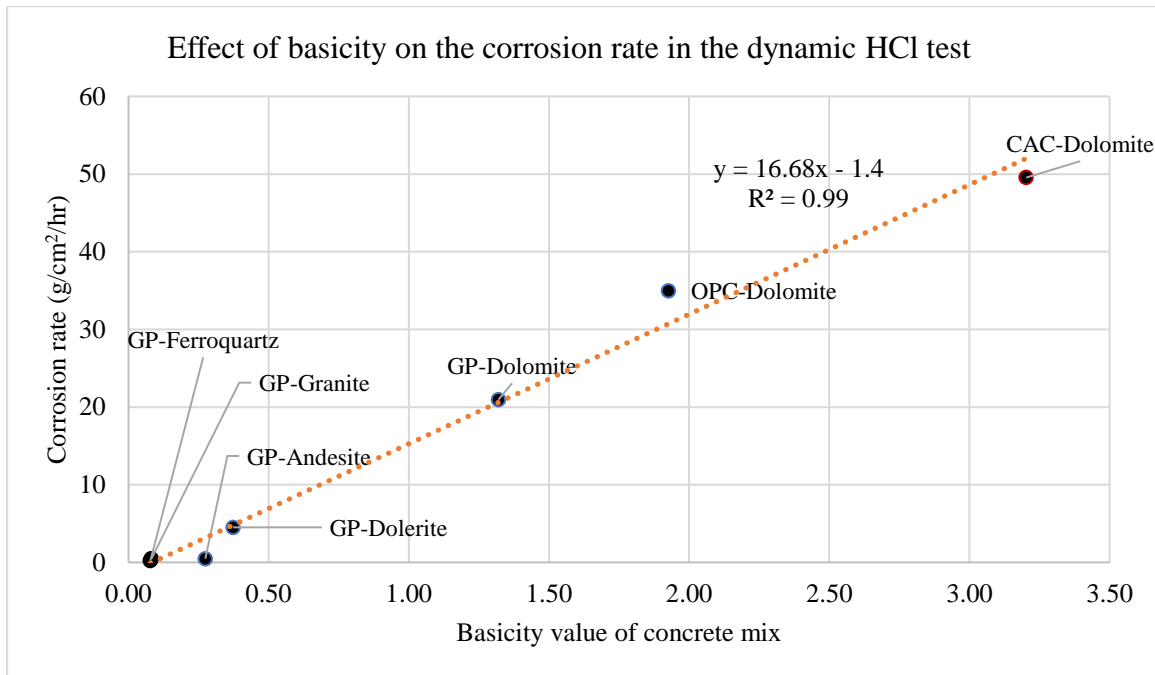| Aggregate type	CaO (%)	MgO (%)	SiO2 (%)	Basicity
Dolomite	23%	16%	25%	1.565
Ferro-Quartz	2%	0%	96%	0.026
Dolerite	11%	6%	52%	0.321
Andesite	8%	4%	55%	0.222
Granite	2%	1%	72%	0.029

Figure 4-4 : Basicity value of concrete mixes compared to the corrosion rate measured in the dynamic HCl test

Figure 4-4 shows the corrosion rate from the dynamic HCl test of the 7 different mixes compared against the calculated basicity value. The graph shows a strong linear relationship between the basicity value and the corrosion rate measured in the dynamic HCl test.

Since the basicity value is a measure of the ratio of basic oxides to acidic oxides, it could be inferred that higher basicity values are associated with higher corrosion rates. However, since corrosion involves dissolution and precipitation, it is also important to attribute to which phase of the corrosion process the basicity value is related. It is argued that the dynamic HCl test provides an aggregated measure of the rate of dissolution of a concrete mix in HCl. Thus it is inferred that the rate of dissolution, measured here in $g/cm^2/hr$ is linearly related to the basicity value of the concrete mixes tested in this study. However this relationship will require further study and verification.

4.5 Effect of basicity on aggregate-binder compatibility in concrete mixtures subjected to the dynamic HCl test

While preferential corrosion of the either the paste or binder fraction of concrete in acidic milieu is undesirable, the effects of preferential corrosion of the binder can be more damaging since it results in aggregate fallout and rapid disintegration of concrete. There is a lack of focus in the literature on this specific problem.

In South Africa, calcareous aggregates are prescribed in the concrete mixes used for sewer pipes in order to spread corrosion over both aggregate and paste. With respect to this SANS 677

suggests that the insoluble portion of the selected aggregate in hydrochloric acid should not exceed 25% by mass [15].

It is argued here that preferential corrosion is strongly related to a disparity in the rate of dissolution between the binder and the paste. Therefore, it would be useful if the difference in the rate of dissolution between the binder and the paste were quantifiable. It is further argued that the combined rate of dissolution of a concrete mix is measurable by the dynamic HCl test. Furthermore, given the highly correlated relationship between the basicity of a concrete mix and the corrosion rate shown in Figure 4-4, it is suggested that the extent of preferential corrosion in a concrete mix may be assessed by calculating the difference between basicity values of the paste and aggregate.

$$\text{Basicity differential} = \text{Basicity}_{\text{aggregate}} - \text{Basicity}_{\text{HCP}} \tag{4}$$

A qualitative assessment of this hypothesis was conducted by comparing the surface characteristics of specimens after they were subjected to the dynamic HCl test. The basicity differentials of the seven concrete mixes was calculated using equation (4). The visual appraisal of the corroded concrete specimens conformed to the hypothesis. The specimen with the largest basicity differential was the CAC-dolomite mix, with a basicity differential value of -7.09. The surface of the specimen displayed a clear preferential corrosion of the binder, with stone and sand sized particles protruding from the specimen. PC-dolomite specimen showed preferential corrosion of the binder however to a reduced extent, which was in keeping with its lower basicity differential (-1.53). The smoothest concrete mixes had basicity differentials close to zero (GP-ferro-quartz, GP-granite, GP-andesite). The concrete mixes that displayed preferential corrosion of the aggregate were GP-dolomite and GP-dolerite. The surface characteristics of these two mixes were characterised by cavities in the binder matrix where aggregates were dissolved by HCl. Therefore, it is suggested that the visual assessment of the specimens subjected to the dynamic HCl test are in agreement with the calculated basicity differential value of the seven mixes tested in this study.
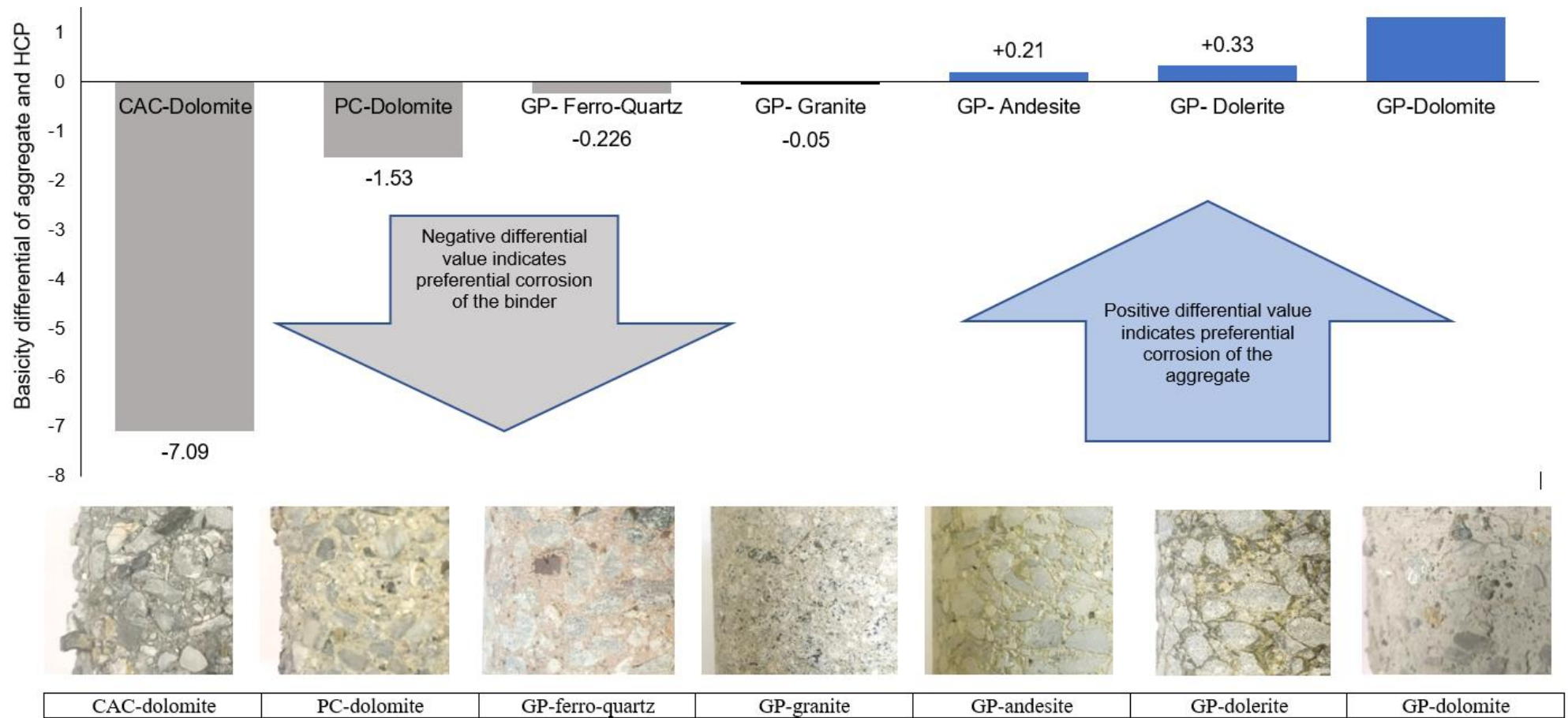
Figure 4-5:Visual examination of surface corrosion in the dynamic HCl test compared to the calculated basicity differential for the concrete mixture.

5. CONCLUSIONS

The performance of geopolymer concrete mixes subjected to mineral acid tests is generally superior to Portland cement and calcium aluminate cements combined with dolomite aggregate.

Results from the static HCl test showed that GP-ferro-quartz concrete, the most acid resistant concrete specimen, provided a 69-fold improvement in resistance when compared to PC-dolomite mixes (control #1) and a 4.72-fold improvement in resistance when compared to CAC-dolomite mixes (control #2).

Results from the dynamic HCl test show that the GP-ferro-quartz mix provided a 180-fold increase in resistance when compared to the PC-dolomite mix and a 275-fold increase when compared to CAC-dolomite mix. The CAC-dolomite mix was found to have the lowest resistance to the erosive-corrosive exposure conditions of the dynamic HCl test. Thus, in terms of the concrete MIC resistance properties identified in this study, it is suggested that the CAC-dolomite mix had poor kinetic resistance to dissolution. However, under the static acid test (static corrosion exposure condition), the CAC-dolomite mix performed better than the PC-dolomite mix and GP-dolomite mix. CAC-dolomite concrete performed inferiorly only to the set of GP-siliceous-aggregate mixes in the static HCl test.

The difference in the performance of CAC-dolomite concrete performance between the static and dynamic test is largely attributed to the formation of alumina gel, an acid corrosion product of CAC hardened paste, which envelopes the concrete specimen and reduces the rate of surface corrosion in the static HCl test. However, under the dynamic HCl test, the gel layer is brushed off the surface of the concrete specimen rendering it ineffective in protecting the concrete specimen from corrosion.

The difference in the rate of corrosion of GP-siliceous aggregate concrete mixes subjected to HCl and H_2SO_4 under dynamic conditions was minute. This finding reinforces the suggestion that the dynamic acid test provides an indication of the rate of dissolution and that the rate of dissolution is not dependent on acid type [12].

A strongly correlated linear relationship between the basicity value of a concrete mix and the corrosion rate from the dynamic HCl test was established. This empirical relationship warrants further investigation and verification, as it would, in principle provide a means to estimate the dissolution rate of concrete by calculating its basicity.

Basicity was also found to be useful in determining the corrosion compatibility of binder and aggregate types. It was found that the difference between the basicity value of hardened cement paste and the basicity value of the aggregate was useful in determining the type and extent of preferential corrosion of a concrete specimen tested under the dynamic HCl test. For ease of reading, this difference was called the "basicity differential". By visually assessing corroded concrete specimens from the dynamic HCl test, it was possible to determine whether the hardened cement paste or aggregate component was preferentially corroded, and to quantify the severity of preferential corrosion.

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