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Chloride-Ion Penetrability and Mechanical Analysis of High Strength Concrete with Copper Slag

Savaş Erdem[1] and Marva Angela Blankson[2,*]
[1]School of Civil Engineering, University of Istanbul, Avcilar Campus, Istanbul-Turkey,
[2]School of Civil Engineering, University of Nottingham, Nottingham- England, UK

Abstract
The use of waste materials and industrial by-products in high-strength concrete could increase the sustainability of the construction industry. In this study, the potential of using copper slag as coarse aggregate in high-strength concrete was experimentally investigated. The effects of replacing gravel coarse aggregate by copper slag particles on the compressive strength, chloride ion- migration, water permeability and impact resistance of high-strength concretes were evaluated. Incorporating copper slag coarse particles resulted in a compressive strength increase of about 14 % on average partly due to the low Ca/Si ratio through the interface area of this concrete (more homogenous internal structure) as confirmed by the energy dispersive X-ray micro chemical analysis. It was also found that the copper slag high-strength concrete provided better ductility and had much greater load carrying capacity compared to gravel high-strength concrete under dynamic conditions. Finally, it was observed that in comparison to the high strength concrete with slag, the chloride migration coefficient from non-steady state migration was approximately 30 % greater in the gravel high-strength concrete.

Keywords: Copper slag; Waste recycling; Sustainable concrete; Chloride-ion penetrability; Mechanical analysis.

I. Introduction

Copper slag is generated in the metallurgical industry as a result of matte smelting process of copper concentrate [1]. During the matte smelting, two separate liquid phases are formed; namely copper-rich matte (sulphides) and slag (oxides). It has been estimated that approximately 2.2 tonnes of slag are generated for every tonne of copper fabrication with a world-wide annual generation about 24.6 million tonnes [2]. Dumping or disposal of such large amounts of copper slag causes serious environmental and health problems as it contains heavy metals [3]. Due to new European environmental regulations, high waste treatment costs and limited availability of disposal sites, there is an urgent need to investigate alternative uses for copper slag as raw material of other processes [1, 3].

In this respect, the reuse of copper slag in the construction industry seems to be a good strategy for satisfying all requirements (reduction of the waste volume and finding new materials) [4]. In the literature, a number of research studies have been performed for investigating the reuse applications of copper slag in the cement and concrete industry [5-9]. In the evaluation of the mechanical and dynamic properties of concrete with copper slag aggregates, Khandazi and Behnood [10] demonstrated concrete with a 28 day compressive strength of 67.7 MPa can be produced using 100 % coarse copper slag particles. However, Wu et al. [11] stressed that if the percentage of fine copper slag is more than 40 % in the batch, the static, tensile and dynamic strength decreases significantly as excessive voids, micro-cracks and capillary channels occur in the micro-structure of concrete beyond this limit.

In recent years, with the development of very tall buildings, larger-sized and long-span concrete structures, high-strength concretes has been widely used in civil engineering [12]. The concrete elements in these structures can be subjected to short-duration dynamic loads and thus, improved impact resistance is much more desirable under such circumstances [13]. High-strength concrete production energy intensive and consumes large quantities of primary aggregate resources. Since approximately 75 % of the volume of concrete is occupied by aggregate, the quality of aggregate is of considerable importance on the performance of concrete. Consequently, it makes sense to find other sources of high-quality and inexpensive aggregates to make high-strength concrete [10].

One of the most important structural characteristics of concrete is its distinctive pore structure associated with a large number of pores of different sizes, shapes and origins. The pore structure of paste, mortar or concrete controls other important properties including permeability, strength, modulus of elasticity, volume stability and durability-related properties and can give insight into material performance [14]. In addition to that, micro-cracks in the cement paste matrix may significantly contribute to the permeability [15].

A review of concrete literature indicates that the use of copper slag in high-strength concrete has been examined in relatively few studies and experimental data are limited. Moreover, to the author‘s best knowledge; there has been no study to evaluate the influence of coarse copper slag on the dynamic properties and durability performance of concrete. An attempt was, therefore, made to evaluate the mechanical properties, impact resistance, water permeability and chloride permeability of high-strength concrete made with coarse copper slag particles.

II. Materials and methodology

High-strength ordinary Portland cement CEM I (52.5 MPa strength) has been used in this work. Natural gravel with a size of 4/14 mm and local river sand with a specific gravity of 2.66 constituted the reference mix. The mix proportions are given in Table 1.

In all mixes, the amounts of cement, sand and free water were the same. Thus, the only difference was the type of coarse aggregate used in the mixtures. The coarse aggregate of the control mix was totally replaced by copper slag particles. The same size percentages were selected for the gravel aggregate and copper slag aggregates to eliminate the effect of grading difference on concrete performance. All concrete mixtures were batched using a mechanical pan mixer, placed in oiled steel moulds in two layers; each layer was compacted by using a vibration table before being covered with plastic sheets. The specimens were left in their moulds for one day before de-moulding and cured at a 20±2 ˚C in a water tank until the day of testing. Four cubes (100x100x100 mm) were used to measure the compressive strengths of the mixtures at the ages of 7, 28 and 56 days in accordance with the relevant British European Standard.

Impact tests were carried out using a Rosand type 5 instrumented falling weight impact tester shown schematically in Fig 1. 150 mm disk specimens were placed vertically on a cylindrical steel base (diameter = 150 mm) located at the centre of the impact machine. The hammer was dropped from 500 mm height to provide a striking velocity of 3 m/s. An accelerometer attached to the impact hammer was used to measure acceleration during the impact process.

The depth of water penetration under pressure was determined according to BS EN 12390-8: 2000 [16] using a commercial water permeability test equipment (the 3 points model C435 Matest). 150 mm cube samples was placed under applied pressure of 5 bar (500 kPa) for 72 h. After that, the cubes were split into two halves, the water penetration was measured, and the average results of three samples was recorded.

The chloride migration test was performed according to the NT BUILD 492 [17] procedure. For each test group, the chloride migration depths of cylinder (100 mm diameter and 50 mm thickness) specimens were measured by means of a silver nitrite indicator solution and the non-steady-state migration coefficients (D_{nssm}) were calculated based on the formulas reported by Luo and Schutter [18]. The reference and real test set-up used in this study were shown in Fig. 2 and Fig.3, respectively.

The average atomic ratios of the hydrous phases (calcium silica hydrates (C-S-H) in the interfacial transition zone (ITZ) between the aggregate and the cement matrix were measured by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray (EDX) Analyzer.

III. Results and discussions

3.1 Strength development

The test results of compressive strength of the concrete mixes are summarized in Table 2. Also, Fig.4 below gives a graphical representation of variation of compressive strength with age. Fig. 4 shows that copper slag concrete consistently had the highest compression strength both at early and later ages.

The replacement of gravel coarse aggregate by copper slag aggregate increased the 28- and 56-day compressive strengths from 52 to 61 MPa and from 55 to 65 MPa, respectively. In general, it can be concluded that the incorporation of copper slag coarse aggregates increases the static strength by about 14 % on average.

The higher strength can be attributed to the strength characteristics (lower impact value) of copper slag aggregates [10] or presumably it may indicate that failure through aggregates is possible for the gravel aggregate concrete so that increased paste strength is not significant for the mix properties.

It is established that normal gravel is inert and further, from X-ray diffraction (XRD) results (Fig.5), it is shown that the copper slag did not possess any compound that was potentially reactive (crystal structure) and hence it can be concluded that changes in the ITZ were not the result of any chemical reaction between the aggregate and the cement paste. It is postulated that the utilization of water in fresh concrete is partly influenced by the surface and geometrical characteristics of the aggregate particles. It is therefore believed that these aggregate characteristics had bearing on the effective w/c ratio and, hence, on the pore water in the ITZ. For example, less free water will be available for the transition zone in the copper slag concrete due to a much higher surface roughness and large overall surface area of the slag particles.

In addition, the EDX chemical analysis revealed that there was significant difference in the

Ca/Si, (Al+Fe)/Ca and S/Ca ratios of the ITZs of the two concretes. The analysis indicates a Ca/Si average atomic ratio of 1.13 and a (Al+Fe) / Ca average ratio of 0.17 in the ITZ of the copper slag high-strength concrete. By contrast, the analysis shows a Ca/Si average ratio of 3.12 in the ITZ of the gravel high-strength concrete, signifying that the ITZ was relatively porous (Fig.7) and rich in ettringite (Fig.8).

3.2 Impact response

Fig.8 shows "load-time" histories for the concrete mixes during the first drop of impact. As can be seen, the magnitude of load for the high strength copper slag concrete was approximately 30 % greater than that of the high strength gravel concrete in the first cycle of wave propagation. The peak value is 22.7 kN compared to a peak load of 16.4 kN for the gravel concrete. Since the loading is constant in this work, different peak heights correspond to different times of loading indicating different dynamic stiffness. Therefore, the copper slag mix is to convey stress waves with less crack propagation (Fig.9) when it is subjected to impact loading.

Based on composite mechanics, the elastic modulus of concrete is, to a great extent, positively related to the modulus of the aggregate. According to this theory, when the specimen is subjected to high rates of loading, the concrete with rigid aggregates would mainly be able to dissipate energy by cracking rather than rebounding or deforming [19]. As cracks preferentially travel through the path of least resistance, the ITZ properties become of major importance for the behaviour of this concrete under loading. The stronger ITZ in the copper slag high-strength concrete would efficiently participate in transferring stress through the composite, resulting in a greater vertical impact reaction force.

It is worth also highlighting that the time taken for the compression stress waves to travel from the impact point to the bottom of the gravel specimen was about 30 % higher than for the copper slag specimen. This is a further demonstration of the lower overall stiffness of the gravel mix and a weaker structural integrity at micro-scale. The variation of "load-displacement" histories of the mixes during the first drop of impact is displayed in Fig.10. In both cases; the specimens exhibited a quite irregular load-deflection response over a relatively large strain range followed by an elastic recovery. The recovered strain lower in the case of the copper slag mix in the same way as it is much stiffer. The figures also indicate that the gravel mix exhibits much higher plastic deformation.

3.3 Water permeability and chloride ion penetrability

In order to determine the durability of the two types of concrete, tests were conducted on the transport properties of each concrete. Injurious substances such as sulphates and chlorides, usually present in aqueous solution, can penetrate the concrete and contribute to the degradation of the concrete. Therefore, it was believed that the water permeability and the non-steady state chloride migration tests would provide good indicators of the durability of the concrete.

Table 3 shows the average results after these two tests were carried out on the representative concrete samples. At 28 days, it is shown that the depth of water penetration was 22% higher in the concrete with gravel than that with slag. It is also shown that, in comparison to the high strength concrete with slag, the computed chloride migration coefficient from non-steady state migration (D_{nssm}) at 90 days was 29% greater in the high-strength concrete with gravel.

According to Table 4 [20], both samples of high strength concrete that were made with gravel and slag can be described as having high resistance to chloride penetration. However, in this particular test, the higher D_{nssm} measurement shows that any steel reinforcement that is placed in the high strength concrete with gravel will be more susceptible to corrosion. Comparison of the transport properties of high strength concrete with gravel indicates that there is a consistently lower level of penetrability in the high strength concrete with slag over time. Generally, as aqueous substances penetrate the surface of the concrete, movement takes place in the pores of the bulk of the mortar, in the interfacial transition zone (ITZ) and in the aggregate particles.

With the mortar in the two high strength concrete samples being the same, (the proportions of the mixes were the same), it is deduced that the higher level of penetrability occurred in the interfacial transition zone and/or in the aggregate. In the case of the latter, absorption test showed that the slag aggregate had an appreciably lower degree of porosity. In the other case, angular particles could have created a more tortuous path for flow, and hence the movement of substances in the ITZ of the irregular slag particles would serve to reduce the movement and minimize the transport mechanism. While other features may have helped to reduce the transport property of the high strength concrete with slag, it is plausible that the porosity and the particle shape of the slag aggregate had impact on the permeability and non-steady state migration properties of the recipient high strength concrete.

IV. Concluding remarks

In the light of the findings obtained from this experimental study, it can be concluded:

- Using copper slag, a high strength concrete can be produced with potential uses in structural applications. Also, the incorporation of copper slag coarse aggregates increases the static strength partly due to the strength characteristics of copper slag and partly due to a better packing of cement particles against aggregate surfaces and less thicker and stronger ITZ.
- The computed chloride migration coefficient from non-steady state migration (D_{nssm}) at 90 days was 29% greater in the high-strength concrete with gravel. This knowledge confirms the importance in the careful selection of aggregate when improved property such as good durability is needed in concrete structures (i.e. marine environment).
- The movement of substances in the ITZ of the porosity and irregular slag particles would serve to reduce the movement and minimize the transport mechanism. This signifies that the pore structure, compressibility, and surface texture of the aggregates are of paramount importance for the permeability and migration properties of concrete.
- Application of fractal theory on the macro-scale evolution of impact-induced damage was carried out for the first time in the concrete literature. The analysis revealed that the fractal dimension of the cracks was positively correlate with the irregularity of surface topography. In addition, for the high strength concrete with less porous and stronger particles, greater fractal energies are dissipated during the dynamic damage.

References

[1] Huanosta- Gutierrez, T.; Dantas, R.F.; Ramirez-Zamora, R.M.; Esplugas, S. Evaluation of copper slag to catalyze advanced oxidation process for the removal of phenol in water. Journal of Hazardous Materials 2012, 213-214, 325-330.

[2] Gorai, B.; Jana, R.K.; Premchand. Characteristics and utilization of copper slag- a review. Resources, Conservation and Recycling 2003, 39, 299-313.

[3] Alp, I.; Deveci, H.; Sungun, H. Utilization of flotation wastes of copper as raw material in cement production. Journal of Hazardous Materials 2008,159, 390-395.

[4] Sani D., Moriconi, G., Fava, G., Corinaldesi, V. Leaching and mechanical behavior of concrete manufactured with recycled aggregates. Waste Management 2005, 25, 177-182.

[5] Tixier, R; Devaguptapu, R; Mobasher, R. The effect of copper slag on the hydration and mechanical properties of cementitious mixtures. Cement and Concrete Research 1997, 27, 1569-1580.

[6] Al-Jabri, K.S.; Al-Saidy, A.H.; Taha, R. Effects of copper slag as a fine aggregate on the properties of cement mortar and concrete. Construction and Building Materials 2011, 25, 933-938.

[7] Al-Jabri; K.S.; Hisada, M.; Al-Saidy, M.; Al-Oraimi, S.K. Performance of high-strength concrete made with copper slag as a fine aggregate. Construction and Building Materials 2009, 23, 2132-2140.

[8] Arino, A.M.; Mobasher, B. Effect of ground copper slag on strength and toughness of cementitious mixtures. ACI Materials Journal 1999. 96, 68-74.

[9] Najimi; Sobhani; Pourkhorshidi. Durability of copper slag contained concrete exposed to sulfate attack. Construction and Building Materials 2011, 1895-1905.

[10] Khandazi, M.; Behnood, A. Mechanical properties of high-strength concrete incorporating copper slag as coarse aggregate. Construction and Building Materials 2009, 23, 2183-2188.

[11] Wu, W; Zhang, W; Ma, G. Mechanical properties of copper slag reinforced under dynamic compression. Construction and Building Materials 2010, 24, 910-917.

[12] Chen, B; Liu, J. Contributions of hybrid fibers on the properties of the high-strength lightweight concrete having good workability. Cement and Concrete Research 2005, 35, 913-917.

[13] Zineddin M; Krauthammer T. Dynamic response and behavior of reinforced concrete slabs under impact loading. International Journal of Impact Engineering 2007, 34, 1517-1534.

[14] Khan, M.I. Nanostructure and microstructure of cement concrete incorporating multicementitious composites. Journal of the Transportation Research Board 2010, 2141, 21-27.

[15] Grassl, P; Wong, H.S.; Buenfeld, N.R. Influence of aggregate size and volume fraction on shrinkage induced micro-cracking of concrete and mortar. Cement and Concrete Research 2010, 40, 85-93.

[16] BS EN 12390-8. Depth of penetration of water under pressure. British Standard Institution 2000.

[17] NT BUILD 492. Concrete, mortar and cement-based repair materials: Chloride migration coefficient from non-steady- state migration experiments. Nordtest, Esbo, Finland, 1999.

[18] Luo, L.; De Schutter, G. Influence of corrosion inhibitors on concrete transport properties. Materials and Structures 2008, 41, 1571-1579.

[19] Erdem, S.; Dawson, A.R.; Thom, N.H. Micromechanical structure-property relationships for the damage analysis of impact-loaded sustainable concrete. ASCE Journal of Materials in Civil Engineering 2013, 25, 597-607.

[20] Najim, K.B. Determination and enhancement of mechanical and thermo-physical behavior of crumb-rubber modified structural concrete. PhD thesis, University of Nottingham, UK, 2012.

Figure captions

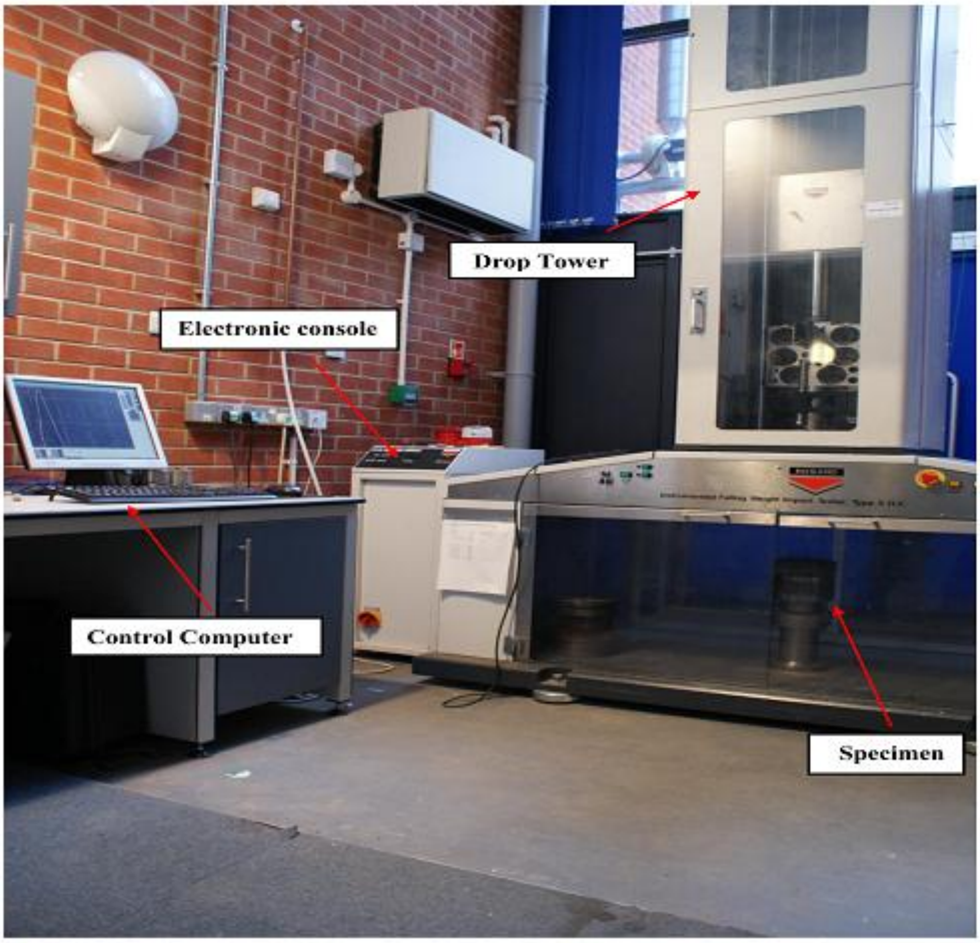


Figure 1 – Drop-weight type impact test device

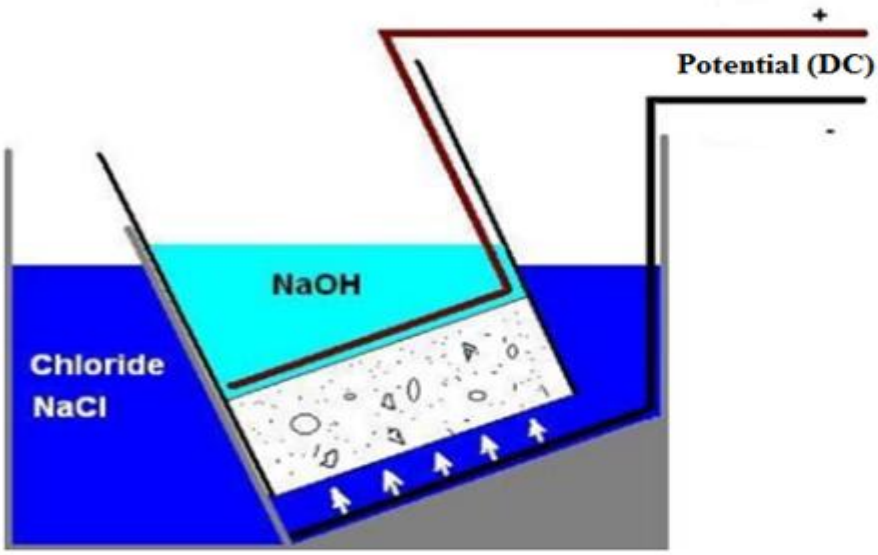


Figure 2 – The reference test set-up for chloride migration measurement (adapted from [18])

Figure 3 – The test set-up used in this study for chloride migration measurement

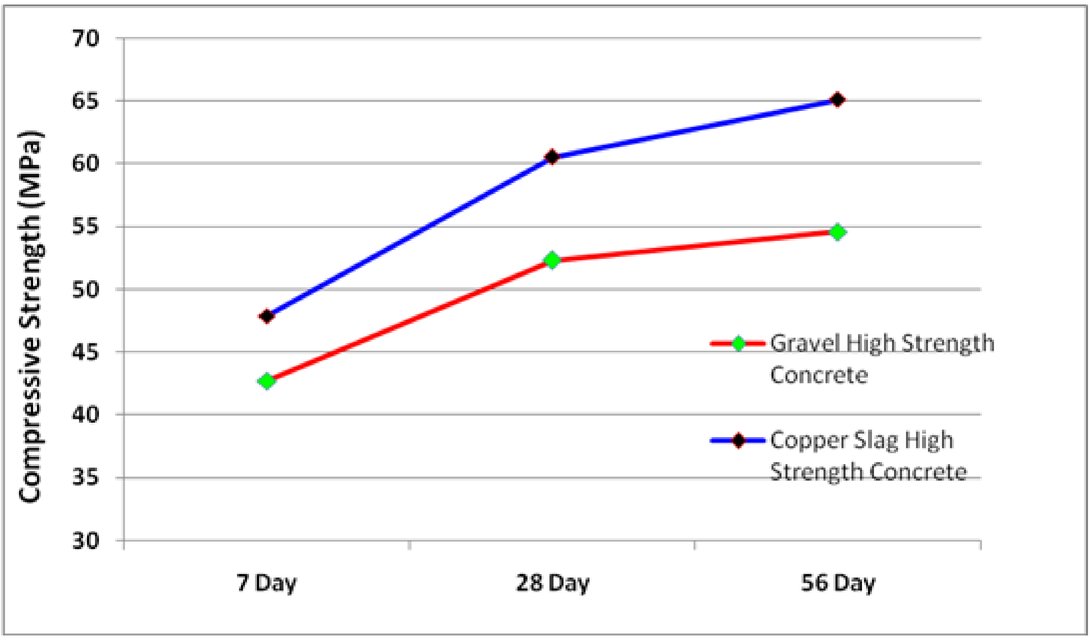


Figure 4 – A graphical representation of the compressive strength results with age

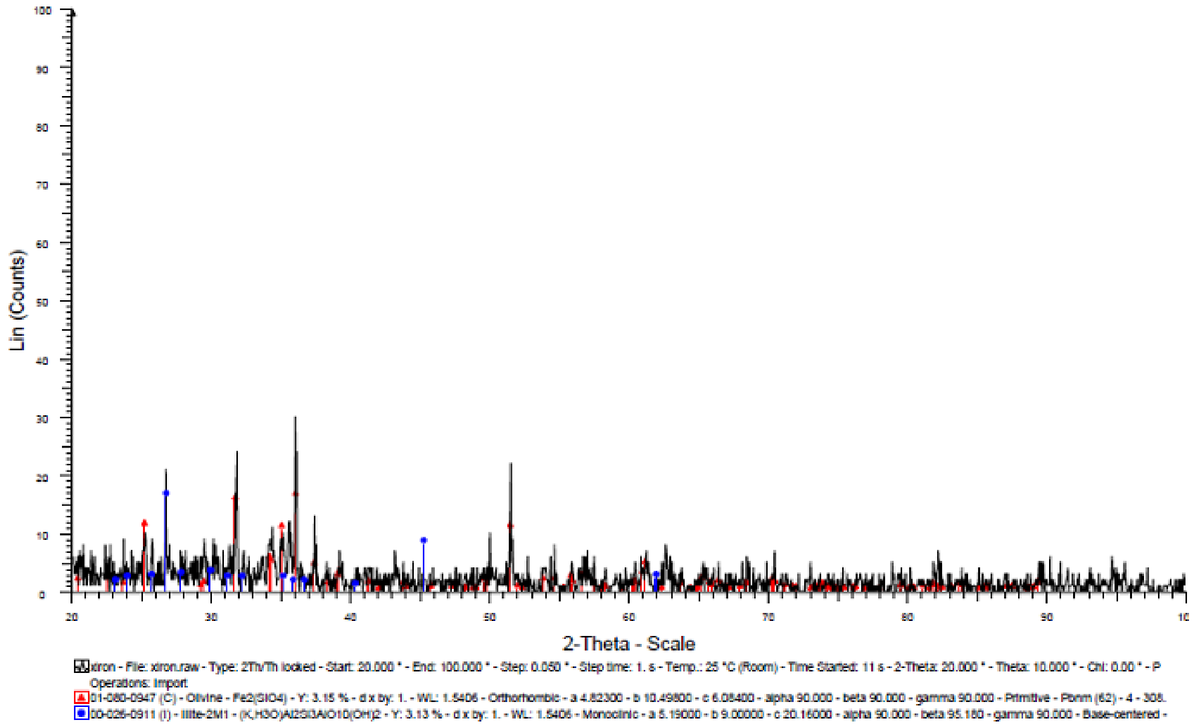


Figure 5 – X-ray diffraction pattern of the copper slag

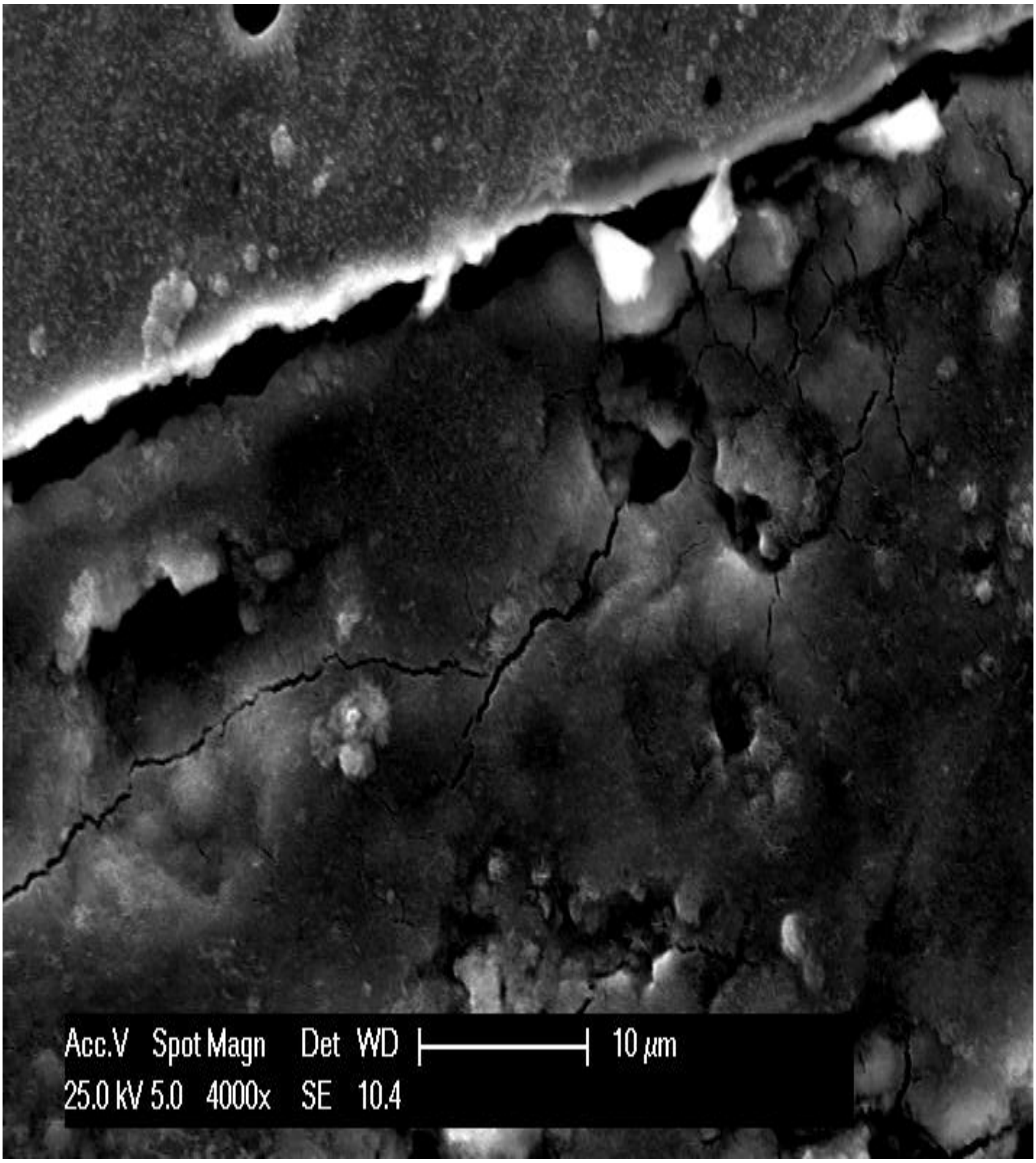


Figure 6 – Porous ITZ in the gravel high-strength concrete sample

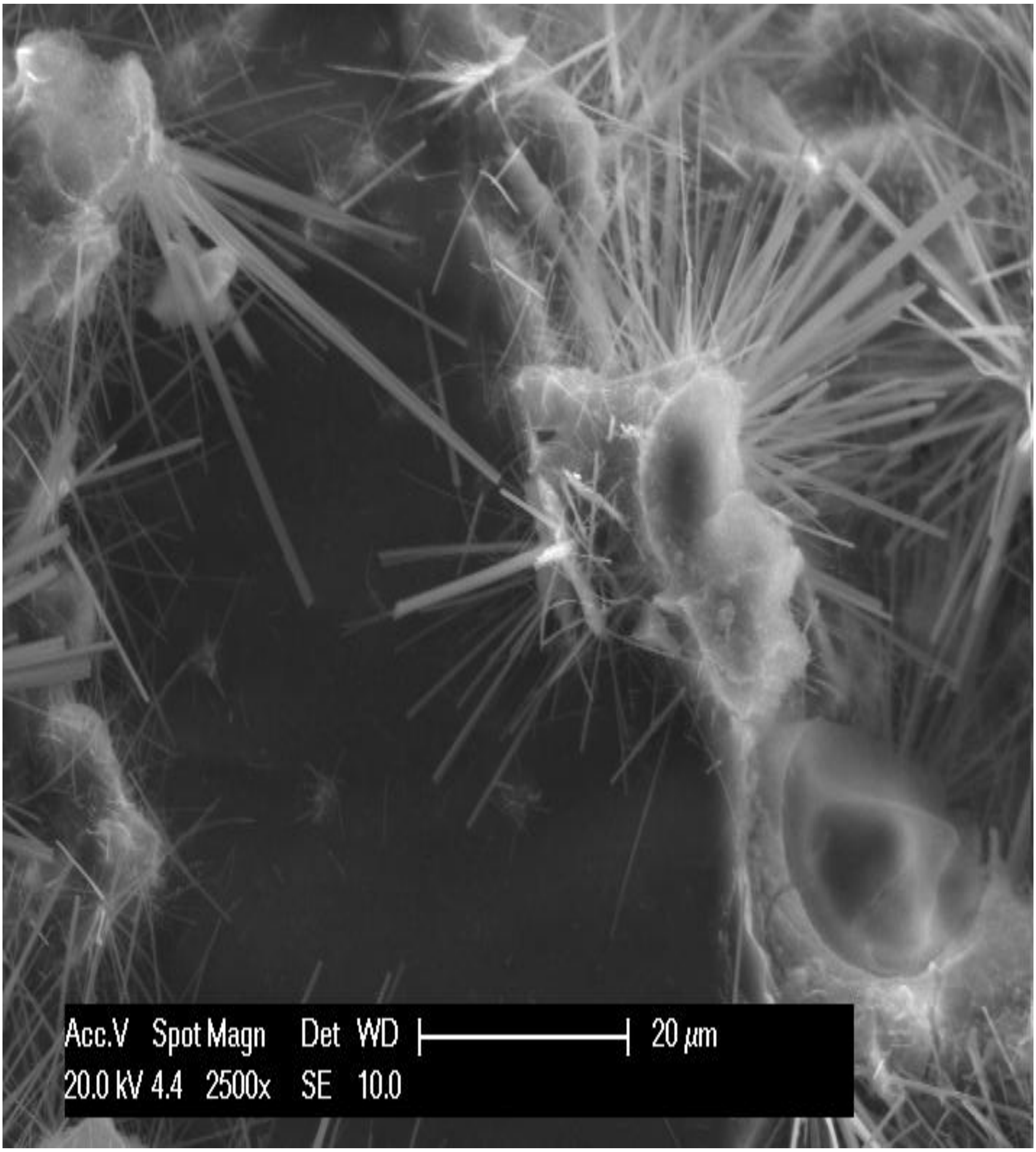
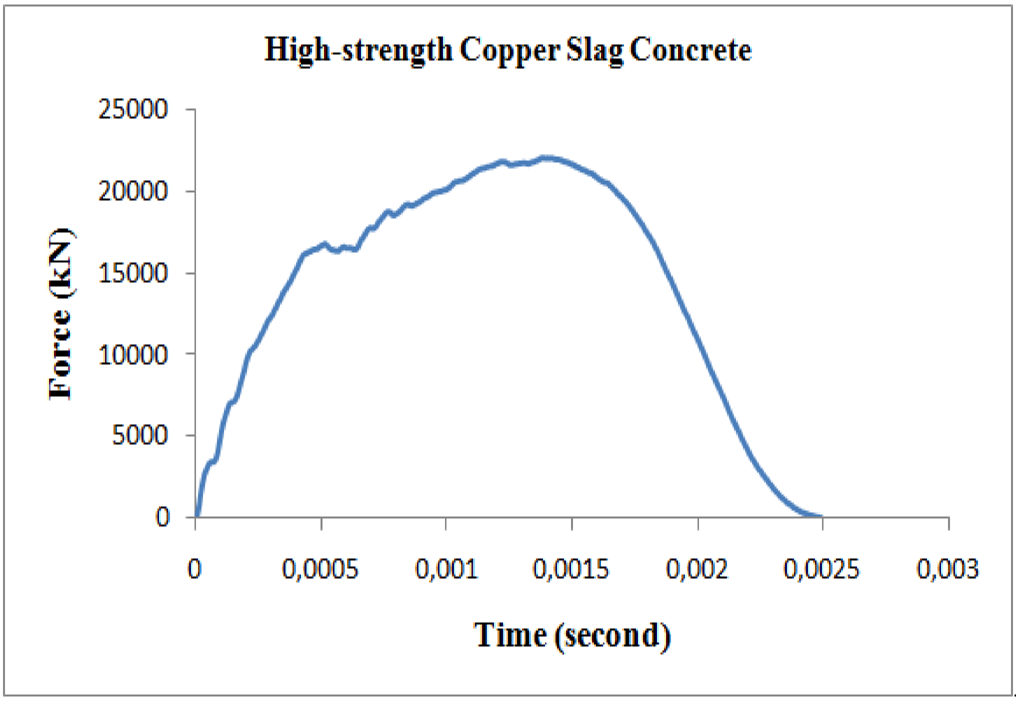


Figure 7 – Ettringite crystals near the ITZ of the gravel high-strength concrete sample



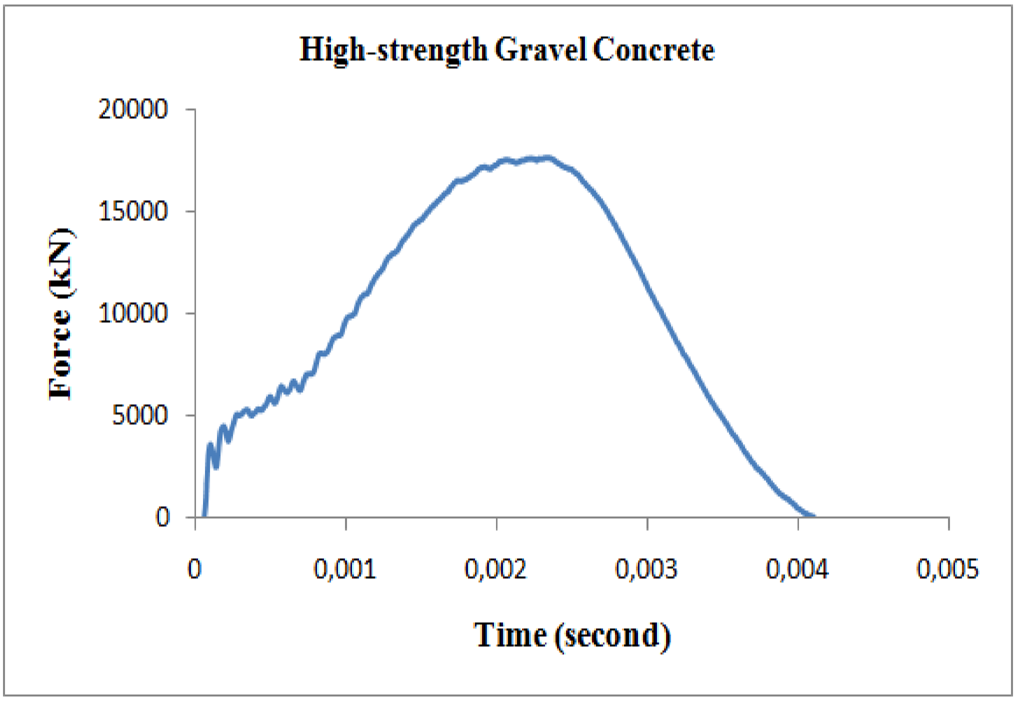


Figure 8 – Nanotech images of fracture surfaces a-) Gravel mix and b-) Copper slag mix

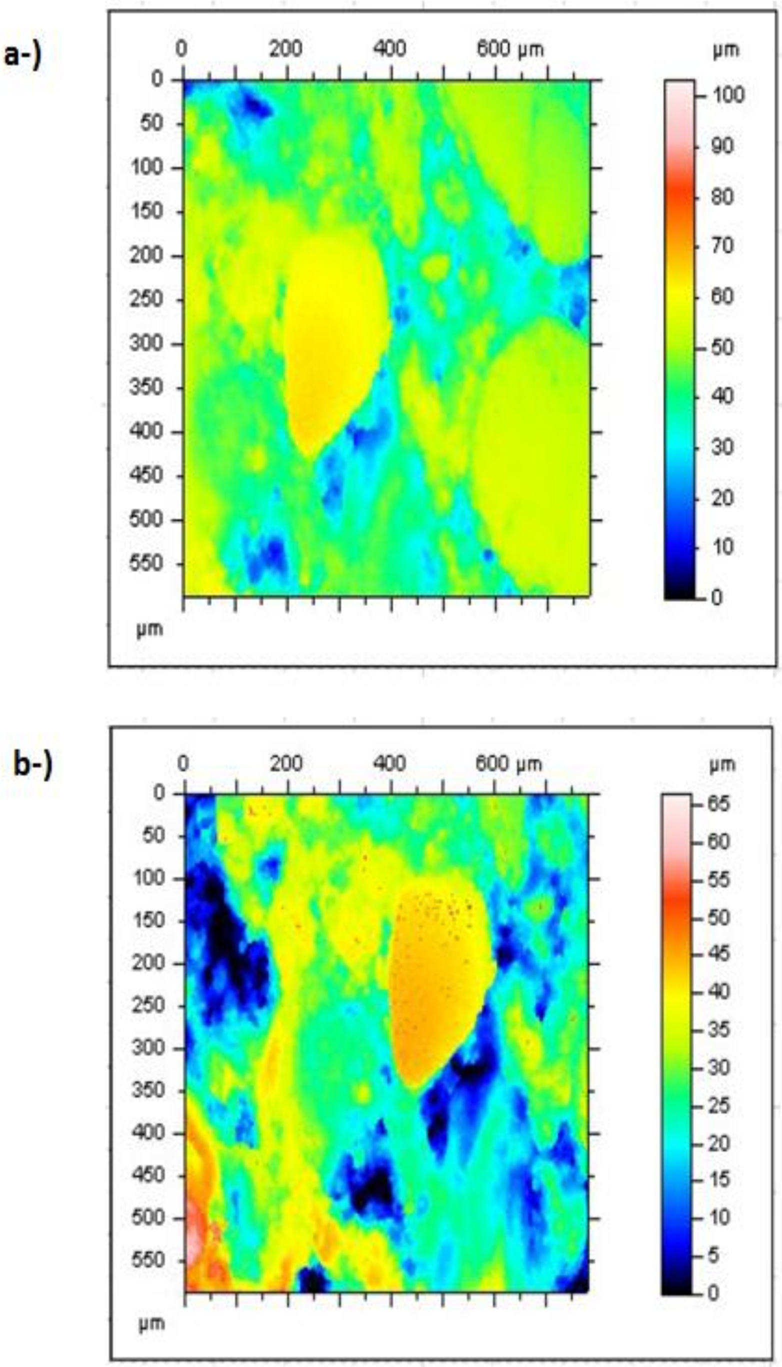
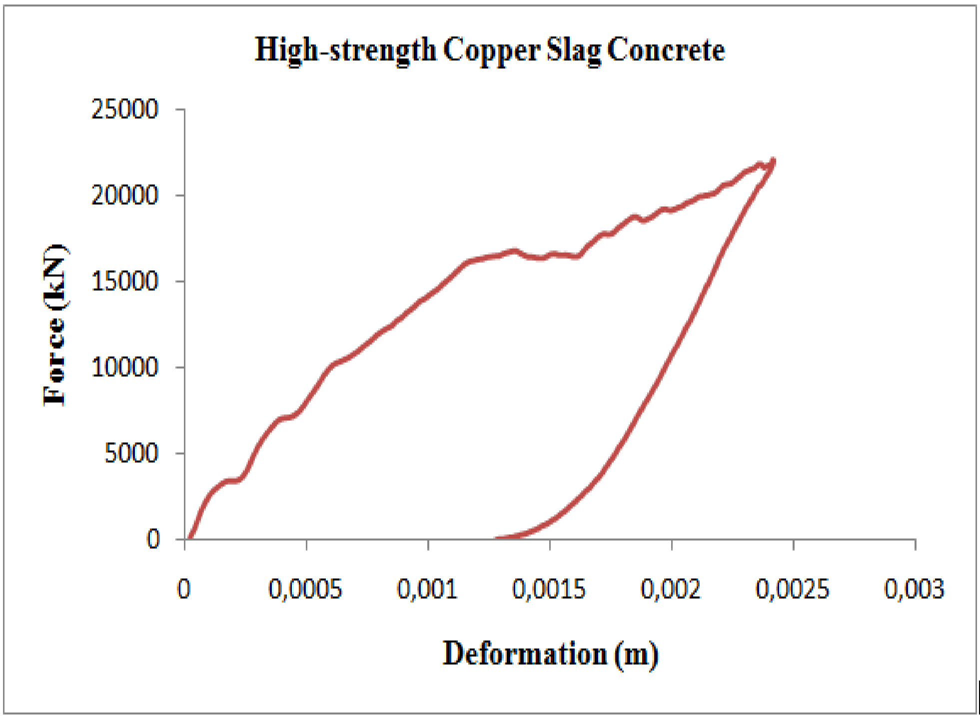


Figure 9 – Load-time histories of the mixes during the first drop of impact



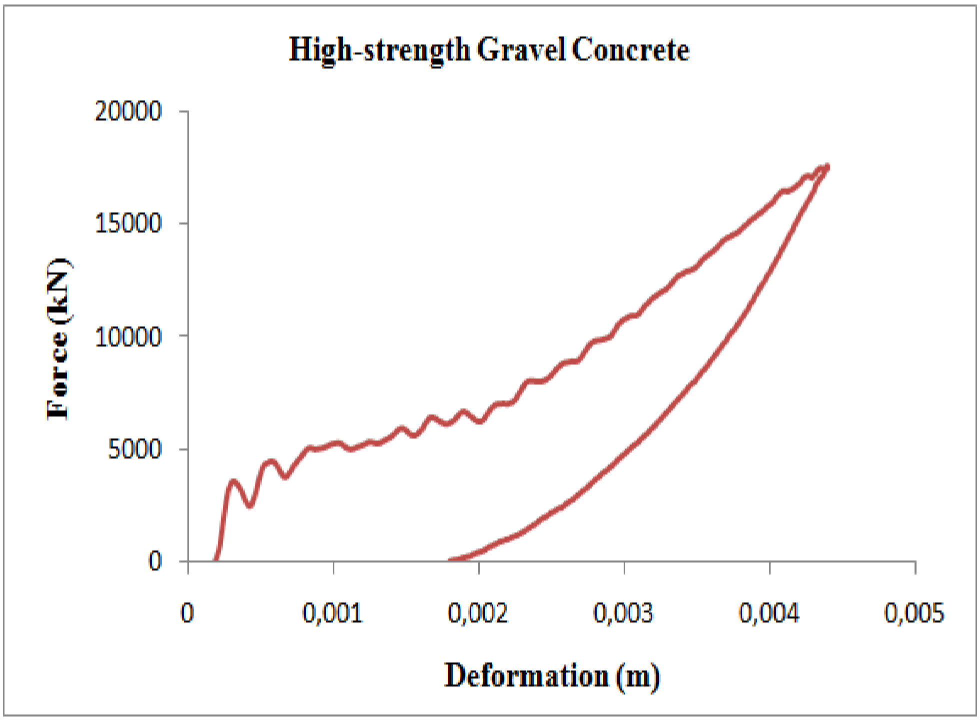


Figure 10 – Load-deformation histories of the mixes during the first drop of impact

Table 1 Mix proportions for 1m³

Material (kg/m³)	Gravel high strength concrete	Copper slag high strength concrete
Cement	390	390
Water	215	215
Sand	810	810
Gravel (coarse aggregate)	1020	0
Copper slag (coarse aggregate)	0	1485

Table 2 Compressive strength test results

Mix ID	7 Day	28 Day	56 Day
Gravel high strength concrete	42.7 MPa	52.3 MPa	54.6 MPa
Copper slag high strength concrete	47.9 MPa	60.5 MPa	65.1 MPa

Table 3 Water permeability and chloride penetrability test results

Mix ID	Water permeability under pressure (mm)	Chloride penetration		
		Depth (mm)	Dnssm x 10^{-12}	Charge passed (coulombs)
Gravel high strength concrete	22	6,0	8,11	1874
Copper slag high strength concrete	18	4,5	5,82	1452

Table 4 Evaluation of the resistance of chloride penetration based on Dnssm and charge passed [20]

Chloride migration coefficient Dnssm x 10^{-12}	Resistance to chloride penetration	Charge passed (coulombs)	Chloride penetration
> 15	Low	> 4000	High
10-15	Moderate	2000-4000	Moderate
5-10	High	1000-2000	Low
2,5-5	Very high	100-1000	Very low
<2,5	Extremely high	< 100	Negligible