University of Dundee

Innovative Processing of Stockpile Fly Ash

Working Draft Report

January 2019

1. Acknowledgements

2. Contributions

Concrete Technology Unit

Dr M J McCarthy

Professor M R Jones

Mr T A Hope

Industrial Partners

Dr R A Carroll

Dr N Cooke

3. Contents

4. Summary

This report describes a 3½ year study carried out to investigate the potential for recovery of wet-stored fly ash, mainly from stockpiles, and processing by various means to meet EN 450-1:2012 requirements. The project was divided into five stages: (I) Review of available literature on wet-storage of fly ash and the various potential beneficiation techniques. (II) Characterisation and use of a selection of fly ashes (8 dry, 8 stockpile, 4 lagoon and 1 beneficiated stockpile) in concrete. (III) Laboratory studies of wet-stored fly ash and evaluation of various processing techniques (assessed by fly ash characterisation and use in concrete). (IV) A visit to a site carrying out beneficiation of wet-stored fly ash and evaluation of material before and after recovery. This was followed by a pilot-scale trial within the UK, beneficiating stockpiled material and evaluating in the same way as (III). (V) Exploring the Practical Implications of the study.

The literature indicates that wet-storage causes changes to the physical and chemical properties of fly ash. Initially, cohesive forces form between moist particles, with chemical reactions then leading to agglomeration. This has been noted to cause an increase in water requirement and reductions in reactivity. Chemically, there is little change observed in the bulk composition and mineralogy of fly ash, although, the formation of calcium sulfate products, such as bassanite and ettringite, may occur. Reductions in consistence between dry and wet-stored fly ash concrete have been noted. However, only minor differences in concrete strength were seen up to 28-days with wet-stored fly ash, although more noticeable effects occur at later test ages after 56-days.

Most beneficiation systems for dry fly ash can be adopted for use with wet-stored fly ash, providing a drying stage is implemented before processing. The most suitable beneficiation systems are a form of drying combined with particle size reduction and carbon removal, as necessary. Although, the required technical performance of the output fly ash and the economic viability of recovery are likely to control the processes selected.

The laboratory studies confirmed that wet-storage of fly ash lead to agglomeration and coarsening of the material, with a reduction in <10 µm content. This tended to increase with fly ash fineness, with the majority of effects occurring in the 6 month period following moistening. In many cases, agglomeration lead to material failing to meet EN 450-1 fineness limits. While the agglomerates appeared to have limited strength, there was little breakdown during normal handling.

The LOI of fly ash was also found to increase slightly during wet-storage, which seemed to reflect the formation of hydration products (e.g. sulfate-based), which decompose during ignition. Wet-storage did not have a significant effect on the bulk oxide composition or mineralogy of fly ash, with only small quantities of calcium sulfate hydrates found in some wet-stored materials. The loss of fine particles and coarsening during agglomeration affected fly ash reactivity. This was reflected in a reduction in activity index of wet-stored fly ash at 28 and 90 days, which in some cases did not meet EN 450-1 limits, although this was material dependent.

When used in concrete of equal mix proportions to a dry Category N fly ash, wet-stored fly ash had a reduced consistence, requiring a larger superplasticizing admixture dose to achieve equivalent slump. However, the wet-stored materials achieved similar strengths to Category N fly ash, at all ages, for the same mix proportions.

Following drying, screening wet-stored materials at 600 µm did not give noticeable benefits to fly ash, however, it reduced material variability and improved repeatability of subsequent tests. Screening improved the dry handling of wet-stored fly ash by removing large agglomerates and also increased the effectiveness of further beneficiation. Screening at 63 µm increased fineness and gave reductions in water requirement, but had little effect on LOI and reactivity. It also gave low yields and little benefit to concrete strength.

Grinding for short durations (20 minutes) in a laboratory ball mill gave reduced particle size, lowered water requirement and increased activity index, but had little effect on LOI, bulk oxide or mineralogical compositions. In concrete, material ground for short durations had a lower superplasticizing admixture requirement compared to unprocessed material, but did not achieve a noticeable increase in concrete strength.

Screening at 600 µm and grinding for a longer duration in the ball mill (120 minutes) increased fineness to <0.5 % retained on a 45 µm sieve and the volume of <10 µm particles to >70 % in wet-stored materials. This did not give any further reductions in water requirement, but increased activity index. Grinding for longer durations had little effect on bulk oxide or mineralogical composition. Long duration grinding had a similar effect on superplasticizing admixture dose for a target slump, to material ground for shorter durations, and gave an increased concrete strength compared to unprocessed material at all ages.

Carbon removal in the laboratory furnace at a temperature of 500°C for 1 hour reduced LOI of most wet-stored materials to below 7 %. This also led to slight increases in fineness, decreases in water requirement and small increases in activity index. No significant effects on bulk oxide and mineralogical composition were observed after this process. When evaluated in concrete, materials after carbon removal had slightly lower superplasticizing admixture requirements and gave small increases in strength.

The initial beneficiation stage of the pilot-scale processing, of drying and de-agglomeration, gave fly ash which met all EN 450-1 requirements except activity index, which may relate to losses of the finest 10 % of particles during this process. Carbon removal by electrostatic separation of the dried and de-agglomerated material, to an LOI of 3 %, resulted in increased reactivity, enough to meet EN 450-1 activity index requirements. Drying and de-agglomeration reduced superplasticizing admixture dose required to achieve a target slump compared to unprocessed material, but had little influence on strength. Therefore, drying and de-agglomeration followed by carbon removal could be used to produce an EN 450-1 Category N fly ash from this wet-stored material feed.

Air-classification after drying and de-agglomeration to remove coarse material produced a fly ash which satisfied all EN 450-1 requirements for Category N material. Air-classification further increased fineness, reduced water requirement and increased activity index, but did not result in strength gains in concrete.

Grinding the dried and de-agglomerated material in a micronising mill led to noticeable increases in the quantity of <10 µm particles, activity index and concrete strength. This gave the highest performance achieved with the wet-stored fly ash, but had a low throughput. Carbon removal by electrostatic separation of the micronised material did not result in any benefits beyond the reduction of LOI.

Preliminary tests for carbonation and chloride ingress suggest little difference between these for wet-stored and beneficiation fly ash in concrete of similar 28 day strength. This represents an area that requires further testing.

Overall, the laboratory and pilot-scale processing trial demonstrated that EN 450-1 material could be successfully produced from a wet-stored UK fly ash. Each fly ash deposit is likely to be different and to require site specific testing. Energy (and cost) requirements between processing techniques will also vary and what can be achieved for fly ash using a particular beneficiation approach would need to be balanced against these.

5. Introduction

5.1. Background

The benefits of fly ash as an addition in concrete have been well known for some time, and the material is an established resource for the construction industry in the U.K. and beyond. Produced during electricity generation in coal-power stations on a large scale for more than 50 years, there has historically been a surplus. However, since the summer of 2014, demand for fly ash has consistently exceeded supply leading to shortages (Carroll, 2015). Combined with a decline of GGBS availability (Alberici, et al., 2017), there has been a lack of both as additions for concrete in the U.K.

Several factors have led to this shortage for fly ash, the most significant of these is the decline in coal power electricity generation in the U.K., with other factors such as the recovery of the construction industry after the 2008 recession and increased utilisation of the material also contributing (U.K. Qualtity Ash Association, 2016). In response, importing fly ash or recovery of existing wet-stored (stockpile and lagoon) materials within the U.K. are considered as potential sources of fly ash for the future.

4.1.1   Importing fly ash

Fly ash is currently imported in countries such as Australia (Infodrive India, 2018) and, more recently, the U.S.A. (The Associated Press, 2017), where, despite using coal for electricity generation, shortages in supply or logistical costs have made importing fly ash viable. Fly ash is usually imported wet, in bulk to prevent dusting, but can also be transported dry in specialised powder vessels, like cements. Importing fly ash is an option for the U.K. if transportation from port to user can be accomplished economically. Alternatively, recovery of wet-stored fly ash may provide enough supply for the U.K. construction industry in the medium term or be used as a reserve during times of low availability.

4.1.1 Recovery of wet-stored fly ash

Historically the U.K. has over-produced fly ash and there exists large reserves of wet-stored material in and around power stations. This may represent a supply of fly ash for the future, provided it can be recovered effectively and retains the physical and chemical properties of freshly produced material (Carroll, 2015). The key technical consideration for recovery of wet-stored fly ash is the deterioration of the material during storage. Wet-stored material has been found to generally fail to meet EN 450-1 or BS 8500 requirements for use in concrete (McCarthy, et al., 1999), therefore, some form of beneficiation is likely to be required.

Recovery of wet-stored fly ash must also be economically and environmentally viable. If recovery requires a significant energy input, any CO_2 saving by replacement of Portland cement (PC) will be lost. High energy requirements will also increase the cost, making recovered fly ash less attractive for use. If these costs exceed that of importing fly ash from overseas, this will not be a practical solution.

5.2. Aims and Objectives

The aim of this project is to investigate the properties of wet-stored fly ash and establish means by which it can be beneficiated for use as an addition to EN 450-1 in concrete.

This will be achieved through the following objectives;

- Examining the physical and chemical characteristics of fly ash following wet-storage and the factors influencing these, by studying both on-site, wet-stored low-lime fly ash from throughout the U.K. and carrying out controlled laboratory wet-storage studies.

- Investigate the effects of wet-storage on fly ash performance in concrete, compared with a variety of dry fly ashes.

- Evaluate various beneficiation processes at a laboratory-scale for recovery of wet-stored fly ash, examining the impact on physical properties, chemical properties and performance in concrete.

- Carry out a pilot-scale trial of the most promising beneficiation processes identified in the laboratory to establish the implications of scaling-up beneficiation and to validate the laboratory findings.

5.3. Scope

This project focussed on the recovery and beneficiation of long-term, wet-stored fly ash for use, as an in concrete. Initially, a review of available literature to identify findings from previous studies on wet-stored fly ash were conducted to gain a greater understanding of the changes in properties occurring due to wet-storage. This was followed by an evaluation of existing mineral beneficiation techniques focusing on; particle size separation, particle size reduction and carbon removal. A review of literature investigating the effects of these processing techniques on dry fly ash was conducted to identify the likely benefits that could be attained.

Physical and chemical characteristics of twelve long-term, wet-stored fly ash materials, covering both stockpile and lagoon fly ash, were evaluated using standardised tests for fineness, loss-on-ignition, activity index, water requirement and established techniques to determine bulk oxide composition, mineralogy and particle size distribution to develop an understanding of the typical range of physical and chemical properties of wet-stored materials.

These were compared to a range of dry materials to identify the characteristics most influenced by wet-storage and confirm observations made in available literature. The performance of these materials was compared in 0.5 or 0.53 water/cement ratio concretes, using 30% fly ash, to evaluate if any losses in strength occurred due to wet-storage. As these materials were of unknown history, produced from different parent coals, subject to different burning conditions and wet-stored for a range of durations only general comparisons could be made between the wet-stored and dry fly ashes.

To further develop an understanding of the effects of wet-storage and allow direct comparison between fly ash before and after this was carried out, selective dry fly ashes were wet-stored for up to 24 months in the laboratory and sampled at regular intervals. This was to examine changes that occur during wet-storage with time and to compare with on-site, wet-stored material to confirm the validity of laboratory storage.

These comparisons were then used to determine the most suitable beneficiation techniques for wet-stored fly ash by identifying the properties that did not meet EN 450-1 requirements. The influence of beneficiation on the characteristics and concrete performance of wet-stored fly ash could then be established.

Wet-stored materials were beneficiated using a variety of different laboratory processing techniques focussing on drying, particle size separation, particle size reduction and carbon removal to meet EN 450-1 requirements. The effects of these processes on fly ash characteristics and concrete performance were studied, with beneficiated material compared to both the original wet-stored and dry materials.

Based on these results, further investigation focusing on particle size reduction, with a view to gain significant increases in concrete strength, was conducted on selected materials.

A pilot-scale trial to recover and beneficiate 5 tonnes of wet-stored fly ash was conducted to confirm results obtained in the laboratory and evaluate the feasibility of large-scale recovery. The wet-stored material was dried and de-agglomerated, then either separated by air-classification, or finely ground using a micronising mill. These materials and the original feed material were characterised and evaluated in concrete. Additionally, selected samples from the pilot-scale trial also underwent carbon removal by electrostatic separation in small quantities.

A limited investigation into carbonation and chloride ingress of beneficiated wet-stored fly ash was conducted on selective dry, wet-stored and beneficiated materials to give an indication of the effects of both wet-storage and subsequent beneficiation on these aspects of durability.

6. Literature

6.1. Introduction

This literature review will outline the main reported differences between dry and wet-stored fly ash, highlighting the effects of wet-storage on material characteristics and performance in concrete. An overview of available fly ash beneficiation systems is also given, detailing the effects these have on wet-stored materials in comparison to dry fly ash, if available.

6.2. Wet-storage

Fly ash can be wet-stored in either stockpiles, at 10 - 20% moisture (Cheerarot & Jaturapitakkul, 2004) or in lagoons, both of which are common in the U.K. (Sear, 2001). Once fly ash lagoons reach maximum capacity they are drained, with the fly ash excavated and left in stockpiles to dewater until achieving a similar moisture content to stockpiles. Wet-stored material is currently recovered for low performance applications such as fill or soil stabilisation directly from stockpiles (Sear, 2001). Previous studies investigating wet-stored fly ash have mostly focused on the environmental impacts of heavy metals leaching from wet-storage locations into surrounding groundwater and weathering (Georgakopoulos, et al., 2002) (Gitari, et al., 2009) (Roy & Berger, 2011). Work conducted at the University of Dundee has investigated the effects of laboratory wet-storage on fly ash characteristics and performance in concrete (McCarthy, et al., 2000). In this study, wet-storage was found to involve both physical and chemical changes, which affected fly ash characteristics and performance in cementitious systems.

When introduced to water, cohesion forces develop rapidly between fly ash particles which keep particles clustered together. As wet-storage continues, chemical reactions occur, believed to be the formation of calcium sulfate hydrates such as gypsum (Gitari, et al., 2009). This was identified as the most likely chemical reaction occurring during wet-storage, as both calcium cations and sulfate anions are most abundant on fly ash surfaces (Helmuth, 1987) and have highest leachability (Gitari, et al., 2009), which in the presence of water can form calcium sulphate hydrates. Several studies have identified calcium sulfate hydrates present in on-site wet-stored fly ash (Gitari, et al., 2009); (P. Eze, et al., 2013); (Georgakopoulos, et al., 2002); (Spears, 1997). McCarthy *et al* (1999) observed small quantities of calcium sulphates hydrates, present in both laboratory and on-site wet-stored materials, in addition to limited quantities of hydration products such as ettringite. It is possible that the formation of calcium sulfate hydrates causes agglomeration of fly ash particles by forming between particles which then remain together after cohesion forces are lost during drying and when gypsum is partially dehydrated (Ballirano & Melis, 2009).

Other studies have suggested alternate mechanisms that may occur during wet-storage involving the dissolution of aluminates and silicates from the amorphous glass of fly ash in the presence of high pH pore solution created by the leaching of alkalis. Aluminates and silicates then precipitate as aluminosilicates back on to the surfaces of fly ash particles when the pH of the pore solution drops (Zevenbergen, et al., 1999), due to the percolation of alkalis into groundwater or carbonation. This is essentially the same mechanism as weathering of volcanic ash but was found to occur much more rapidly in wet-stored fly ash, with the level of deterioration observed, in some instances, transforming fly ash into an amorphous clay, like a zeolite.

Carbonation is also known to occur in on-site wet-stored fly ash due to the formation of portlandite from calcium cations and water which then reacts with atmospheric carbon dioxide to form calcite (Sear, 2001) (Schramke, 1992).

Investigation of the influence of wet-storage on fly ash characteristics by McCarthy *et al* (1999) observed an increase in 45 μm sieve retention, an increase in water requirement and a reduction in strength factor but no significant changes in bulk oxide or mineralogical compositions. Evaluation of the performance in concrete of these materials indicated that up to 28-days there was little difference in compressive strength between wet and dry fly ash. Beyond 28-days, a slight reduction in concrete strength of wet-stored fly ash was observed compared to dry materials.

6.3. Drying

Previous beneficiation of wet-stored fly ash in the U.K. conducted using wet processing has been of limited success in both the laboratory and commercially, due to issues with material separation and water usage (McCarthy, et al., 2013) (Insider Media Limited, 2013). Therefore, by drying the material prior to beneficiation it can be handled and processed in the same manner as a freshly produced dry fly ash. Drying fly ash can be accomplished in multiple ways, however, the most practical for wet-stored fly ash would be a flash drying system that includes a form of agitation. Flash drying relies on exposing wet material to hot air whilst applying external action that breaks cohesion forces and exposes more particle surface area, increasing the rate and efficiency of drying (Borde & Levy, 2006). Agitation can be accomplished using baffles within the drying system, which cause collisions that break cohesion forces, or mechanical action such as an impact mill, where the material is ground and dried at the same time (Atritor Ltd, 2018). Flash drying is more effective than bulk drying, however, still requires a high energy input to remove moisture (Borde & Levy, 2006).

6.4. Particle size separation

Particle size distribution is well established as a reliable indicator of dry fly ash performance on several characteristics namely; water requirement, reactivity and concrete strength (Ramezanianpour, 2014) (McCarthy, et al., 2013). By separating fly ash at a chosen particle size, improvements to the above can typically be achieved. Air-classification is a commonly used separation process at coal power stations to remove coarse particles, often including carbon, to meet EN 450-1 requirements (Sear, 2001).

Particle size separation is typically carried out on dry fly ash by either air-classification or screening. Air-classification uses centrifugal forces inside a cyclone to separate particles at a desired 'cut' size, generally operating at a high yield and degree of efficiency (Shaprio & Galperin, 2005). Screening fly ash retains particles greater than the screen mesh size, allowing finer ones to be separated and collected (Soong, et al., 2002). Screening systems often include a form of agitation to reduce mesh blocking by particles, improving throughput.

Particle size separation can also be conducted on wet-stored fly ash in an excess of water by wet screening, hydraulic classifiers or settling tanks, which use the differing settlement rates of fly ash particles in a fluid to separate the material into various particle size fractions.

Previous research at the University of Dundee has investigated air-classification, dry screening and hydraulic classification of various wet-stored materials. Hydraulic separation required the fly ash to be slurried in water and did not achieve distinct separation of fly ash particles, with many fine particles remaining trapped with larger particles due to flocculation and lost in the oversize (McCarthy, et al., 2013). Recovered material then required drying before use, increasing the overall processing time and energy requirements. Although, another study by McCarthy *et al* (2000) demonstrated, by adjusting the water content of the concrete mix to account for moisture in fly ash, an equal strength concrete could be produced to that with dry material.

6.5. Particle size reduction

Particle size reduction is a well-established beneficiation technique for dry fly ash. Numerous studies exist examining the impact of various grinding systems on a wide range of dry fly ash characteristics including particle size, consistence and reactivity (Kiattikomol, et al., 2001); (Paya, et al., 1996); (Sun, et al., 2013). These studies are generally in agreement that the main benefits of grinding on dry fly ash are an increase in volume of fine fly ash particles and surface area (Kiattikomol, et al., 2001). This results in increased pozzolanic reactivity, seen as greater mortar and concrete strengths, especially at early ages of <56-days. Particle size reduction also typically results in slight increases in water requirement due to higher surface area and the breaking of spherical particles, reducing the lubricating effect of the fly ash (Paya, et al., 1996).

While capable of improving properties, grinding of dry fly ash on an industrial-scale is rarely conducted in the U.K., due to the costs outweighing benefits to performance. Fly ash produced in the U.K. typically meets EN 450-1 with minimal processing, usually requiring carbon removal rather than grinding. Any fly ash produced that fails to meet EN 450-1 fineness requirements due to coarse particles is air-classified to remove the oversize rather than being ground.

There has been limited investigation into particle size reduction of wet-stored fly ash, with results indicating that the effects of grinding are the same as for dry fly ash. Grinding of wet-stored materials was found to increase the volume of <10 μm particles, improve consistence and increase concrete compressive strengths (McCarthy, et al., 2018) However, these materials were evaluated at a single grinding duration preventing any relationship between improvements to the material and degree of grinding from being established.

A wide variety of grinding systems exist that can be used successfully with fly ash depending on the input and desired output material particle size. Many grinding systems need a dry feed material, therefore, wet-stored fly ash will be likely to require a pre-processing drying stage if grinding is to be utilised as a beneficiation process.

Wet-stored fly ash is known to agglomerate, causing an increase in particle size (McCarthy, et al., 1999), therefore a form of grinding that can accept large agglomerates and reduce particle size without requiring long residence times would be suitable. The grinding systems best suited for the particle size range of fly ash are; impact, hammer, ball and micronising mills (Saravacos & Kostaropoulos, 2016).

Impact and hammer mills induce collisions between particles and surfaces within the mill to reduce particle size. These systems are typically used in series with an air-classifier which recycles any particles that exceed the required size back into the mill for further grinding. This system is effective at grinding to a particle size of around 30 µm, beyond which, throughput decreases due to the volume of particles that must be recirculated through the mill for additional grinding (Hosokawa Micron Powder Systems, 1998). These systems are, therefore better suited to quickly reducing agglomeration, rather than grinding particles to increase the volume of fines.

Ball mills use the crushing action between the grinding medium and mill walls to reduce particle size. These mills are most frequently used in cement manufacture, as they can operate on a large scale and provide a high throughput with a consistent output material. Ball mills can achieve particle sizes of <10 µm, although, finer output requires longer grinding durations and lower throughputs to achieve this (Metso Corporation, 2018) (Jaturapitakkul, et al., 2004). These mills can be adjusted to produce a range of output particle sizes depending on configuration, from high throughput with coarse output to low throughput with very fine output.

Micronising mills use contrasting high pressure air-flows to create a turbulent air vortex inside the mill (Morales, et al., 2012). These turbulent conditions cause inter particle collisions, which break particles by abrasion. Particles are retained within the vortex of the mill due to centrifugal forces, the effect of which reduces as particles become lighter as they are ground. Once a particle is light enough it moves to the centre of the vortex and falls out of the air-stream into a collection vessel at the base of the mill, while large particles remain in the vortex for further grinding (Atritor Ltd, 2018). This system is controlled by the input material feed rate, with higher rates reducing the degree of grinding and vice versa. This system requires sighting runs to calibrate the material feed rate for maximum throughput at the desired output particle size. Like ball milling, this system is suitable for creating very fine materials to levels of 1 μm (Morales, et al., 2012).

The most suitable grinding process will depend on the degree of particle size reduction required to meet EN 450-1 or achieve enhancements in concrete properties. Therefore, the deterioration of the wet-stored material will be a significant factor and will need to be evaluated before a beneficiation system can be selected.

6.6. Carbon removal

Carbon removal of dry fly ash is currently conducted at several power stations due to the high unburned carbon contents in the fly ash produced (Cangialosi, et al., 2005). Carbon removal can be conducted by various systems, the most common of which are oxidation or electrostatic separation.

Oxidation is the simplest method of removing unburned carbon, introducing fly ash to conditions of 700 to 900°C in a furnace or fluidised bed reactor causing combustion of unburned carbon present. Fluidised bed reactors are the most commonly used system as these allow a stable throughput and control over the degree of carbon removal by manipulation of fly ash feed rate, temperature and oxygen supply (Cammarota, et al., 2008). This allows almost all carbon to be removed, by increasing residence time and temperature, or only marginal quantities to be removed to meet standards, as required. The disadvantage of oxidation is the high energy needed, often requiring a supply of gas to maintain the high temperatures required, while also producing CO_2 and in some cases NO_x (Fedorka, et al., 2013). As a major advantage of fly ash for the construction industry is the CO_2 reduction compared to Portland cement alone, producing CO_2 during beneficiation would result in a higher embodied CO_2 for recovered fly ash, potentially making it a less attractive addition for use in concrete. Similarly, any NO_x produced would have to be managed. For these reasons oxidation may not be suitable as a large-scale carbon removal system, unless specially designed with the coal power station to recycle heat and pollutants like the STAR Process (Fedorka, et al., 2015).

The alternative to oxidation is electrostatic separation, which exploits the difference in surface charge between fly ash and carbon to separate the two. When tribo-electrostatically charged by frictional contact with a charging surface, fly ash particles take on a negative surface charge and carbon a positive charge (Zhang, et al., 2012). The charged particles then pass electromagnetically charged plates, one positive and one negative, at a potential difference of 50 kV. As the particles pass these plates, they are attracted to that of opposite charge and hence are separated. Dry fly ash particles are attracted to the positive plate and unburned carbon to the negative plate. This allows the two to be separated with a reasonably high efficiency and throughput (Bittner, et al., 2009).

While electrostatic separation must be carried out on dry material, as fly ash and unburned carbon cannot be charged and separated in wet form due to cohesion forces. Research carried out on electrostatic carbon removal of wet-stored fly ash after drying has found that a charge reversal occurs, with fly ash taking on a negative charge and unburned carbon positive (Cangialosi, et al., 2005). The two materials could still be separated effectively but were collected at opposite electrodes (Baker, et al., 2014).

6.7. Combined systems

Processing systems can also be combined, such as drying and particle size reduction, where the natural agitation and exposure of new surface area caused by grinding, also improves the effectiveness of the drying stage (Kudra & Mujumdar, 2006). Whether beneficiation systems can be combined to reduce the number of processing stages will depend on the level of beneficiation required by wet-stored fly ash. Some wet materials may require little particle size reduction, screening or carbon removal, while others which may require extensive processing to meet EN 450-1 requirements.

6.8. Summary

Wet-storage causes several changes to both the physical and chemical properties of fly ash. Physically, cohesive forces form between moist particles which then give way to chemical reactions causing agglomeration of fly ash particles. This is observed as an increase in particle size and affects the finest fly ash particles giving a loss of these in the material. Agglomeration also causes an increase in water requirement due to coarsening of the material. Chemically, there is little change observed in oxide composition and mineralogy, although, the formation of calcium sulfate products such as bassanite and ettringite were found in wet-stored materials, suggesting reactions occur. Little reduction in concrete strength was seen up to 28-days in wet-stored fly ash when compared to dry material, with greater differences observed after 56-days.

Most current beneficiation systems for dry fly ash can be adopted for use with wet-stored material, providing a drying stage is implemented before further processing. The most suitable beneficiation systems are a form of drying combined with particle size reduction and carbon removal, as necessary. The characteristics of the feed wet-stored material, the required technical performance of the output fly ash and the economic viability of recovery will be likely to control the processes selected.

7. Experimental Details

7.1. Materials

7.1.1. Portland cement, aggregates and admixture

The cement used throughout the project was a CEM1, strength class 52.5 N, Portland cement (PC) conforming to EN 197-1 (BSI, 2011). The mineralogical, oxide composition and particle size distribution data of the PC are shown in Appendix A, Table 2 and Figure 1. The aggregates used during concrete mixing were 4/10 mm and 10/20 mm natural uncrushed gravel aggregate, supplied locally from Fife, Scotland. The properties of these are shown in Table 3, along with the two medium grade sands used during the study.

To achieve the desired consistence (slump), at fixed water content, of the concrete mix, Glenium 51 polycarboxlylic ether superplasticizer admixture was used (BSI, 2012).

When mixing mortar, the same PC was used in conjunction with standard sand in accordance with EN 196-1 (BSI, 2011).

7.1.2. Dry Fly Ash

The main characteristics of the dry fly ashes obtained from the U.K. are given in Table 4.

7.1.3. On-site wet-stored Fly Ash

The main characteristics of on-site wet-stored fly ash materials from the U.K. and Germany are shown in Table 5, for stockpiled material, and Table 6, for lagoon material.

7.2. Laboratory wet-storage of fly ash

Dry fly ash materials were moistened and stored in a controlled laboratory environment for up to 24 months. Water was added at either 10, 15 or 20 % by dry mass before being mixed in 2 kg batches using a Creteangle Multi-Flow 14 litre pan mixer for 4 minutes and hand mixing with a metal paddle thereafter to ensure homogeneity and remove material from the drum walls. The wet material was then sealed in plastic bags, inside sealed plastic containers before being placed into a controlled exposure environmental chamber of 20 ± 2°C at 65 ± 5 % relative humidity. Small samples of this wet-stored fly ash were taken at 1 day, 7 days, 1 month and 3 months for characterisation. Larger samples of between 5 – 10 kg were taken at 6 months and 24 months for further characterisation, beneficiation and use in concrete.

Once sampled, all laboratory wet-stored fly ash was oven dried for 24 hours at 105 ± 5°C, to determine moisture content and bagged for future use to prevent re-ingress of moisture from the surroundings. All testing and processing was conducted on the material after oven drying.

7.3. Laboratory Processing

Both, on-site and laboratory wet-stored materials were beneficiated at a laboratory-scale using various processing techniques. These were divided into three main categories depending on the mechanism of beneficiation; particle size separation by sieving, particle size reduction by grinding, and carbon removal by oxidation.

7.3.1. Sieving

Selected fly ash materials were screened at 600 μm as a precursor to further beneficiation, such as, grinding or carbon removal, to reduce the variability of the wet-stored materials by removing the largest agglomerates.

Screening at 600 μm was achieved by brushing wet-stored fly ash through a standard 600 μm mesh in a slow rotational motion. This was found to be the most effective way of preventing mesh blocking, giving the fastest throughput, while also minimising dusting. It should be noted that no crushing force was applied when screening to force agglomerates through the mesh, by breaking them against the screen. This was to remove agglomerated material greater than 600 μm and allow particle size separation to be evaluated independently of particle size reduction as far as practically possible.

Screening at 63 μm was also evaluated by hand-sieving in the same manner. Due to low yields and throughput, only small quantities of <63 μm material could be obtained in a reasonable time-scale. Therefore, only a limited number of materials screened at 63 μm were characterised and tested in concrete.

7.3.2. Grinding

Particle size reduction was carried out using a ball or micronising mill. The ball mill was a Fritsch Pulverisette laboratory ball mill, using 20 mm diameter hardened stainless steel balls as the grinding medium in 2 x 250 ml drums. This ball mill uses a planetary system to grind material by both impact and friction between the balls and the interior walls of the drums.

Wet-stored material, in dry form, was initially added unscreened in 125 g batches to each drum for 10 to 40 minutes to establish the optimum grinding duration for maximum throughput, whilst producing material that met EN 450-1 (BSI, 2012) for Category S.

Based on an evaluation of this material in concrete, a further investigation using smaller batch sizes of 100 and 50 g after screening at 600 μm, with selective wet-stored material was conducted. Grinding in 50 g batches gave the highest degree of particle size reduction for a given duration, although, several batches were required to produce sufficient quantities for use in concrete.

An example of the labelling system used for the grinding variables was as follows: **SFA 1 < 600 μm BM 120 50 g.** This denotes that the on-site, wet-stored (**SFA**) fly ash SFA 1 had been screened at 600 μm (**<600 μm**) and ground for 120 minutes (**BM120**) in the ball mill using batches of 50 g.

A limited amount of grinding was also conducted in the laboratory using a 150 mm diameter Atritor micronising spiral jet mill. This system uses two airflows to create vortex conditions inside the mill, wherein, fly ash particles collide and breakdown by inter-particle abrasion. When in the mill, material is split by air-classification between fine particles, which travel towards the centre of the vortex and coarse particles which remain on the outside. The fine particles in the centre are discharged downwards towards a vessel by gravity as the vortex forces weaken in the centre for collection. The coarse particles remain in the vortex and continue to be subject to inter-particle collisions until fine enough to be move to the centre of the mill and be discharged. The effectiveness of this system is dependent on the input air pressure and material feed rate, with greater raw material to input air ratios increasing throughput, but decreasing the degree of grinding and vice-versa.

Issues arose when using this system in the laboratory, the most significant of which was a loss of <10 μm material which became trapped in the exhaust gases, travelling vertically upwards to the exhaust filter, rather than falling into the collection vessel at the base of the system. Much smaller increases in fineness were achieved than expected due to this loss of fine particles. Therefore, only small quantities of fly ash were beneficiated using this system in the laboratory. Material ground in the spiral jet mill microniser is denoted as SJM, for example **SFA 1 SJM** was on-site, wet-stored material SFA 1 passed through the mill a single time.

A larger version of this system was used to beneficiate fly ash successfully during the pilot-scale trial which is discussed in the 'Pilot-scale processing' section of this report.

7.3.3. Carbon Removal

Carbon removal was carried out in the laboratory by oxidation using a Carbonlite OAF laboratory furnace. Initial tests were conducted at temperatures ranging from 500 – 700 °C at durations of 45 minutes to 4 hours to find suitable conditions for carbon removal. These tests identified that 500°C for an hour was adequate to reduce the LOI of fly ash to meet EN 450-1 in most materials. Due to practical limitations of the furnace, batches of fly ash materials could not be inserted and removed from the furnace while it was at the burning temperature. Therefore, materials were placed into the furnace and allowed to reach temperature before timing was started. When the heating duration was over, the furnace was turned off and the door opened to cool the fly ash within the furnace. As a result, materials heated in the furnace for a stated 1 hour, are likely to have been exposed to high temperature for slightly longer, while the furnace reached the burning temperature and cooled. A chart showing the time taken for the furnace to reach and subsequently cool from 950°C is given in Figure 2. Once the metal container had reached <200°C, the material and container could be removed from the furnace safely using oven gloves to allow more rapid cooling outside the furnace.

Wet-stored materials were screened at 600 μm before oxidation in the furnace, for ease of handling and to increase the exposed surface area and improve oxidation. Fly ash was heat treated in batches of between 400 - 500 g, giving a material depth in the container of around 15 mm, i.e. the minimum depth that still gave a reasonable throughput.

The labelling system used to for carbon removal was as follows: **SFA 1 <600 μm 500°C/1 hr H&C.** This denotes the on-site, wet-stored material SFA 1 that has been screened at 600 μm, then placed in the furnace for 1 hour at 500°C, while also allowed to heat and cool in the furnace.

7.3.4. Mix proportions

The mix proportions of the concretes described in the report are shown in Table 7, at 0.5 w/c used from September 2014 until May 2016 for materials laboratory wet-stored, screened at 63 µm and ball milled in 125 g batches. After May 2016 a change in laboratory sand necessitated a change in mix proportions to those outlined in Table 8, at 0.53 w/c, for materials ball milled in 50 g batches, screened at 600 µm, undergone carbon removal and the pilot scale-processing materials.

Selected mixes of the pilot-scale processed materials used the mix proportions outlined in Table 8 but had adjusted w/c ratios, achieved by reducing the water content to reach higher concrete strengths, whilst still reaching S3 slump.

7.3.5. Mixing

Concrete was mixed in the laboratory in accordance with BS 1881-125 (BSI, 2013), using a Croker Cumflow RP50XD 35 litre rotating pan mixer.

7.3.6. Curing

Concrete samples were stored under damp hessian/polythene sheeting for 24 hours immediately after being cast. After 24 hours, these were demoulded, and the concrete placed in water baths at 20 ± 2°C (BSI, 2009), until required for testing.

7.4. Test Methods

The properties described in this section were determined using test methods given in appropriate British/European Standards, or following established techniques at the University of Dundee. A summary of the methods used during the study is given in Table 9.

7.4.1. Fineness

Fineness was measured using the 45 µm sieve retention test specified in EN 451-2 (BSI, 2017). Fly ash samples of 1 g were screened under a water pressure of 80 ± 5 kPa for 60 ± 10 seconds. The retained material was then oven dried at 105 ± 5 °C until at constant mass and the percentage retained calculated. The Standard specifies the mean of at least two test results within 0.3% should be taken as the fineness value.

Whilst the maximum range of 0.3 % for fineness was generally obtained for dry fly ash within four tests, the range of results obtained for wet-stored material could be up to 25 %, between minimum and maximum values. Therefore, obtaining results which met the 0.3 % requirement proved to be impractical. Additionally, some wet-stored materials could return more than one group of test results within 0.3 %, with significantly different means. An example of this is given in Table 10 for SFA 1. According to EN 450-1, the fineness of this material could be either 49.0 or 58.2 %. Therefore, an overall mean of the sieve retention values, omitting outliers that differed significantly from the other values recorded, was taken as the material fineness, with the minimum and maximum values obtained for each material also reported, as shown in Table 10. Typically, six tests were required before minimum, maximum and mean values could be established.

Wet-stored materials that had undergone beneficiation, such as screening or grinding, were generally found to meet the 0.3 % limit, and therefore, the fineness of these were reported as outlined in EN 451-2.

7.4.2. Particle size distribution

Particle size distributions of materials were found by laser diffraction using a Malvern Mastersizer 2000 LASER particle size analyser. This system measures the deflection of light scatter off particles, which range from small angles for large particles to large angles from small particles. The data generated is then used with Mie theory of light scattering to calculate the overall particle size distribution.

Small quantities of fly ash were added to a dispersant, in this case water, and subject to ultrasonic displacement for 2 minutes. The ultrasonic displacement aides the dispersal of fly ash but also influences the particle size of wet-stored material by causing some de-agglomeration, which results in smaller particle sizes recorded. However, ultrasonic displacement is required to prevent excessive variation between tests.

Five measurements of each material were taken to create an average and allow outlying results to be identified. Malvern software was then used to compute the particle size distribution, d_{10}, d_{50} and d_{90} of the tested material.

7.4.3. Loss-on-ignition

Loss-on-ignition was evaluated using the chemical test for cement, EN 196-2 (BSI, 2013) with the method modified as described in EN 450-1, with a 1-hour ignition time. Oven dried fly ash samples of 1.00 ± 0.05 g were weighed into crucibles and placed in the furnace at 950 ± 25 °C for 1 hour. The crucibles were then allowed to cool before the mass of fly ash after ignition was measured, and the change in mass and LOI determined.

7.4.1. Bulk oxide composition

Bulk oxide composition was evaluated using a Panalytical Zetium X-ray fluorescence spectrometer. X-ray fluorescence uses high energy, short wavelength radiation to excite the inner electrons of atoms, which become unstable, leaving their orbit to be replaced by an outer electron. This exchange gives off energy in the form of fluorescent radiation, of which each atom will produce a unique amount. Measurement of this radiation allows identification of the type and quantity of atoms present, given as an oxide content.

Samples were oven dried prior to testing and mixed by mortar and pestle with a small amount of Movoil, used as a binding agent. These were compacted in a press at 75 kPa for 10 minutes and 150 kPa for a further 10 minutes, to provide a smooth surface for testing. Samples could then be placed into the x-ray fluorescence spectrometer and tested.

7.4.2. Mineralogical composition

The mineralogical composition of the fly ash materials was evaluated by X-ray diffraction using a SIEMENS X-Ray Diffractometer D5000. This uses the pattern produced by diffraction of X-rays through closely spaced lattices of atoms in crystalline structures, to produce peaks at angles between 3 to 60 degrees 2θ. This information is then used to identify crystalline phases present, based on knowledge of the material and known diffraction angles of mineral phases. The inclusion of 5%, by mass, of corundum, Al_2O_3, allows the percentage composition of mineral phases to be identified and calculated using Rietveld analysis.

Fly ash was oven dried and mixed in a mortar and pestle with corundum, then compacted on to a plastic slide to obtain a uniform, flat surface for testing. X-ray diffraction is conducted on sample surfaces, so care was taken when preparing the samples to avoid surface irregularities that would affect results.

7.4.3. Morphology

The morphology of selected fly ash samples was investigated using scanning electron microscopy (S.E.M.). This system scans samples with a concentrated beam of electrons, producing signals that are returned from the sample in a raster scan pattern, which is used to build up an image of the sample surface.

Samples were coated in a palladium – gold (Pd-Au) layer to prevent charging during analysis, which enables better image quality at greater magnifications.

7.4.4. Water requirement

Water requirement of fly ash was evaluated using the method outlined in EN 450-1 Annex B (BSI, 2012) and the mortar mixing procedure in EN 196-1 (BSI, 2005).

Mortars using 30% replacement of fly ash were mixed at an initial w/c ratio of 0.5 and the flow compared to that of a PC only reference of equal mix proportions (BSI, 2005). The w/c ratio of the fly ash mix was then increased or decreased to match the reference mortar flow within ±10 mm. This water content was then used to find the water requirement for the fly ash as a percentage of the reference mortar.

7.4.5. Activity index

The activity index of fly ash materials was evaluated on mortar prepared following the mixing procedure outlined in EN 196-1 (BSI, 2005), at 0.5 w/c ratio using 52.5 N PC at a 25 % fly ash level in cement. Mortars were cast into six 40x40x100 mm prisms and cured in a water bath at 20 ± 2°C until testing. The prisms were tested at 28 and 90 days using three per age, split in half to provide 6 test specimens. Measurements were made at a loading rate of 2400 N/s, the compressive strengths recorded, and the average strength at each age found. The maximum acceptable variation between the maximum and minimum strength values should be no greater than 10 % of the mean of all 6 results. If the range exceeds this, an average of the 5 closest results is permitted, providing that the range between the new maximum and minimum values are within 10 % of the new mean.

The mean strength of the fly ash mortar was then given as a percentage of the reference PC mortar, which is the activity index of the fly ash at each test age. Fly ash is deemed to satisfy the EN 450-1 requirements if activity index is ≥ 75 % at 28 days and ≥ 85 % at 90 days (BSI, 2012).

7.4.6. Specific surface area by nitrogen adsorption

Specific surface area, by nitrogen adsorption, was evaluated using a Quantachrome NOVA 3000e Surface Area & Pore Size Analyzer. Fly ash samples were oven dried and placed in test cells in quantities of 3 – 5g, recorded to 0.001 g. These were then de-gassed and heated in the instrument for a minimum of 4 hours at 105 ± 5°C, plugged with glass rods and transferred to the nitrogen adsorption terminals of the instrument. Samples were then exposed to nitrogen, whilst the cells were immersed in liquid nitrogen, to obtain the nitrogen adsorption and desorption curves. The surface area, in m^2/g, could then be calculated from the maximum nitrogen adsorption and sample mass.

7.4.7. Foam index

The foam index test was used to estimate the air-entraining agent (AEA) requirement of fly ash. A 2 g mass of fly ash and 8 g of Portland cement were mixed with 25 ml of distilled water for 50 seconds using a standardised system outlined in Gao *et al* (1997). The AEA, Sodium dodecyl benzene sulfonic acid, was added in 20 µl increments and the mixture shaken for 25 s, after each addition, in a IKA MS3 digital vortex mixer. After each increment of AEA and shaking, the mixture surface was observed and if a stable foam was maintained for 45 s then the total AEA dose was recorded and the test finished. If the foam collapsed during the 45 s, additional increments of air-entrainment were added, and the procedure repeated until a stable foam maintained for 45 s. The foam index of each fly ash is expressed as the AEA dose required to satisfy the test in ml.

7.4.8. Thermo-gravimetric analysis

Thermo-gravimetric analysis was conducted using a Netzsch STA 409 instrument. Samples were heated to 950°C in a nitrogen rich environment, to prevent oxidation, and the mass loss during heating recorded. Mass loss observed at specific temperatures enabled identification of dehydration and decomposition occurring and the nature of products present. These were identified using a database of dehydration and decomposition curves for various common minerals (Foldvari, 2011).

7.4.9. Carbon content

Selective fly ash materials were sent to STEAG Building Materials Laboratory, Galbeck, Germany, to be measured for carbon content using LECO analysis from CO_2 evolved during oxidation in a furnace at 1450 °C by infrared detectors.

7.5. Concrete

7.5.1. Consistence

The consistence of concrete was assessed using the slump test described in EN 12350-2 (BSI, 2009). A dampened slump cone was filled with freshly produced concrete in three layers and tamped using a metal rod of 16 mm diameter and 600 mm length, 25 times after the first and second layer. The final layer was tamped 15 times, topped up with concrete and tamped a final 10 times. The slump cone was then removed, and the difference in height from the top of the slump cone to the top of the concrete recorded as the slump to the nearest 5 mm. All concrete mixes discussed in this report had a target slump class of S3, 100 – 150 mm.

7.5.2. Sample Preparation

Concrete cubes of 100 mm in size were prepared in accordance with EN 12390-1 (BSI, 2012). Moulds were oiled before use and filled in two equal layers of concrete, with each compacted on a vibrating table, specified EN 12390-2 (BSI, 2009). Excess concrete from the top layer was removed and smoothed using a steel float.

Samples were then placed under damp hessian for 24 hours before being demoulded and water cured at 20 ± 2°C until testing.

7.5.3. Compressive strength

Compressive strength testing of the concrete cubes was carried out in accordance with EN 12390-3 (BSI, 2009) using a cube testing machine meeting EN 12390-4 requirements (BSI, 2000).

7.5.4. Carbonation

Selected fly ashes were tested in concrete under the accelerated carbonation conditions outlined in BS 1881-210 (BSI, 2012). Concrete specimens were cast, into 2 prisms of 100x100x500 mm, and cured as described previously for 100 mm cubes. At 28 days, the specimens were removed, air-dried for 14 days in the laboratory, and sealed on two opposing faces with paraffin wax, to prevent ingress of CO_2. These prisms were then placed in a carbonation chamber at 4.0 ± 0.5 % CO_2, 55 ± 5 % relative humidity and 20 ± 2°C temperature for up to 10 weeks. Sections of the prisms were broken off after 1 week, 2 weeks, then every 2 weeks thereafter up to 10 weeks and sprayed with phenolphthalein indicator. Measurements were taken with digital callipers at 10 points per prism, 5 from each unsealed prism face, to the point of carbonation ingress, marked by the indicator colour change. The mean of these 20 results was taken as the depth of carbonation at each test age.

7.5.5. Chloride diffusion

Selected fly ash materials were tested for chloride diffusion resistance in concrete using the accelerated chloride ingress test, outlined in EN 12390-11 (BSI, 2015) (NT Build, 1999). Concrete specimens were cast into two 100 mm cubes and cured for 28-days as outlined previously. These were then sliced at a depth of 75 mm, parallel to the cast face, sealed in wax on all sides except the exposed cut face, and placed into a 3 % sodium chloride solution for 90 days. After 90 days exposure, the cubes were removed and allowed to air dry before being cut in half, perpendicular to the exposed face. The newly cut faces were sprayed with 0.1 M silver nitrate solution and the depth of chloride penetration measured from the exposed face in 10 mm increments along the cube as outlined in NT BUILD 492 (NT Build, 1999). The average chloride ingress depth for both cubes could then be found.

While the procedure for the evaluation of chlorides ingress was initially to be conducted in accordance with EN 12390-11, practical limitations prevented the layered grinding of the exposed cubes required for the test. The NT BUILD 492 method for assessing chloride provided a general comparison between fly ash concretes.

8. Wet-storage

8.1. Wet-storage effects

To investigate the effects of wet-storage, various dry materials were moistened and stored in the laboratory. Most of these materials were wet-stored for up to 24 months, however, due to time limitations DFA 6 and DFA 8 were wet-stored for only 6 months. The results of the other wet-stored materials indicate that little change occurs in wet-stored material between 6 and 24 months, with much of the physical and chemical effects occurring in the first few months of storage.

The influence of laboratory wet-storage on the characteristics of fly ash are examined in the sub-sections below for the materials outlined in Table 12.

8.1.1. Moisture content

The change in moisture content with storage duration for laboratory wet-stored materials are shown in Figure 3 to 8. These show a decrease in log scale moisture content as storage duration increases, with large reductions seen up to 30 days and a more gradual decrease thereafter. In some cases, higher moisture contents were recorded at later storage ages, which is likely to be due to material variability.

The moisture loss up to 30 days was not attributed to evaporation as these materials were sealed in air-tight bags and buckets in a controlled environmental chamber at 20°C and 65 % relative humidity to limit evaporation, as far as practical. Therefore, the reduction in moisture content at early storage ages, suggests water is quickly bound within fly ash, and is not removed during drying at 105°C. This suggests a reaction is taking place between elements within the fly ash and water during wet-storage. The mechanism of this reaction could not be determined with certainty during this project.

8.1.2. Particle size

Effect of moisture content

The change in particle size with storage duration for each laboratory wet-stored material is given in Figure 9 to 14 for 45 µm sieve retention and Figure 23 to 28 for the quantity of <10 µm particles. These figures are shown on a log scale for clarity between storage durations and include R^2 values giving the correlation for each material and age.

The effect of the initial moisture content on the rate of change of particle size is shown in Figure 11 for DFA 4 and Figure 12 for DFA 5 wet-stored at 10, 15 and 20 %. The rate of agglomeration was found to be higher with increased initial moisture content, suggesting that at lower moisture contents of 10%, water availability may be limiting agglomeration. Although, these differences were generally small and may have been due to material variability within wet-stored fly ash.

Fineness

The change in 45 µm sieve retention with storage duration are shown on a log scale in Figure 9 to 14. These show the mean fineness result as well as the maximum and minimum values of the materials with storage age, given as error bars to illustrate the variability of the material.

Fly ash becomes cohesive when mixed with water, even at low moisture contents (McCarthy, et al., 1999). When wet-stored, this cohesion gives way to agglomeration of fly ash particles, which remain after oven drying removes free water. All laboratory wet-stored material evaluated showed signs of agglomeration, observed as an increase in particle size. Figure 9 indicates the increase in fineness due to agglomeration of DFA 1 LS 10% (laboratory wet-stored with an initial moisture content of 10%). The rate at which agglomeration occurred varied between materials, as shown in Table 13 which gives the logarithmic gradient of increasing particle size with storage duration. However, in each case the most significant increases in fineness occurred in the first month of wet-storage, with further increases at a slower rate.

Particle size distribution

The changes in particle size distribution with laboratory wet-storage duration are given in Figure 15 to 21. The laboratory stored materials, except DFA 6 and DFA 8, had volumes of <10 μm particles of between 10 to 20 % after 6 months storage, irrespective of the volume of dry <10 μm particles. Particle size distribution data obtained by laser diffraction shows a decrease in the volume of particles <10 μm, and a corresponding increase in those between 10 to 100 μm, as storage duration increases. Changes in particles greater than 100 μm were not consistently observed, although agglomerates of this size or greater were noted in the material.

This may be due to the ultrasonic displacement applied before laser diffraction, to aid particle dispersal, causing agglomerates to break down reducing the particle size, or agglomerates settling within the dispersal media and not being evaluated.

As noted during fineness testing, variability within samples should also be considered. While ultrasonic displacement before testing reduced variability before laser diffraction, the particle size distribution may also change depending on the sample location within the wet-stored material. These samples were taken, after oven drying, from around 1 kg of wet-stored material up to 6 months and 5+ kg after 6 months. Variability in particle size distribution test results were seen in both laboratory and on-site wet-stored materials, an example of this is given for SFA 2 in Table 18 and Figure 22 which show the difference in d_{10}, d_{50}, d_{90} and particle distribution of three sample of SFA 2. Therefore, the particle size distributions given should be considered as indicative for each material.

Quantity of <10 μm particles

The change in quantity of <10 μm particles with storage duration for the laboratory wet-stored materials are given in Figure 23 to 28. These show the fine fly ash particles rapidly agglomerate, either with other fine particles, or the surfaces of larger particles, probably reflecting their high available surface areas. Once a large proportion of these fine particles have agglomerated, the rate of agglomeration slows due to the reduction in surface area for the formation of reaction products. This usually occurs after 6 months storage, although, in materials with a high quantity of <10 μm particles such as DFA 3, Figure 24, this can happen more rapidly.

The volume of fine particles in the dry material was found to be an influencing factor on the rate of agglomeration, but not necessarily the ultimate degree of agglomeration. Of the materials laboratory wet-stored, DFA 3 saw the largest reduction in quantity of <10 μm particles, but did not have the highest 45 μm sieve retention after 24 months. In comparison, DFA 1 had a low quantity of <10 μm particles and agglomerated at a much slower rate, but reached a higher 45 μm sieve retention after 24 months. This suggests that while <10 μm particles agglomerate most readily, this also occurs with larger particles but at a slower rate.

8.1.3. Carbon

Loss-on-ignition

Figure 29 to 34 show the change in loss-on-ignition (LOI) with storage duration. Laboratory wet-stored materials typically experienced an increase in LOI of 0.3 – 1.5 % in the first 7-days of wet-storage. This change is unlikely to occur due to an increase in unburned carbon present, as laboratory stored materials were sealed to prevent ingress of CO_2 during wet-storage.

The increase in LOI observed is likely to be the result of moisture bound in the fly ash during wet-storage and corresponds to the reductions in moisture content observed during early wet-storage tests. The reduction in moisture content and increase in LOI suggest that while physical cohesion occurs initially, there follows chemical reaction between moisture and fly ash. This bound water is not removed during typical oven drying at 105°C, but does during LOI testing at 950°C, resulting in higher LOI values being recorded.

The increase in LOI did not uniformly increase with storage duration, shown in Figure 29 for DFA 1, which gave decreases at 7 days and 6 months storage. These are likely to represent variability within the wet-stored materials, as seen in the 45 µm sieve retention results.

Carbon content

Figure 35 gives the results of CO_2 evolution testing of DFA 1, DFA 3 and DFA 5 before and after 6 months wet-storage. These confirm that no change in actual carbon content occurred as a result of wet-storage and any increase in LOI is component changes in the material other than carbon.

8.1.4. Morphology

S.E.M Images

S.E.M. images of DFA 1, DFA 3 and DFA 5 before and after wet-storage are given in Figure 36 to 48. DFA 5 before and after 24 months wet-storage is shown in Figure 47 and 48, as an example. The fly ash particle surfaces have become rougher, due to the formation of surface products, as observed by McCarthy *et al* (1999) who referred to this as 'furring'. These surface products are likely to be involved in agglomeration and appear to hold particles together, after oven drying removes any cohesion forces. These can be seen to form between groups of small particles giving larger agglomerates, or between small particles and the surfaces of large particles.

CT scan

Figure 49 shows a cross-section of a small agglomerate of around 4 mm in diameter of DFA 5 after laboratory wet-storage for 24 months. The white areas indicate solid fly ash particles, while grey areas show particles or reaction products formed during wet-storage, and black areas are voids between particles. Some of these are internal within large hollow fly ash particles, indicated by their circular shape and grey or white perimeter outline. However, many are voids created between fly ash particles during agglomeration, which exist in a wide range of sizes and are distributed throughout the whole agglomerate.

The presence of these voids is likely to be a contributing factor to the increased water requirement of wet-stored fly ash, as water may be absorbed within the agglomerate and unable to lubricate particles. These also influence the overall w/c ratio by reducing the available water within a cementitious mix, which may also result in higher strengths at the expense of consistence.

8.1.5. Water requirement

Figure 50 shows the change in water requirement of DFA 1, 3 and 5 after 6 months' wet-storage at 10 % initial moisture content. None of the dry materials satisfied EN 450-1 Category S requirements of <95 % prior to wet-storage, with water requirements of 97 to 104 %. The water requirement of the laboratory wet-stored materials increased to similar levels to those of the on-site wet-stored materials given in Table 16. Increases of 3 to 13 % were seen compared to the initial dry materials, giving water requirements after 6 months storage of between 107 to 110 %. This increase was attributed to agglomeration creating voids between particles as seen in Figure 49 and an increased quantity of coarse, angular particles.

8.1.6. Air-entrainment

Foam index test

Figure 51 shows the change in air-entraining admixture (AEA) requirement during the foam index test with storage duration, for DFA 1, DFA 3 and DFA 6. The AEA required to achieve a stable foam was found to decrease as wet-storage duration increased. For some materials, this occurred after just 1 day of wet-storage, however, it was more commonly seen after 7 days to 1 month. Material with the highest initial AEA requirement, usually a result of a high unburned carbon content, saw the greatest decrease in AEA requirement after wet-storage.

The decrease in AEA requirement did not consistently correlate to other characteristics of the laboratory wet-stored materials such as fineness, quantity of <10 μm particles, LOI or specific surface area by nitrogen adsorption, given in Figure 52 to 55 respectively. Of these, AEA requirement correlated best to fineness and specific surface area by nitrogen adsorption.

The quantity of unburned carbon has the largest influence on the AEA demand of fly ash. Unburned carbon adsorbs AEA, reducing the quantity and stability of air-bubbles that form, increasing the dose required. As there is no change in unburned carbon content during laboratory wet-storage, the decrease in AEA requirement cannot be due to this. It must therefore occur due to a change in interaction between carbon and AEA.

This is likely to be due to a change in polarity of the surface of unburned carbon during wet-storage from non-polar to polar. Directly from the power station, unburned carbon in fly ash is non-polar, therefore, attracting the polar end of AEA molecules (Hachmann, et al., 1998). As it is the polar end of the AEA molecule that facilitates the formation of air bubbles, any adsorbed by the carbon cannot be used to entrain air. When the carbon becomes wet, the surfaces exchange electrons with water and become polar (Menendez, 2014). This means, when AEA is introduced to fly ash, the carbon particles now repel the polar end of the molecules reducing the quantity of AEA lost to the carbon and decreasing the dose required to form stable air bubbles.

Air-entrainment of mortar

Figure 56 gives a comparison of the air content of mortars of DFA 1, DFA 3, DFA 6 and DFA 8 before and after wet-storage. After wet-storage, higher air-contents were reached at equivalent AEA doses than before wet-storage. This shows the decrease in AEA requirement observed during the foam index test also occurs in mortar.

Specific surface area

Specific surface area measured by B.E.T., of the laboratory wet-stored materials increased with storage duration shown on a logarithmic scale in Figure 57 to 62 and generally with particle size shown in Figure 63 to 71.

The specific surface area of fly ash was expected to remain unchanged after wet-storage, as nitrogen adsorption is heavily influenced by the quantity of unburned carbon which remained unchanged. However, wet-storage was found to cause a significant increase in specific surface area which increased with storage duration. This is likely to be a result of voids formed within agglomerates, as seen in the CT scan given in Figure 49, absorbing nitrogen. This gives an insight into the unstructured and porous nature of wet-stored fly ash agglomerates, which for DFA 3 shown in Figure 58 increased the specific surface area (by B.E.T.) by a factor of 3 after 24 months laboratory wet-storage.

8.1.7. Activity index

The change in reactivity with storage duration for the laboratory wet-stored materials is given in Figure 72 to 78. Reactivity was found to generally decrease linearly on a logarithmic scale with storage duration, although, due to material variability higher activity index values were sometimes seen at later storage durations.

Fineness and activity index

Comparing reactivity to 45 μm sieve retention in Figure 79 for all materials before and after laboratory wet-storage indicates a statistically significant relationship at both 28 and 90 days. However, in satisfying a 95% confidence interval, the correlation factor was low (R^2 <0.5). Wet-stored fly ash appears to follow the trend of reduced activity index with increasing particle size, however, there is greater variability. EN 450-1 requirements for activity index, at 28 and 90 days, and 45 μm sieve retention for Category N fly ash are also given in Figure 79 to show the number of materials that met these requirements. All dry materials met fineness and reactivity requirements before wet-storage, showing that a loss of reactivity occurs during wet-storage and some form of beneficiation would be required to meet EN 450-1.

While a general trend was seen for all laboratory wet-stored materials collectively, comparing particle size and activity index of each dry fly ash separately typically gave stronger correlations.

37

Figure 80 to 86 show the relationship between fineness and activity index for each of the laboratory wet-stored materials. Wet-storage had the greatest effect on the property at 28-days, giving higher percentage differences between the dry and laboratory wet-stored material results at this age. Wet-storage had less of an effect at 90-days, where the difference in activity index was smaller than seen at 28-days. This suggests that wet-storage affects the rate of pozzolanic reaction, explained by the loss of <10 μm particles due to agglomeration. Which mainly involves fine particles, reducing available surface area for pozzolanic reaction, reducing the rate of reaction.

Quantity of <10 μm particles and activity index

Figure 87 shows the relationship between the quantity of <10 μm particles and activity index for the laboratory wet-stored materials collectively and Figure 88 to 94 which give this separately for each material. These show the trends as observed with fineness, although, with generally stronger correlations.

8.1.8. Bulk oxide composition

The bulk oxide composition of DFA 4 during laboratory wet-storage at 20% moisture is given in Table 14 as an example.

The bulk oxide composition of the laboratory wet-stored materials remained largely unchanged during wet-storage. Small variations were observed in the main oxides of SiO_2, Al_2O_3 and Fe_2O_3, which is likely to be due to a combination of test and material variability. Some minor oxides such as soluble SO_3 did change between storage ages, possibly reflecting variability, due to surfaces rich in calcium or alkali sulfates. Differences in this region may also explain the variation observed in the main bulk oxides of SiO_2, Al_2O_3 and Fe_2O_3, where a higher quantity of SO_3 on the surface obscured the presence of other oxides.

The only oxide limit of EN 450-1 that wet-stored materials frequently failed to meet was a maximum of 3.0% SO_3, which may be due to their increased surface concentrations as discussed above.

8.1.9. Mineralogy

X-ray diffraction results for DFA 4 during laboratory wet-storage at 10% moisture are given in Table 15 and Figure 95 as an example.

A comparison between XRD data of dry and wet-stored material shows little difference in peak locations, implying there is little change in the materials with wet-storage. Although, the volumes of the minerals identified by Rietveld analysis were found to vary, there were no identifiable trends. This suggests that the effects observed were a result of test and sample variations, rather than changes due to wet-storage. Differences in volume between storage ages observed are likely to result from errors during Rietveld refinement, such as shifts in diffraction angle between samples, or errors in the quantity of 5% reference corundum. This may have led to the composition being inaccurately calculated, although, every effort was taken to reduce these errors.

8.1.10. Concrete

Materials were tested in concrete after 6 months laboratory wet-storage, using the mix proportions outlined in Table 7. These materials were used 'as recovered' without any screening or beneficiation and compared to dry fly ash to evaluate the changes in concrete performance.

Fresh properties

Laboratory wet-storage generally increased SP dose required to achieve an S£ slump, shown in Figure 96 as superplasticizer dose per kg of cement. Mirroring the trends of the water requirement test results, admixture doses increased after wet-storage. This is to be due to agglomeration, which may have several detrimental effects on consistence. Agglomeration will; reduce the volume of fine particles leaving fewer fine particles to displace water between coarse aggregates, cause a roughening of particle surfaces due to product formation reducing the lubricating effect of the fly ash and lead to the formation of voids which absorb water reducing consistence.

The superplasticizing admixture demand generally increased with both particle size and LOI shown in Figure 97 to 98, however, no distinct trends could be identified.

Cube strength

The change in hardened concrete strength after 6 months wet-storage is given in Figure 99 to 104 for DFA 1, DFA 3, DFA 4 and DFA 5.

A reduction in strength occurred after wet-storage, with differences generally increasing with concrete age and were between 1 and 6 MPa in all materials except DFA 3, which saw reductions of between 6 and 15 MPa. These results suggest that most wet-stored material could still achieve comparable concrete strength to that of a Category N dry material, except for DFA 3.

The large loss of compressive strength was seen in DFA 3, due to a significant loss of <10 μm particles (62 % to 13 % after 6 months storage). In comparison, the other dry materials had volumes of <10 μm particles of 24 to 30 % which decreased to 13 to 20 % after 6 months wet-storage, and therefore, less reduction in strength.

The change in 28-day concrete strength, compared to the loss in <10 μm particles due to wet-storage, is given in Figure 105. This shows the relationship between the reduction of <10 μm particles and concrete strength and is similar to that observed for activity index in Figure 87 to 94, where a decrease in volume of <10 μm particles resulted in reduced reactivity.

8.2. On-site wet-storage

A summary of the characteristics of the on-site, wet-stored materials is given in Table 16 and discussed in the following sections.

Eight on-site wet-stored materials, seven from the U.K. and one from Germany, were evaluated to find the typical characteristics and performance of materials currently available. These were also compared to the laboratory wet-stored materials to check their suitably in replicating on-site conditions.

Laboratory wet-stored materials at 6 months, or longer, were found to have similar characteristics and performance in concrete to on-site wet-stored materials. Both laboratory and on-site wet-stored materials also had a similar degree of variability, most notably in fineness, where individual tests of laboratory wet-stored materials varied by 3 to 17 % at 6 months and by 5 to 25 % for the on-site materials.

8.2.1. Moisture content

The moisture content of the on-site wet-stored materials typically ranged from 10 to 20 %, as shown in Table 16, except SFA 5, which had a moisture content of 6 %. This range of moisture contents confirm the suitability of using 10 to 20 % initial moisture content during laboratory wet-storage to replicate in-situ on-site conditions.

8.2.2. Particle size

Fineness

The fineness results of the on-site wet-stored materials are given in Table 17 and are presented in the same way as the laboratory wet-stored, with the mean, minimum and maximum results shown. On-site wet-stored materials generally had a wide range of 45 μm sieve retention values between tests due to agglomeration, similar to that found for the laboratory wet-stored materials. Of the on-site materials evaluated during this project, none met EN 450-1 Category N requirements for fineness.

Particle size distribution

The particle size distribution data of the on-site materials are given in Figure 106 to 107 and Table 17.

Comparing particle size distributions of DFA 1 wet-stored in the laboratory for 6 months, and SFA 1, an on-site material, in Figure 108, shows similarities between the two. Both have low volumes of <10 μm particles, high concentrations of 10 – 100 μm and a small proportion of >100 μm due to agglomeration.

The particle size distribution data for the on-site materials given in Table 17 typically indicate lower d_{50} values than would be expected from the corresponding 45 μm sieve retention results. This was attributed to the ultrasonic displacement applied before analysis, to disperse the fly ash particles, which may have broken apart some agglomerates reducing particle size. Additionally, agglomerates were often too large to be circulated around the system, settling to the bottom of the dispersal solution. These agglomerates were, therefore, not tested which would also result in a finer material being analysed.

Quantity of <10 μm particles

The quantity of <10 μm particles of the on-site wet-stored materials are given in Table 17. These ranged from 19 to 24 % and were lower than the dry Category N materials evaluated, which ranged from 24 to 31 %. The quantity of <10 μm particles of on-site wet-stored materials were generally similar to those of the laboratory wet-stored materials after 3 months wet-storage.

8.2.3. Carbon

Loss-on-ignition

The loss-on-ignition result of the on-site materials are given in Table 16. These ranged from 3.5 to 15.9 % and were generally greater than 7 %.

Carbon content

To establish the quantity of actual carbon present, selective materials were sent for analysis to STEAG's Building Materials Laboratory, Gladbeck, Germany. This enabled an evaluation of the contribution to LOI values from non-carbon organics. These results, where available, are given in Table 16.

The LOI of on-site material was found to be greater than the carbon content, as found during laboratory wet-storage. The relationship between carbon content and LOI is shown in Figure 109, including a best fit line for dry fly ash materials, DFA, laboratory wet-stored materials, DFA LS, and on-site wet-stored materials, SFA.

These relationships had a gradient greater than 1, indicating that for every 1 % of carbon, slightly more than 1 % was found in the LOI tests. On-site wet-stored materials had the largest difference between LOI and carbon contents, which is likely to be due to the formation of products during agglomeration and carbonation.

8.2.4. Morphology

S.E.M. images

Figure 111 to 116 show S.E.M. images of on-site materials at magnifications of x1000 and x3000. Comparing these to S.E.M. images of dry materials shows the changes to particle surfaces occurring during wet-storage.

Images of DFA 1 and SFA 1, two different fly ash materials from the same power station are shown in Figure 36 and 38. The particle surfaces of SFA 1 are rougher, with large quantities of products present. Both DFA 1 and SFA 1 show particles joined together. However, this appears to be caused by fusing during cooling in the boiler for DFA 1, while, in SFA 1 distinct individual particles are joined by surface products between particles.

The highlighted area in Figure 114 of SFA 1 shows an example of the extent of surface products between particles. Comparing these to a S.E.M. image obtained of DFA 1 LS - 6M 10% in Figure 37, shows similarities between the two materials. In both, the fine fly ash particles have become attached to the surface of larger fly ash particles, giving a visual example of the reduction in the volume of <10 μm particle in laboratory wet-stored materials during storage.

8.2.1. Water requirement

Table 16 gives the water requirements of the on-site wet-stored materials. As with laboratory wet-stored samples, these materials were not pre-screened prior to testing, to evaluate the condition of the material directly following storage. The water requirements ranged from 100 – 109 %, in line with those observed in laboratory materials after 6 months wet storage. No relationship with water requirement could be established for particle size or carbon content, although, water requirement typically increased with both 45 µm sieve retention and LOI.

8.2.2. Air-entrainment

Foam index

Using the foam index test, the air-entraining agent dose required to achieve a stable foam for the on-site wet-stored materials is given in Table 16. These generally required less AEA than dry fly ash of similar LOI. A comparison of foam index results for dry and on-site wet-stored materials is given in Figure 118.

The lower AEA dose required by on-site wet-stored materials reflects the trend observed during testing of laboratory materials, in which, fly ash required less AEA after wet-storage. This is believed to be caused by interaction between water and unburned carbon reducing the adsorptive capacity of carbon by changing its surface charge. It is likely that the same mechanism occurs on-site as in the laboratory, with both having a low AEA demand compared to dry fly ash.

8.2.2.1. Specific surface area

The specific surface areas of the on-site wet-stored materials, measured by B.E.T., are given in Table 16. These were higher than dry materials of equivalent LOI, most probably due to internal voids within agglomerates, as observed in the laboratory wet-stored materials.

The surface areas of the dry and on-site wet-stored materials compared with LOI are shown in Figure 119. These show a general trend between surface area and LOI, suggesting that LOI also still has an influence on specific surface area, by nitrogen adsorption, after wet-storage.

44

8.2.3. Activity index

The activity index results of the on-site wet-stored materials are given in Table 16. These were generally lower than that of the dry materials shown in Table 4. With only SFA 5 and SFA 7 meeting EN 450-1 requirements of 75 % at 28 days and 85 % at 90 days. The on-site wet-stored materials had activity index values of between 70 to 83 % at 28-days and 80 to 90 % at 90-days, compared with 79 to 92 % at 28-days and 87 to 109 % at 90-days, for the dry materials.

The relationship between particle size and activity index for the on-site wet-stored materials is given in Figure 120 for 45 µm sieve retention and Figure 121 for the quantity of <10 µm particles. Wet-stored materials followed the same general trend observed for dry fly ash in the literature, of decreasing fineness resulting in a reduction in activity index, however, no strong correlation could be established for the on-site materials.

Both laboratory and on-site wet-stored materials show wet-storage causes a reduction in activity index. This loss is likely to be due to reduced surface area available for reaction, caused by agglomeration, reducing the pozzolanic activity and the rate of strength gain. There may also be a loss of chemical reactivity, due to the formation of surface products, although further work is required to confirm this.

8.2.4. Bulk oxide composition

The bulk oxide compositions of the on-site wet-stored materials are given in

Table 19. These were similar to the dry materials, satisfying all EN 450-1 requirements. Comparing the dry and wet-stored materials collectively highlights that the bulk oxide composition of fly ash is largely unchanged by on-site wet-storage, with only small reductions in CaO and Na_2O found. These remain within the typical oxide composition of U.K. fly ash given in Table 1 (Feng & Clark, 2011).

8.2.5. Mineralogy

The mineralogy of the on-site wet-stored materials is given in Table 21 and Figure 122. These were as expected for low lime fly ash and like the dry materials given in Table 11. The most unusual material was SFA 6, a German fly ash, which was high in both quartz and mullite, with a corresponding lower amorphous glass content, which is likely to reflect the parent coal.

8.2.6. Concrete

Fresh properties

The superplasticizing admixture requirement for the on-site wet-stored and dry materials are compared with fineness in Figure 123 and quantity of <10 μm particles in Figure 124. On-site wet-stored material typically had a higher admixture requirement to achieve a S3 slump, compared to dry materials for an equivalent LOI and fineness. As both 45 μm sieve retention and LOI increased, the superplasticizing admixture dose required also increased.

The data points DFA 4 and DFA 5 are labelled, as these materials had a high admixture demand for comparatively low 45 μm sieve retentions, due to high LOI, as porous unburned carbon appear to adsorb superplasticizer.

Cube strength

Table 22 shows the cube strengths of the on-site wet-stored materials at various ages using the 0.53 w/c ratio mix outlined in Table 8, while Figure 125 makes a comparison between fineness and 28-day strength for dry, on-site wet-stored, and laboratory wet-stored materials. These had similar 28-day strengths, regardless of fineness, except for DFA 3 which had a very high strength and is omitted from Figure 125 for clarity.

The on-site wet-stored materials gave comparable strength performance in concrete to Category N dry materials, even though most of their characteristics did not meet EN 450-1 requirements. There was also no relationship identified between fineness and 28-day cube strength for either dry or on-site wet-stored materials, as shown in Figure 125.

Therefore, any beneficiation of wet-stored fly ash is likely to be required to meet EN 450-1 limits for fineness, LOI and activity index.

9. Laboratory processing

Various processing techniques were evaluated at a laboratory-scale and could be categorised as; particle size separation, particle size reduction and carbon removal. Laboratory-scale processing was initially carried out to beneficiate wet-stored material to satisfy EN 450-1 requirements, after which, further laboratory-scale processing to improve the strength gain in concrete was considered.

9.1. Pre-screening

Screening at a larger mesh size of 600 μm was identified as a suitable pre-processing stage to remove large agglomerates, improve material homogeneity and increase the efficiency of grinding or carbon removal.

9.1.1. Yield

The yields for various wet-stored materials are given in Table 23. Screening at 600 μm gave a high yield and throughput, which allowed material to be processed quickly before any further beneficiation. Screening at 600 μm also improved the dry handling of the material by removing the large agglomerates resulting in a material which would flow like a dry Category N fly ash.

9.1.2. Variability

Screening at 600 μm also reduced the variability of the wet-stored materials, seen as a reduction in the range of 45 μm sieve retention results obtained for a single material, shown in Table 24. The 45 μm sieve retention results obtained for on-site wet-stored materials ranged from 5 to 24 % before screening at 600 μm to 1 to 7 % after. While data for the range of material variations is not available for other tests, such as water requirement and activity index, it is likely that this variability will reduce after screening as the material becomes more homogeneous.

9.1.3. Particle size

Fineness

A comparison of the fineness results of the on-site wet-stored materials before and after screening at 600 μm is given in Figure 126. Screening at 600 μm reduced 45 μm sieve retention of all on-site wet-stored materials. In SFA 2 and SFA 5 this was enough to meet Category N requirements for fineness.

Particle size distribution

Examples of the change in particle size distribution of selected on-site wet-stored materials after screening at 600 μm is given in Figure 127 and 128, showing the removal of agglomerates <600 μm and the corresponding small increase in fine particles.

Quantity of <10 μm particles

The change in quantity of <10 μm particles of selected on-site wet-stored materials after screening at 600 μm is given in Figure 129. Screening at 600 μm typically resulted in an increase in the volume of <10 μm particles by 2 to 3 % in each material.

9.1.4. Carbon

Loss-on-ignition

Figure 130 shows the change in LOI of selected materials after screening at 600 μm. Screening at 600 μm had no effect on the LOI of the on-site wet-stored materials. This suggests that unburned carbon is evenly distributed between the <600 μm and >600 μm fractions of wet-stored fly ashes, as screening did not result in an increase or decrease in the LOI of <600 μm material. Since unburned carbon present in fly ash will be <600 μm in size, no change in LOI after screening suggests that a portion of unburned carbon must be held within agglomerates. If unburned carbon was not present agglomerates, screening at 600 μm would have led to an increase in LOI by removing fly ash particles in the form of agglomerates, therefore, increasing the volume of carbon particles in the screened material.

9.1.5. Air-entrainment

Specific surface area

The specific surface area, measured by nitrogen adsorption, of on-site wet-stored materials remained unchanged after screening at 600 μm, except SFA 1 which increased by 2 m^2/g, as shown in Figure 131. The increase in surface area of SFA 1 may be an erroneous as it does not follow the behaviour of the other on-site wet-stored materials.

9.1.1. Activity index

The change in activity index of the on-site wet-stored materials after screening at 600 μm is given in Figure 132 for SFA 2 and SFA 5. Screening at 600 μm, generally resulted in decreases in activity index at 28 and 90 days of 1 – 4 %, except SFA 2 which saw a 9 % increase at 28-days. The differences in activity index before and after screening were generally small and it is likely that screening at 600 μm has only a marginal effect on the reactivity of wet-stored fly ash, with some of these changes due to material/test variability.

9.1.2. Bulk oxide composition

The change in bulk oxide composition of SFA 1, SFA 2 and SFA 4 after screening at 600 µm is given in Table 25. No significant changes occurred in bulk oxide composition after screening at 600 µm.

9.1.3. Mineralogy

The mineralogy of SFA 1, SFA 2 and SFA 4 before and after screening at 600 µm is given in Table 26 and for SFA 4 <600 µm in Figure 133. No change in mineralogical composition or volumes was found to occur as a result of screening at 600 µm.

9.1.4. Concrete

Fresh properties

The change in superplasticizing admixture dose required to achieve S3 slump for the on-site wet-stored materials after screening at 600 µm is given in Figure 134. Generally, small reductions were observed after screening due to the removal of agglomerates, except SFA 1 which required a higher dose than the unscreened material. After screening, SFA 1 had an increased specific surface area measured by nitrogen adsorption, which suggests that this material contained a high volume of voids within agglomerates of <600 µm in size.

Cube strength

The concrete cube strength of the on-site wet-stored materials before and after screening at 600 µm is given in Figure 135, using a 0.53 w/c mix, outlined in Table 8. Screening generally led to an increase in cube strength of 1 to 4 MPa between 28 and 90 days, with the largest increases seen at 56 and 90 days.

9.2. Particle size Separation

The characteristics of wet-stored materials after screening at 63 µm sieve are given in Table 27. This mesh size was selected to reduce particle size to <40 % retained on a 45 µm sieve and meet EN 450-1 Category N fineness requirements. Selected <63 µm screened materials were characterised and evaluated in concrete.

9.2.1. Yield

The throughput and ultimate yield obtained during screening at 63 µm for various wet-stored materials are given in Table 28. After investigating several methods of screening, to achieve optimal throughput, the quantity of <63 µm wet-stored material produced per hour remained low. The yields obtained for SFA 1 to 4 when screening at 63 µm were less than 50 %, the lowest of which was for SFA 3 of 17 %. Therefore, screening at 63 µm was considered impractical and not evaluated in further detail.

9.2.2. Particle size

Fineness

Figure 136 shows the change in fineness of wet-stored materials after screening at 63 µm. Screening led to large reductions in 45 µm sieve retention to <12 % producing Category S fineness material, as seen by McCarthy *et al* (2018).

Particle size distribution

The change in particle size distribution of SFA 4 after screening at 63 µm is given in Figure 137 as an example of the effects of this process. The figure shows the removal of material greater than 100 µm and the slight loss of <10 µm particles increasing those in the 10 to 63 µm range.

Quantity of <10 µm particles

The change in quantity of <10 µm particles after screening at 63 µm for wet-stored materials is given in Figure 138. While screening reduced 45 µm sieve retention, increases in the quantity of <10 µm particles were observed only in some cases. The quantity of <10 µm particles of SFA 2 and LFA 5 were found to increase, whereas, SFA 1 and SFA 5 remained largely unchanged, and SFA 3 and SFA 4 lost <10 µm material. The reduction of <10 µm particles after screening may have occurred due to fine particles becoming trapped in large agglomerates and removed with the oversize material.

9.2.3. Carbon

Loss-on-ignition

The change in LOI of selected wet-stored materials after screening at 63 μm is shown in Figure 139. Screening gave small reductions in LOI ranging from 1 to 3 %, depending on the quantity and particle size of the unburned carbon present (McCarthy, et al., 2018). Screening reduced LOI of SFA 2 from 9 to 6 %, to satisfy EN 450-1 requirements, but did not lead to large enough reductions in the other materials to be useful as a dedicated carbon removal process.

9.2.4. Water requirement

Figure 140 shows the change in water requirement of wet-stored materials after screening at 63 μm. The reduction in water requirement observed is likely to be due to the removal of porous carbon and large agglomerates, both of which may take up water. Screening reduced water requirement, the extent of which varied between materials and could not be related to changes in particle size. However, this did not reduce water requirement of any wet-stored material to ≤95 %, the limit for a Category S material.

9.2.5. Air-entrainment

Foam index

The change in foam index of wet-stored materials after screening at 63 μm is given in Figure 141. Screening generally led to a reduction in AEA required to achieve a stable foam. The greatest reduction after screening was seen in SFA 4, whereas, only small changes were observed in SFA 1 and SFA 3. The reduction in SFA 4 may be due to removal of unburned carbon, but the changes in AEA requirement could not be related to the change in LOI after screening.

Specific surface area

The specific surface area, measured by nitrogen adsorption, was found to decrease slightly after screening at 63 µm, as shown in Figure 142. These reductions are likely to be due to reduced unburned carbon and removal of large agglomerates, both of which influence specific surface area. However, the change in LOI or particle size could not be related to that in specific surface area for the materials evaluated.

9.2.6. Activity index

The change in activity index of SFA 5 and LFA 5 after screening at 63 µm is shown in Figure 143. Small increases in activity index were observed in both materials at different ages, however, these increases were inconsistent, and any influence of screening may be masked by material variability. It should also be noted that these materials had a high activity index at both 28 and 90 days before screening and may not have been wet-stored for a long duration before testing.

9.2.7. Bulk oxide composition

Table 29 shows the bulk oxide composition of wet-stored materials before and after screening at 63 µm. No significant changes, beyond material and test variability, were found to occur as a result of screening.

9.2.8. Mineralogy

The mineralogy of the wet-stored materials before and after screening at 63 µm is shown in Figure 144 and Table 30.

9.2.9. Concrete

A comparison of the concrete cube strengths achieved, using a 0.5 w/c mix outlined in Table 7, before and after screening at 63 µm are shown in Figure 145. A small reduction in strength occurred in SFA 5 <63 µm material compared to SFA 5, of between 0.5 and 1.5 MPa at all ages, however, LFA 5 <63 µm had significantly lower strengths compared to LFA 5, of between 4 and 8 MPa at 3 to 28 days. Screening at 63 µm did not give any benefits to concrete cube strength.

9.3. Short duration particle size reduction

On-site wet-stored materials were initially ground in the laboratory ball mill, in batch sizes of 125 g at grinding durations of 10 to 40 minutes to achieve a 45 µm sieve retention of <12 %, satisfying Category S requirements. The on-site materials were dried before grinding and 125g batch sizes used to maximise throughput and minimise material wastage.

9.3.1. Particle size

Fineness

The change in fineness of selected on-site wet-stored materials after ball milling for 10 to 40 minutes is shown in Figure 146. The 45 µm sieve retentions of the ground materials were evaluated to determine the minimum grinding duration reached to achieve a fineness of <12 %. These results show that irrespective of initial 45 µm sieve retention of the materials, after 10 minutes grinding each had a fineness of between 10 and 14 %. The results show that 20 minutes ball milling would be suitable to achieve <12 % retained on a 45 µm sieve mesh.

Particle size distribution

The changes in particle size distribution of SFA 1 and SFA 2 after ball milling for 10 to 40 minutes are given in Figure 147 and 148. These show a large decrease in particle size after grinding for 10 minutes, mainly due to the de-agglomeration of large and medium sized agglomerates, with longer grinding durations up to 40 minutes resulting in further, but smaller decreases in particle size.

Quantity of <10 µm particles

The change in quantity of <10 µm particles after ball milling for 10 to 40 minutes for the on-site wet-stored materials is given in Figure 151. Although large decreases in 45 µm sieve retention were observed after short grinding durations, the corresponding increases in <10 µm particles were smaller, at between 15 to 20 %. Grinding for 20 minutes resulted in an increase in volume of <10 µm particles to a level of 35 to 40 %, i.e. like those of the dry Category N materials evaluated during the project.

54

9.3.2. Carbon

Loss-on-ignition

The change in LOI after ball milling is given for SFA 1 in Figure 154. As laboratory ball milling is a closed system, allowing full recovery of material, LOI was expected to remain unchanged. This was confirmed by the results of SFA 1, with only small variations recorded between grinding durations. These were attributed to material variation, rather than a change in quantity of unburned carbon.

9.3.3. Morphology

S.E.M. images

Figure 156 to 159 show the S.E.M. images of SFA 1 after ball milling for 10 to 40 minutes. These indicate an increase in the number of fractured particles with grinding duration, however, fine fly ash particles, of <10 µm appear to remain intact. These images also show a reduction in the number of large agglomerates as grinding duration increases, although, some fine fly ash particles appear agglomerated together. This suggests that ball milling for 10 to 40 minutes causes the breakdown of agglomerates of >10 µm, but is less effective in reducing the size of fine agglomerates.

9.3.4. Water requirement

The change in water requirement after ball milling for 10 to 40 minutes is given in Figure 161. Ball milling resulted in reductions in water requirement of typically 9 %, however, these could not be related to grinding duration or fineness. Reductions of 9% were obtained in all materials irrespective of grinding duration except SFA 1 BM30 where this was 10 %. This suggests the reduction in water requirement is likely to be a result of de-agglomeration.

Although, these materials have similar fineness, quantity of <10 µm particles and particle size distributions to that of Category S fly ash, the water requirements of the ground material could not achieve the ≤95 % limit required for Category S materials. It appears that 100 % water requirement was the limit of what could be achieved by grinding in 125 g batches for 10 to 40 minutes. There is no water requirement limit placed on Category N fly ash, however, any reductions that can be achieved would be of benefit.

9.3.5. Activity index

The changes in activity index, after 20 minutes balling milling for SFA 1 to 4 are given in Table 35 and compared with fineness and quantity of <10 µm particles in Figure 164 and 165. Increases of 7 to 10 % were observed at 28 days and 8 to 20 % at 90 days in these materials, and related well to both fineness, in Figure 164, and quantity of <10 µm particles, in Figure 165. This increase in activity index is the result of increased surface area for pozzolanic reaction due to de-agglomeration and exposure of new particle surfaces of the wet-stored material.

9.3.6. Air entrainment

Specific surface area

Table 34 shows the change in specific surface area, by nitrogen adsorption, for SFA 1, SFA 2 and SFA 4 after ball milling. Ball milling led to a slight increase in specific surface area after 10 - 30 minutes grinding before decreasing at 40 minutes in SFA 1, and gave slight reductions in SFA 2 and SFA 4. The decrease in specific surface area is likely to be the result of de-agglomeration giving a reduction in the number of voids associated with fly ash agglomerates, which were seen in CT scans of both laboratory and on-site wet-stored materials.

9.3.7. Concrete

Fresh properties

The superplasticizing admixture doses required to achieve S3 slump with SFA 1 and SFA 2 after 10 to 30 minutes ball milling are given in Figure 168, using a 0.5 w/c mix outlined in Table 7. The change in admixture requirement with particle size for SFA 1 and SFA 2 after 10 - 30 minutes ball milling is given in Figure 169 for fineness and Figure 170 for the quantity of <10 µm particles. Ball milling significantly reduced superplasticizing admixture requirements, as seen during water requirement testing, due to de-agglomeration and the associated reduction of voids. The reduction in superplasticizing admixture dose also correlated well with both fineness and quantity of <10 µm particles, with decreasing particle size giving a lower superplasticizer requirement.

Cube strength

The concrete strength results of SFA 1 and SFA 2 after ball milling are given in Table 38, and Figure 173 and 174. These show that little difference occurred between the wet-stored and ball milled material allowing for test and material variability. While small increases in strength were observed in SFA 2 BM20 compared to SFA 2, at all concrete ages, of between of around 2 - 5 MPa, this was not observed in SFA 1 or SFA 2 at other durations. Therefore, ball milling for short durations appeared to have no noticeable effect on concrete strength.

9.4. Long duration particle size reduction

A further evaluation of grinding after screening at 600 µm, was conducted to determine whether an increase in concrete strength could be obtained after grinding for longer durations.

To identify a suitable grinding duration and batch size to significantly increase fineness, a variety of different wet-stored materials were ball milled at batch sizes of 50 and 100 g. The particle size distributions of these materials were then evaluated by laser diffraction, to find a grinding duration and batch size that would give a large increase in the quantity of <10 µm particles.

Figure 152 and 153 show the volume of <10 μm particles of on-site wet-stored materials after grinding in 50 and 100 g batches. A grinding duration of 120 minutes was found to give a volume of <10 μm particles of >70 % in each material at a batch size of 50 g and was selected for further study.

9.4.1. Particle size

Fineness

The fineness values of the on-site wet-stored materials after ball milling for 120 minutes are given in Table 31. Grinding for 120 minutes in 50 g batches reduced particle size to <0.5 %, therefore, the quantity of <10 μm particles were used to give a better comparison between materials.

Particle size distribution

The particle size distributions of SFA 1, SFA 2 and SFA 6 before and after ball milling for 120 minutes are given in Figure 149 and 150. These show significant increases in fine particles compared to material after screening and ball milling for 20 minutes. The 120 minutes ball milled materials generally had maximum particle sizes of 40 to 50 μm, compared to the screened material which had a maximum particle size of 600 μm and the material ball milled for 20 minutes, which had a maximum particle size of around 100 μm. There was also a large increase in <1 μm particles in both SFA 1 and SFA 2, although, this was not seen to such an extent in SFA 6.

Quantity of <10 μm particles

The quantity of <10 μm particles of the on-site wet-stored materials after ball milling for 120 minutes are given in Table 31. These ranged from 71 to 79 %, classifying them as super-fine fly ashes.

9.4.2. Carbon

Loss-on-ignition

Table 33 gives a comparison of the LOI values for selected wet-stored materials before and after ball milling for 120 minutes. LOI after ball milling for 120 minutes, was found to be slightly higher than that of the input <600 µm materials. As ball milling is a closed system, the small increases in LOI are likely to be due to variability, as observed when grinding at 10 – 40 minutes.

Morphology

S.E.M. images

S.E.M. images of SFA 1 before and after ball milling for 120 minutes are given in Figure 155 and 160 respectively. Before grinding, SFA 1 has a large quantity of misshapen particles and surface products on particle surfaces forming agglomerates. After ball milling, SFA 1 BM120 consists largely of small, irregular particles, with few intact spherical particles remaining. Ball milling for 120 minutes does not appear to break apart all of the smallest agglomerates, but seems to fracture large fly ash particles creating fine irregular particles and exposing new surfaces.

Comparing the S.E.M. images of SFA 1 <600 µm BM120 and SFA 1 BM20 at x1000 magnification, highlights the differences between the two durations. Figure 157 of SFA 1 BM20 shows mostly intact particles, with only the largest broken apart, whereas, SFA 1 <600 µm BM120 in Figure 160 has only very fine particles remaining unbroken and contains a greater number of fine fragments of broken large particles.

9.4.3. Water requirement

A comparison of the water requirements for SFA 1 and SFA 2 unscreened, after screening at <600 µm and after 120 minutes ball milling is given in Figure 162.

Ball milling for 10 to 40 minutes was found to decrease the water requirement of wet-stored materials to 100 %. Ball milling for 120 minutes gave a smaller reduction, of around 1 to 4 % when compared to <600 µm material, and 4 to 5 % when compared to the unscreened wet-stored materials.

This suggests that while grinding for short durations causes de-agglomeration, improving consistence, longer grinding durations start to break the fly ash particles, which increases surface area and therefore water requirement. This results in a decrease in water requirement compared to the on-site wet-stored materials, but an increased water requirement compared to these materials ground for shorter durations.

9.4.1. Air-entrainment

Specific surface area

The change in specific surface area, measured by nitrogen adsorption, with grinding duration of SFA 1 and SFA 2 is shown in Figure 163.

Material ground for 120 minutes had slightly lower surface areas than the unscreened wet-stored materials and those ground for short durations. This suggests that grinding in smaller batch sizes for longer durations causes de-agglomeration of smaller particles than shorter durations, reducing internal voids and, therefore, specific surface area. If further de-agglomeration did not occur the specific surface area would be likely to increase due to the increased particle surface area from the reduction in particle size.

9.4.2. Activity index

The activity index results of the 120 minutes ball milled materials are given in Table 31 and compared to other grinding durations and particle size in Figure 166 and 167. Ball milling for 120 minutes increased activity index, as seen in the short duration ball milled materials, with longer durations giving greater increases at both 28 and 90-days.

Figure 166 shows the trend between fineness and activity index at both ages between the on-site wet-stored and ball milled materials. A general trend of increasing activity index with decreasing particle size is seen, however, by comparing activity index and quantity of <10 μm particles in Figure 167, a much stronger correlation is found. This shows that for very fine materials, the volume of <10 μm particles is a more appropriate measure of particle size.

9.4.3. Bulk oxide composition

Table 36 gives the bulk oxide composition data of SFA 1 and SFA 2 <600 μm before and after ball milling for 120 minutes which remained unchanged.

9.4.4. Mineralogy

Table 37 gives the mineralogy of SFA 1 and SFA 2 < 600 μm before and after ball milling for 120 minutes. Mineralogy remained largely unchanged, with only small increases in quartz and mullite observed after grinding. This is likely due to quartz and mullite phases being identified during X-Ray diffraction as particles are broken and the crystalline phases, usually at the centre, are exposed to surface testing as seen by McCarthy et al (2018) when ball milling fly ash.

9.4.5. Concrete

Fresh properties

The change in superplasticizer admixture dose required to achieve an S3 slump after 120 minutes ball milling is shown in Figure 171, for a 0.53 w/c mix, outlined in Table 8. The superplasticizer admixture requirement reduced after 120 minutes ball milling, as seen with shorter durations. Although, the reduction achieved after ball milling for 120 minutes was less than that for 10 to 30 minutes, due to the increased surface area with the longer period.

Cube strength

The cube strength results of SFA 1, SFA 2 and SFA 6 after ball milling for 120 minutes are given in Figure 175 at 28-days and Table 39 at 28, 56 and 90-days for a 0.53 w/c mix of proportions outlined in Table 8. While no strength gains were achieved after ball milling for 10 to 30 minutes, 120 minutes led to increases of 5 to 10 MPa at 28 to 90-days.

9.5. Microniser

Selected materials were ground in the laboratory-scale microniser and evaluated to allow for a comparison between ball milling and micronising. Due to practical limitations operating the microniser, only SFA 6 was ground in a sufficient quantity for use in concrete, and only a limited selection of characterisation tests were conducted on the micronised material.

9.5.1. Particle size

The change in particle size distribution and quantity of <10 μm particles of SFA 1, SFA 5 and SFA 6 after micronising are given in Table 32.

Micronising resulted in an increase in quantity of <10 μm particles of around 15 to 18 %, similar to the gains seen during grinding for short durations in the ball mill.

9.5.2. Concrete

Fresh properties

Figure 172 shows the change in superplasticizer dose required to achieve an S3 slump in SFA 6 after micronising. The superplasticizing admixture requirement decreased from 6.8 g/kg of cement to 4.3 g/kg, although, this was less than observed by ball milling SFA 6 for 120 minutes, which reduced to 3.6 g/kg.

Cube strength

The concrete cube strengths of SFA 6 after micronising are shown in Figure 176. Little difference in cube strength was observed after micronising, with both materials reaching comparable strengths at each age. Based on these results and the difficulty in operating the microniser, no further processing was conducted using this system in the laboratory.

9.6. Carbon removal

9.6.1. Temperature selection

Figure 177 and 178 show the reduction in LOI of various on-site wet-stored materials after carbon removal in the laboratory furnace at temperatures of 500, 600 and 700 °C for 1 hour, allowing the sample to heat and cool in the furnace. From these results a furnace temperature of 500 °C after screening at 600 μm was found to be suitable to reduce LOI to <7 % in most materials, except very high LOI materials such as SFA 3 and SFA 4

This section discusses the results of carbon removal at 500°C for 1 hour, as this was the lowest furnace temperature that would remove carbon and appeared to have no additional effects on fly ash. At higher temperatures, most notably 700°C, a distinct colour change was observed in the fly ash, from dark grey/black to a burnt orange/brick red, which seemed to be due to oxidation of the iron mineral phases. While, this did not appear to affect the fly ash characteristics or performance in concrete, a low carbon removal temperature was more desirable to reduce energy requirements as far as possible.

9.6.2. Particle size

Fineness

A comparison between fineness values of selected on-site wet-stored materials, before and after carbon removal at 500°C for 1 hour, is given in Figure 179. Carbon removal led to an increase in fineness in most fly ashes, the degree of which varied between materials, which is likely to be due to differences in the size of carbon particles present. The larger the carbon particles, the greater the increase in fineness after carbon removal.

A reduction of 7 % was seen in SFA 5, whereas, SFA 7 had no reduction suggesting that the carbon present in SFA 5 is generally coarse (>45 μm), whereas, SFA 7 contains carbon that is more evenly distributed throughout the whole particle size range. This is shown by the reduction in LOI of SFA 7 of 2 % resulting in no change in fineness.

Particle size distribution

Figure 180 shows the change in particle size distribution of SFA 5 <600 µm and SFA 7 <600 µm after carbon removal at 500 °C for 1 hour. These show little difference after carbon removal with only a small decrease in particle size observed.

Quantity of <10 µm particles

The change in quantity of <10 µm particles of the on-site wet-stored materials after carbon removal at 500 °C for 1 hour is shown in Figure 181. Carbon removal led to an increase in quantity of <10 µm particles in SFA 2, however, there was no significant effect on the other materials.

9.6.3. Carbon

Loss-on-ignition

Figure 182 and 183 show that the change in LOI of wet-stored materials after carbon removal at 500 °C for 1 hour. The materials shown in Figure 183 were screened at 600 µm prior to carbon removal, which slightly increased effectiveness. Without screening, carbon removal reduced LOI of SFA 2 by 3% by including screening this increased to 4%.

Oxidation in the furnace at 500°C for 1 hour was suitable to reduce the LOI of most materials, except for particularly high LOI materials such as SFA 3 and SFA 4. These would require higher temperatures to remove sufficient unburned carbon to meet EN 450-1 requirements.

Only a limited study of carbon removal by oxidation was conducted in the laboratory as this is less likely to be considered for industrial-scale carbon removal of wet-stored fly ash due to the energy requirement and CO_2 produced.

9.6.4. Water requirement

The change in water requirement of SFA 5 and SFA 7 before and after carbon removal at 500°C for 1 hour is given in Figure 184. Carbon removal led to reductions in water requirement of 14 % in SFA 5 and 5 % in SFA 7. It should be noted that these materials were screened at 600 μm before carbon removal which may have reduced water requirement, to a small degree, the reductions in water requirement observed in SFA 5 and SFA 7 are likely to reflect carbon removal.

9.6.5. Activity index

A comparison of the activity index results of SFA 5 and SFA 7 before and after screening and carbon removal at 500°C for 1 hour is given in Figure 185. Carbon removal led to an increase in activity index at both 28 and 90 days due to the removal of carbon.

9.6.6. Bulk oxide composition

Table 40 shows the bulk oxide compositions of SFA 5 and SFA 7, before and after carbon removal for 1 hour. Carbon removal was found to have no effect on the oxide composition of either material.

9.6.7. Mineralogy

Table 41 and Figure 186 show the mineralogy of SFA 5 and SFA 7, before and after carbon removal at 500°C for 1 hour. Carbon removal was found to lower the quantity of quartz observed in both SFA 5 and SFA 7 and mullite in SFA 7. These results are likely to be the result of material and test variation, as the carbon removal temperature used was too low to have any effect on the mineral phases.

9.6.8. Concrete

Fresh properties

Figure 187 shows the change in superplasticizing admixture dose required to achieve S3 slump after screening and carbon removal at 500°C for 1 hour. Carbon removal led to a decrease in superplasticizer demand, with the greatest reduction seen in SFA 5 which also saw the largest reduction in water requirement after carbon removal. These materials were also screened at 600 μm before carbon removal which was found to give small reductions in superplasticizing admixture demand, therefore, a proportion of the reductions shown in Figure 187 is probably the result of removing large agglomerates.

Cube strength

A comparison between the 28-day concrete cube strengths of the wet-stored materials before and after screening and carbon removal at 500°C for 1 hour is shown in Figure 188, with the remaining strengths given in Table 42. Screening and carbon removal led to increases in cube strength at 28 days of between 2.5 to 3.0 MPa.

10. Pilot-scale processing

Approximately 5 tonnes of wet-stored fly ash from a U.K. stockpile was beneficiated at Atritor Ltd in Coventry, England, using a dryer-pulveriser, air classification and a micronising mill. The output products and a sample of the feed stockpile material were sent to the laboratories in Dundee for characterisation and evaluation in concrete.

Additionally, small samples of the dried and de-agglomerated material (PFA 2) and the micronised material (PFA 4) were sent to STET in the U.S.A. to undergo electrostatic separation to remove carbon. These were then characterised, however, limited sample sizes prevented them from being evaluated in concrete.

10.1. Materials

Table 43 outlines the various beneficiation techniques carried out and the abbreviations used for each. An image of the as-received material prior to processing is also given in Figure 212. Although this material was screened at 500 µm on site, it appears that a degree of re-agglomeration caused by compaction and cohesion had occurred during transport.

10.2. Drying and de-agglomeration

The stockpile on-site wet-stored feed material was dried using the Dryer-Pulveriser shown in Figure 213, which uses a de-agglomeration and flash drying system to achieve beneficiated material to a targeted output moisture content or throughput. This was achieved using an inlet air temperature of 500°C and a material feed rate of 1184 kg/hr to give output material of 0.5 % moisture content at a throughput of 1000 kg/hr. This stage beneficiated the feed wet-stored material (SFA 8) to a dry, de-agglomerated material (PFA 2), which was collected in bag filters for use or further processing.

During this stage, some super-fine material was carried away in exhaust gases and collected in a separate fine bag filter. This was found to be around 10 % of the mass collected in the primary bag filter, however, it could not be recovered due to contamination with other materials from previous trials using the dryer-pulveriser. Therefore, the ultimate weight of collected material from this pilot-scale trial was 3658 kg from the input feed mass of 4965 kg, with 369 kg of ultra-fine material lost during drying.

10.3. Classification

Dried and de-agglomerated material (PFA 2) was further beneficiated by air-classification to produce a Category S material. This was established by calibrating the air-classifier, shown in Figure 214, to give an output product of <12 % greater than 45 µm by laser diffraction. This gave a classified product (PFA 3) at a yield of around 60 %, with the remaining material as oversize (PFA 5). When PFA 3 was tested for fineness in the laboratory it was found that laser diffraction during calibration over-estimated the volume of >45 µm material compared to the 45 µm sieve retention test.

10.4. Microniser

A microniser, shown in Figure 215, was used to grind PFA 2 to produce an ultra-fine material (PFA 4). This material had a similar fineness to those ball milled in the laboratory for 120 minutes. However, the throughput required to achieve this fineness was 2.5 kg/hour, too low to be suitable for mass processing of recovered fly ash.

10.5. Electrostatic Separation

Both PFA 2 and PFA 4 from the pilot-scale trial was sent to STET in the U.S.A. for carbon removal by electrostatic separation. These materials were tested for fineness, LOI, particle size distribution and activity index to evaluate the effects of carbon removal by electrostatic separation, and allow comparisons to be made with carbon removal in the laboratory.

10.6. Results

The characteristics of the pilot-scale processed materials are given in Table 44 for the materials processed at Atritor and Table 45 for the materials sent to STET.

10.6.1. Particle size

Fineness

A comparison of the fineness values of the pilot-scale processed materials is given in Figure 189 for the materials processed at Atritor and Figure 190 for the STET materials. PFA 2 met Category N fineness requirements after flash drying and de-agglomeration, with a 45 μm sieve retention of 31 % reduced from 62 % retained for the feed wet-stored material. This suggests that a large quantity of agglomerates were broken down after drying and de-agglomeration, producing an output material similar in particle size to a dry Category N material.

The air-classified material (PFA 3) had a fineness of 1.5 % and the over-size material (PFA 5) of 56 %. The micronised material (PFA 4) had a fineness of 0.6 %.

Electrostatic separation led to a slight decrease in fineness in PFA 4 LC of around 4 %, which is likely to be due to a loss of fine particles during processing and led to a decrease in particle size of PFA 2 LC. Both PFA 2 HC and PFA 4 HC gave a decrease in fineness after electrostatic separation, due to an increase in unburned carbon.

Particle size distribution

Figure 191 shows the particle size distribution curves of the feed and pilot-scale processed materials. Both PFA 2 and SFA 8 have a similar shaped curve, with the most significant difference between the two being a lower proportion of >100 μm particles present in PFA 2 after de-agglomeration. The slight reduction in <10 μm particles in PFA 2 compared to SFA 8 is due to the loss of very fine particles outlined previously.

Comparing PFA 2 and PFA 3 shows the effective separation of almost all >100 μm particles after air-classification. The oversize (PFA 5) contained no particles <10 μm, with most between 40 - 80 μm in size. The majority of PFA 4 comprised of <10 μm particles with a maximum particle size of around 20 μm.

The particle size distribution curves for PFA 2 and PFA 4 after carbon removal by electrostatic separation are shown in Figure 192. PFA 2 LC gave a reduction in 30 – 100 μm material and corresponding increase in <30 μm material after carbon removal, suggesting that the unburned carbon particles present were typically between 30 - 100 μm in size. Whereas, PFA 4 LC saw a reduction in <10 μm particles, which is likely to be due to a loss of fines during processing.

Quantity of <10 μm particles

The quantity of <10 μm particles of the pilot-scale processed materials are given in Figure 193 for the Atritor materials and Figure 194 for the STET materials. The quantity of <10 μm particles of PFA 2 was slightly lower than that of the feed wet-stored material (SFA 8), due to the loss of very fine particles during drying and de-agglomeration. It is likely that if this material had been recovered, the quantity of <10 μm particles of PFA 2 would exceed that of SFA 8 due to the de-agglomeration stage.

Air-classification of PFA 2 to PFA 3 led to an increase in quantity of <10 μm particles from 20 % to 36 %, similar to the volume of <10 μm particles of wet-stored materials after ball milling for 20 minutes in the laboratory. Micronising PFA 2 to PFA 4 significantly increased the volume of <10 μm particles from   20 % to 72 %, giving a very fine output product.

Electrostatic separation of PFA 2 to PFA 2 LC led to a slight increase in quantity of <10 μm particles to 26 % due to the removal of coarse carbon, increasing the fines content of the overall fly ash. The high carbon output material PFA 2 HC was found to have a corresponding decrease in quantity of <10 μm particles to 14 %, due to the increased quantity of coarse carbon.

Electrostatic separation of PFA 4 led to a reduction in quantity of <10 μm particles in both the low and high carbon output products. The quantity of <10 μm particles reduced from 72 % to 63 % and 55 % for PFA 4 LC and PFA HC respectively. This is likely to be due to the loss of fine particles during electrostatic separation or handling. Electrostatic separation may prove unsuitable for very fine material, if a large portion of fine particles are lost during processing.

10.6.2. Carbon

Loss-on-ignition

The LOI values of the pilot-scale processed and STET materials are given in Table 44 and 45. The LOI of SFA 8 was 6.3 %, which remained unchanged after drying and de-agglomeration to PFA 2 which had a LOI of 6.1 % and air-classification to PFA 3 of 6.3 %. The LOI of the micronised material (PFA 4) was slightly higher at 6.6 %, however, this is unlikely to represent an increase in actual carbon content and may be due to finer carbon particles undergoing more complete oxidation during LOI testing because of an increased surface area, or variability.

It is of note that the oversize (PFA 5) after air-classification had a lower LOI than PFA 2, the input feed material, at 4.7 %. This suggests that carbon particles in the stockpile material were fine or of low density, remaining with the fine product after classification. As particle size distribution analysis of PFA 2 LC gave a reduction in 40 to 80 µm particles after carbon removal, it is likely that this carbon was low density and separated with the fine particles during air-classification.

Electrostatic separation reduced LOI to a target of 3.0 % for low carbon output material. After electrostatic separation PFA 2 LC had an LOI of 3.1 % and PFA 4 LC of 3.3 %. The high carbon materials had a slightly greater LOI than the input material of 7.2 % for PFA 2 HC and 6.7 % for PFA 4 HC.

Carbon content

Table 46 gives a summary of the carbon contents, measure by CO_2 evolution, of the pilot-scale processed materials and Figure 195 shows the relationship between carbon content and LOI.

The carbon contents of SFA 8, PFA 2, PFA 3 and PFA 4 were found to be around 5.5 % and remained largely unchanged after drying, de-agglomeration, classification and micronising. The LOI results of these materials were typically 1 to 2 % higher, indicating that a proportion of material removed during LOI testing was non-carbon.

10.6.3. Water Requirement

The change in water requirement with fineness and quantity of <10 µm particles, are shown for the pilot-scale processed materials in Figure 196.

The water requirement of the feed stockpile material, SFA 8, was 103 %. This reduced, after drying and de-agglomeration, to 102 % for PFA 2, to 100 % after air-classification for PFA 3 and to 98 % after micronising for PFA 4. Whilst a reduction in water requirement was achieved, EN 450-1 requirements for Category S material were not reached with any form of beneficiation.

A good relationship between water requirement and particle size, most notably 45 μm sieve retention was found, with the finest material giving the lowest water requirement. This increased with particle size, before levelling off above 30 % for 45 μm sieve retention.

Mortar flow

Due to limited sample sizes, the water requirements of the materials processed at STET could not be evaluated, however, material was available to compare the mortar flow of these materials using a 0.5 w/c ratio mortar mix at 30 % in cement.

Figure 197 gives a comparison of the mortar flows for PFA 2, PFA 4 and the materials processed at STET, with PFA 2 and PFA 4 after carbon removal at 500°C for 1 hour in the laboratory furnace also included. These show, electrostatic carbon removal increased mortar flow in PFA 2 LC and PFA 4 LC by 10 – 15 mm, similar to the mortar flows of PFA 2 and PFA 4 after carbon removal in the laboratory. The high carbon materials, PFA 2 HC and PFA 4 HC, had similar or slightly lower mortar flows than that of PFA 2 and PFA 4, which is likely to be due to the comparatively small increase in LOI between the materials, as shown in Table 44 and 45.

10.6.4. Air-entrainment

Foam index

The air-entraining agent dose required to achieve a stable foam during the foam index test for the pilot-scale processed and electrostatically separated materials is given in Figure 198.

No change in AEA requirement was observed between the pilot-scale processed material and the wet-stored feed material, except the micronised material PFA 4 which increased significantly. This may have arisen due to the grinding of carbon particles opening new surfaces of carbon which were not exposed during wet-storage, and therefore, had no interaction with water during wet-storage and remained non-polar. These non-polar surfaces would attract the polar end of AEA molecules much like a dry fly ash, leading to the large increase in AEA required to create a stable foam.

After electrostatic separation, the processed materials also had slightly higher AEA requirements. PFA 2 LC had the same dose to that of PFA 2, despite a lower carbon content, PFA HC had a higher requirement for a similar LOI and both PFA 4 LC and HC needed larger doses than PFA 4. This may be due to electrostatic charging or separation processes affecting the surface charge of the carbon particles, which also affects adsorption of AEA molecules. However, this would require further investigation and the increase found in PFA 4 of the low carbon material was small.

Specific surface area

The specific surface area, measured by nitrogen adsorption, of the pilot-scale processed and STET materials are given in Table 44 and 45. The specific surface area of PFA 2 and PFA 3 were similar to the feed wet-stored material (SFA 8) at around 6.0 m^2/g, with PFA 4 found to be 4.5 m^2/g. This suggests that not all agglomerates in PFA 2 and PFA 3 were broken or removed during these beneficiation processes, with voids between particles still contributing to specific surface area. After a large degree of grinding, in the microniser, a reduction in specific surface area was observed suggesting that the majority of agglomerates broke down, as found after ball milling for 120 minutes in the laboratory.

The specific surface area of PFA 2 and PFA 4 after carbon removal by electrostatic separation were lower than PFA 2 and PFA 4 due to the removal of unburned carbon. The specific surface area results of the high carbon materials after electrostatic separation were also lower than PFA 2 and PFA 4, despite having a higher carbon content. It is unknown why these materials had lower surface areas when measured by nitrogen adsorption.

10.6.5. Activity index

The activity index of the feed wet-stored and pilot-scale processed materials are given in Table 47, and were found to correlate well with quantity of <10 μm particles, shown in Figure 200. As the quantity of <10 μm particles increased, due to beneficiation, the activity index at both 28 and 90 days also increased. The activity index of SFA 8 and PFA 2, failed to meet EN 450-1 requirements at both 28 and 90-days, however, after carbon removal, PFA 2 LC met these which may be due to the increased volume of fine particles, seen as an increase in quantity of <10 μm particles.

Both PFA 3 and PFA 4 met 28 and 90-day activity index requirements, however, carbon removal of PFA 4 had little influence on the reactivity of PFA 4 at both 28 and 90 days. This may be due to the loss of fine particles during electrostatic separation, offsetting any gains from the removal of carbon.

10.6.6. Bulk oxide composition

The bulk oxide composition of the pilot-scale processing materials are given in Table 48 and were found to remain unchanged after beneficiation.

10.6.7. Mineralogy

The mineralogy of the pilot-scale processing materials is given in Table 49, Figure 201 and 202. No change in mineralogy occurred as a result of pilot-scale processing or electrostatic separation.

10.6.8. Concrete

The pilot-scale processed material, SFA 8, PFA 2, PFA 3 and PFA 4 were evaluated in a 0.53 w/c concrete, mix proportions given in Table 8. SFA 8 was evaluated at the same mix proportions, in a wet condition by adjusting the mix water to maintain a 0.53 w/c ratio.

Based on these concrete results, additional mixes were prepared which utilised a water saving, achieved using a fixed superplasticizing admixture dose needed in SFA 8 at 0.53 w/c ratio to reach S3, and decreasing the w/c ratio while maintaining equal consistence for the beneficiated materials. These used the same mix proportions as outlined in Table 8 with water held back until a S3 slump was achieved and the new w/c ratio calculated.

Fresh properties

The admixture demand of the pilot-scale materials increased with fineness as shown in Figure 203. This was a strong relationship due to the materials originating from the same fly ash and highlights the importance of particle size on consistence, the effect of wet-storage on consistence and the extent to which this can be recovered by beneficiation.

The largest reductions in admixture requirement were seen in PFA 3 and PFA 4, requiring just over half that of SFA 8 to achieve S3 slump.

Cube strength

Equal w/c ratio

The concrete cube strengths of the feed wet-stored and processed materials are given in Figure 204 and Table 50. These materials had equivalent strengths at all ages except for the micronised material (PFA 4) which had strengths of 2 to 3 MPa higher at 28-days or later. No relationship between particle size, measured by either fineness or quantity of <10 μm particles, and concrete strength for the pilot-scale materials could be identified, with no strength increases in PFA 2 and PFA 3.

Water saving mixes

The concrete strength results of the water saving mixes for the pilot-scale processed materials are given in Table 51 and Figure 205 compared to SFA 8 at 0.53 w/c ratio using a fixed superplasticizer dose of 5 g/kg of cement.

A w/c ratio of 0.51 was reached in PFA 2 and PFA 3, with a further reduction to 0.49 in PFA 4. This led to increases in strength of 2.0 to 3.5 MPa in PFA 2, 2.5 to 4.5 MPa in PFA 3 and 6.0 to 10.0 MPa in PFA 4.

While beneficiation did not lead to large gains in concrete strength using equal mix proportions, the overall improvement in fly ash characteristics, most notably in consistence, allowed higher cube strengths to be obtained by adjusting the w/c ratio of the mix.

11. Durability

Selected materials were also used to carry out a limited investigation into two common concrete durability concerns; carbonation and chloride ingress. Due to the limited nature of the studies, these results should be considered as an indication of how beneficiated, wet-stored materials will perform, and it should be emphasised that further testing is required to fully evaluate durability performance.

11.1. Carbonation

Figure 206 gives the depths of accelerated carbonation ingress of the pilot-scale processed materials with duration at the exposure conditions outlined in Concrete Test Methods section. These show that after some initial variation the materials performed similarly, with carbonation depths of around 15 mm at 10 weeks seen in each.

Little significant difference between wet-stored and pilot-scale processed materials was observed, regardless of beneficiation. These results suggest that beneficiation does not result in a direct improvement to carbonation resistance at equal strength, but can increase resistance if beneficiated to improve reactivity and give higher strengths in concrete.

11.2. Chloride ingress

Figure 207 gives a comparison of chloride ingress depths for the pilot-scale processed materials. As seen during the carbonation study there appeared to be little difference between wet-stored and beneficiated materials. Therefore, the results suggest beneficiation has little effect on chloride diffusion resistance.

12. Collective analysis of materials

12.1. Particle size and consistence

Figure 208 shows the admixture dose required to achieve S3 slump, compared to the quantity of <10 μm particles of various wet-stored, screened and ball milled materials. While no relationship between the quantity of <10 μm particles and superplasticizing admixture dose could be obtained, visually two trends appear to exist. The wet-stored and <600 μm wet-stored materials with low quantities of <10 μm particles have high superplasticizer requirements, which then decrease significantly after short grinding durations of 10 to 30 minutes. With longer grinding durations, of 60 to 120 minutes, reductions are also achieved, although, this is less than materials ground for shorter durations.

This increase in superplasticizer requirement at longer grinding durations is the result of the significantly increased particle surface area of these materials due to individual fly ash particles being fractured. In comparison, shorter grinding durations have been found to mainly cause de-agglomeration, leaving most individual fly ash particles intact. This can been seen by comparing S.E.M. images of SFA 1 after 10 minutes ball milling in Figure 156 to SFA 1 after ball milling for 120 minutes in Figure 160.

Figure 209 gives the superplasticizer admixture dose and quantity of <10 μm particles of DFA 3, the finest reactive dry material, compared to wet-stored materials after 120 minutes ball milling at equal mix proportions. The ball milled materials had slightly lower, but similar superplasticizer requirements as DFA 3, with slightly higher quantities of <10 μm particles.

12.2. Particle size and concrete cube strength

The relationship between the change in volume of <10 μm particles and 28-day cube strength after ball milling for various durations is given in Figure 210. A general trend was found between the increase in quantity of <10 μm particles and that of 28-day strength, suggesting that the change in <10 μm volume could be used as an indicator of the likely strength increase in concrete after particle size reduction.

While a general relationship was found for all ground materials, some gained greater strength for equivalent increases in volume of <10 μm particles than others due to differences in material characteristics, such as, chemical composition and LOI. Therefore, for significant strength gains of >5 MPa to be reliably achieved at 28-days, an increase in quantity of <10 μm particles of 50 % or greater was required. Wet-stored materials typically have a volume <10 μm particles between 20 – 25 %, which means that to reliably gain strength in concrete, the quantity of <10 μm particles for these materials was required to be ≥70 %.

Figure 211 gives the 28-day strength and quantity of <10 μm particles of DFA 3, the most reactive dry material, compared to the wet-stored materials after 120 minutes ball milling for equal mix proportions. The beneficiated, wet-stored materials exceeded the strength of DFA 3 by 2 – 3 MPa, although, these were finer, with a 10 to 17 % higher volume of <10 μm particles.

13. Summary of results and practical implications

13.1. Laboratory wet-storage

Laboratory wet-storage was found to cause an increase in particle size with storage duration, identified as a decrease in quantity of <10 μm particles and a decrease in fineness. This occurred due to agglomeration of fine fly ash particles as surface products form between particles, as seen in S.E.M. images of both on-site and laboratory wet-stored materials. The fineness values of the laboratory wet-stored materials after 6 months were comparable to that of the on-site wet-stored material and did not decrease much further after 6 months storage. Laboratory wet-storage caused a slight increase in LOI, due to the formation of non-carbon hydrate products that dehydrate during LOI testing. Laboratory wet-storage also led to an increase in water requirement and a corresponding decrease in the consistence of concrete. Laboratory wet-storage led to a decrease in activity index and a slight reduction in concrete strength for most wet-stored fly ash, however, it led to significant reductions in concrete strength of DFA 3 due to a large loss of <10 μm material from agglomeration. Laboratory wet-storage had no notable effect on the bulk oxide composition or mineralogy.

Overall, laboratory wet-storage for 6 months led to a reduction in activity index and a decrease of fineness in most materials, in many cases, to the extent where the materials fail to meet the EN 450-1 limits for these requirements.

13.2. On-site wet-storage

On-site wet-stored materials were found to have similar characteristics to material wet-stored for 6 months or longer in the laboratory. On-site wet-stored materials had undergone agglomeration, as observed during laboratory storage, with carbonation also likely to have occurred to some extent (Sear, 2001) (Schramke, 1992). On-site wet-stored materials typically had a low fineness value (>40 % retained on a 45 μm sieve), a low fines content, high LOI and low reactivity. The bulk oxide composition and mineralogy of dry and on-site wet-stored materials were comparable. On-site wet-stored materials had reduced external surface area, but increased internal surface area due to voids within the fly ash agglomerates. This causes an increased water requirement and reduced consistence in concrete when compared to dry fly ash, as observed during laboratory wet-storage. No significant reductions in concrete strength were observed between the Category N dry fly ash materials and on-site wet-stored materials (in a dry state) at equal w/c ratio.

Overall, on-site wet-stored materials failed to meet many of the requirements in EN 450-1 but could still achieve a similar strength in concrete to that of category N fly ash, requiring only an increased superplasticizing admixture dose to account for the loss of consistence.

13.3. Laboratory processing

13.3.1. Pre-screening

Screening at 600 μm generally gave small improvements to the characteristics and concrete performance of wet-stored materials, as well as improving material homogeneity. Therefore, screening at 600 μm was suitable as a pre-processing stage before further beneficiation such as particle size reduction and carbon removal.

13.3.2. Particle size separation

Screening at 63 μm led to small increases in fineness and in some cases to a small decrease in LOI and increase in activity index. Screening at 63 μm did not result in any strength gains in concrete and was found to be of limited effectiveness as a beneficiation process due to the low throughput and yield obtained from the wet-stored materials.

13.3.3. Particle size reduction

Short duration ball milling

Grinding at durations of 10 to 40 minutes in batches of 125 g was found to increase fineness, increase reactivity and reduce water requirement, while having no effect on LOI. Grinding led to an increased external surface area and a reduction in internal voids by breaking agglomerates, which also led to improved consistence. Grinding for 10 to 40 minutes did not result in any significant strength gains in concrete, when compared to the original wet-stored materials, but did significantly reduce superplasticizing admixture dose require to achieve S3 slump.

Overall, grinding for 20 minutes allowed the wet-stored materials to meet EN 450-1 category N requirements for fineness and activity index.

Long duration ball milling

Grinding for 120 minutes in batches of 50 g was found to significantly increase fineness, creating a high fineness material. This led to increased reactivity and reductions in water requirement. Grinding for 120 minutes gave a large increase in external surface area and reduction in volume of internal voids, by breaking apart a large proportion of agglomerates which also led to an improvement in consistence. Grinding for 120 minutes resulted in reductions in the superplasticizer dose required to achieve an S3 slump and strength gains of 5 MPa or greater at 28 days in concrete, when compared to the original wet-stored materials.

Overall, grinding for 120 minutes allowed wet-stored materials to meet EN 450-1 category N and S requirements for fineness and activity index, while also giving increases in concrete strength.

Micronising

Micronising wet-stored materials in the laboratory increased fineness to a similar degree as ball milling for 20 minutes and increased consistence in concrete, but did not result in any increases in concrete strength.

During processing with the microniser, fine <10 µm material was lost after being suspended in exhaust gases and removed, reducing the yield and effectiveness of the process. Therefore, only limited processing was conducted with this system on a laboratory scale, with further evaluation conducted during pilot-scale processing.

13.3.4. Carbon removal

Carbon removal at 500°C for 1 hour reduced the LOI of most wet-stored materials sufficiently to meet EN 450-1 requirements, except for very high LOI (>13 %) materials. Carbon removal increased activity index, reduced water demand and in some cases increased fineness. Carbon removal also led to small increases in concrete strength at 28 days of 3 MPa and led to improvements in consistence when compared to wet-stored materials.

Overall, carbon removal cannot be adopted as a single beneficiation technique for wet-stored materials to meet EN 450-1 requirements other than LOI, but does give additional small benefits to fly ash characteristics by removing inert, porous carbon.

13.4. Pilot-scale processing

13.4.1. Drying and de-agglomeration

Drying and de-agglomeration increased fineness and improved material handling, by breaking agglomerates and removing moisture, but had little effect on LOI, water requirement or activity index. Dry and de-agglomeration did improve consistence, reducing the quantity of superplasticizer required to achieve an S3 slump, but gave no strength gains in concrete at an equal water/cement ratio.

13.4.2. Air-classification

Air-classification further increased the fineness of dried and de-agglomerated material giving additional benefits, such as; reducing water requirement and increasing activity index, however, it did not result in any appreciable reduction of LOI. Air-classification also led to reductions to superplasticizer dose required to meet S3 slump, but did not give any increases in concrete strength.

13.4.3. Micronising

Micronising produced a high fineness fly ash, further reducing water requirement and significantly increasing activity index compared to the dried and de-agglomerated material. Reductions in superplasticizer dose were also achieved, along with small increases in concrete strength.

13.4.4. Electrostatic separation

Electrostatic separation typically led to a small increase in fineness and activity index, in addition to, reductions in LOI and water requirement. Drying and de-agglomeration, followed by electrostatic separation allowed the feed wet-stored material (SFA 8) to satisfy all EN 450-1 requirements for a Category N fly ash.

13.5. Durability

No significant differences were observed between wet-stored and beneficiated fly ash in carbonation and chloride resistance, with the most important factor for both found to be concrete strength, irrespective of whether the material had been wet-stored. A further detailed study of durability resistance of wet-stored and beneficiated material is required.

14. Conclusions

14.1. Wet-storage

The greatest effect of wet-storage on fly ash is the agglomeration of particles, which leads to further detrimental effects on a range of fly ash characteristics and performance in concrete. As agglomeration occurs, the typical particle size of fly ash increases, often beyond the limits in EN 450-1, and there is a loss of reactive <10 μm material.

During wet-storage, fly ash particles are initially in contact due to cohesion, with chemical reactions then giving surface products between fly ash particles joining them together. These surface products remain after cohesion forces are lost during drying and although they have limited strength, there is little breakdown under normal handling conditions, with a particle size reduction process required to achieve this.

The rate of agglomeration is influenced by the particle size of dry fly ash and localised availability of moisture in the wet-storage location. Materials with a large volume of fine (<10 μm) particles will agglomerate at a faster rate than coarser fractions. The overall rate of this process reduces with time and beyond 6 months little increase is observed.

Agglomeration results in a decrease in fineness, often beyond EN 450-1 limits of 40%, and a reduction in fines content. Both have further implications on other material characteristics and performance in concrete. As agglomeration occurs, the consistence of concrete with wet-stored materials decreases, due to voids within the agglomerates that absorb water. These voids were identified as an increase in specific surface area by nitrogen adsorption with storage duration, as agglomeration occurred, and in CT scans of wet-stored fly ash agglomerates, which show their presence.

The loss of fine particles during agglomeration reduces the reactivity of fly ash due to a loss of surface area available for reaction. This leads to a reduction in activity index of wet-stored fly ash, which can result in failure to meet EN 450-1 limits, although, this also depends on the individual material. The loss in reactivity can be related to reductions in the quantity of <10 μm particles by agglomeration, with greater losses leading to larger reductions in activity index at both 28 and 90 days.

The LOI of fly ash also increases to a small degree during wet-storage, although, this is not a result of an increase in unburned carbon. The increase in LOI during wet-storage is caused by the formation of hydration products, which are also likely to be involved in agglomeration of particles, and do not fully de-hydrate at normal drying temperatures and result in increased LOI values. On-site wet-stored materials will also undergo carbonation which also increases LOI to a small degree but was not seen in the laboratory wet-stored materials.

Wet-storage does not have a significant effect on the bulk oxide composition or mineralogy of fly ash, with only small quantities of calcium sulfate hydrates identified in some wet-stored materials.

The unburned carbon within wet-stored fly ash was found to undergo a change in surface potential, due to electron exchange occurring with water. This appears to cause a reduction in air-entraining agent required to achieve a fixed air-content in fly ash mortar, suggesting that the polar carbon particles now repel the polar end of the air-entertaining agent molecules, compared to the unipolar carbon particles in dry fly ash which adsorb air-entraining agent.

When used in concrete of equal mix proportions to a dry Category N fly ash, wet-stored fly ash had a much lower consistence, requiring a larger superplasticizing admixture dose to achieve equivalent slump. However, the wet-stored materials achieved similar strengths to Category N fly ash using the same mix proportions at all ages.

14.2. Processing

14.2.1. Screening at 63 μm

Screening at 63 μm was unsuitable for beneficiating wet-stored fly ash as it resulted in very low yields, of less than 50 %, and had no benefits to concrete strength performance. Screening at 63 μm increased fineness and gave reductions in water requirement by removing large agglomerates. However, screening at 63 μm gave no significant increases in reactivity or reduction in LOI of most materials. Screening at 63 μm led to reductions in concrete strength, believed to be the result of fine fly ash particle losses during screening.

14.2.2. Screening at 600 μm

Screening wet-stored materials at 600 μm did not give any significant benefits to fly ash characteristics, however, it reduced material variability, improving repeatability of subsequent tests. Screening at 600 μm achieved yields, of typically 75 %, which could be increased further with a form of de-agglomeration before screening. Screening improved the dry handling of wet-stored fly ash by removing large agglomerates, which also increased the effectiveness of further beneficiation, such as, particle size reduction or carbon removal.

Screening at 600 μm gave small benefits increases to fineness, quantity of <10 μm particles and consistence in concrete but had no significant effect on LOI, activity index, specific surface area by nitrogen adsorption, bulk oxide composition, mineralogical composition, or hardened concrete performance.

14.2.3. Grinding

Grinding wet-stored fly ash gave to several fly ash characteristics and performance in concrete. Grinding for short durations in a laboratory ball mill led to reduced particle size, lowered water requirement and increased activity index but had no effect on LOI, bulk oxide composition or mineralogical composition. When evaluated in concrete, material ground for short durations had a significantly lower superplasticizing admixture requirement compared to wet-stored materials, but did not achieve increases in concrete strength.

Screening at 600 μm and grinding for a longer duration in the ball mill of 120 minutes resulted in benefits to fly ash characteristics while also giving increases in concrete strength. Long duration grinding increased fineness to <0.5 % retained on a 45 μm sieve and increased the volume of <10 μm particles to >70 % in the wet-stored materials. This did not give any further reductions in water requirement, but increased activity index, due to greater particle surface area. Grinding for longer durations had no effect on bulk oxide or mineralogical composition, as seen during short durations. Long duration grinding led to a similar reduction in superplasticizing admixture dose required to achieve S3 slump, to material ground for shorter durations, and gave an increase in concrete strength compared to wet-stored material at all ages.

14.2.4. Carbon removal

Carbon removal in the laboratory furnace at a temperature of 500°C for 1 hour reduced LOI of most wet-stored materials to below 7 %. Carbon removal also led to slight increases in fineness, decreases in water requirement and small increases in activity index. When evaluated in concrete, materials that had undergone carbon removal had slightly lower superplasticizing admixture requirements and gave small increases in cube strength. No significant effects on bulk oxide and mineralogical composition were observed after carbon removal.

14.3. Pilot-scale processing

The pilot-scale processing trial demonstrated that EN 450-1 material could be successfully produced from a wet-stored U.K. fly ash, as well as confirming the results observed during laboratory beneficiation are achievable on a larger scale. The initial beneficiation stage, of drying and de-agglomeration produced fly ash which satisfied all EN 450-1 requirements except activity index, which it failed to meet at both test ages. Although, it is of note that the finest 10 % of the material was lost during drying and de-agglomeration, which if collected, may have allowed the dried and de-agglomerated material to satisfy activity index requirements. Drying and de-agglomeration did not result in any strength gains in concrete, compared to wet-stored material, however, they did reduce the superplasticizing admixture dose required to achieve an S3 slump. Carbon removal by electrostatic separation of the dried and de-agglomerated material, to an LOI of 3 %, resulted in increased reactivity, enough to meet EN 450-1 activity index requirements. Therefore, drying and de-agglomeration followed by carbon removal could be used to produce an EN 450-1 Category N fly ash from a wet-stored feed material.

Air-classification after drying and de-agglomeration to remove coarse material produced a fly ash which satisfied all EN 450-1 requirements for Category N material. Air-classification further increased fineness, reduced water requirement and increased activity index, but did not result in strength gains in concrete.

Grinding the dried and de-agglomerated material in a micronising mill led to large increases in the quantity of <10 µm particles, activity index and concrete strength. This system produced the highest performance output fly ash, but had a low throughput. Carbon removal by electrostatic separation of the micronised material did not result in any benefits beyond the reduction of LOI.

14.4. Durability

Wet-storage and the beneficiation of wet-stored materials did not appear to significantly affect resistance to carbonation or chlorides ingress for materials of similar concrete strength. The performance of the materials evaluated depended on the concrete strength. It should be recognised that the durability tests were carried out to provide an initial insight to behaviour and further work is required in this area.

15. Future Work

Laboratory evaluation of wet-stored fly ash in concrete suggests comparable strengths to a EN 450-1 Category N dry fly ash can be achieved, provided adjustments are made for the increased water demand with a higher superplasticizing admixture dose. Further study to identify the optimal fly ash replacement level for beneficiated, wet-stored material for a variety of applications would be of benefit. Higher replacement levels are likely to be suitable for low performance applications, however, wet-stored fly ash may prove unsuitable for high performance applications, even at low replacement levels of <15 %. There may also be an upper limit of percentage of wet-stored material that can be included as an addition in concrete before detrimental effects are seen during strength development or for durability. A study evaluating the effects of replacement level and w/c ratio on concrete performance would allow beneficiated, wet-stored material to be fully compared to dry fly ash.

The limited durability investigation carried out in this project was made on a small group of materials, using accelerated test methods. A full durability study investigating natural carbonation, chloride diffusion, freeze-thaw resistance, alkali-aggregate reaction, sulfate resistance and permeability should be established to determine wet-storage effects on the use of fly ash for concrete in aggressive environments. Additionally, a small investigation into drying shrinkage, creep and abrasion resistance of concrete could be conducted to identify if wet-storage has a detrimental effect on these properties.

Finally, establishing a standardised test regime that can be implemented when evaluating a wet-storage location before large-scale recovery and beneficiation is recommended. The ability to evaluate the degree of beneficiation required and the suitability of the material for recovery would allow for more confidence when selecting suitable wet-storage locations or adjusting the beneficiation for specific materials.

This report has outlined the typical characteristics and performance of wet-stored materials and the relationships found between the quantity of <10 µm particles and mortar reactivity and concrete strength. However, these relationships were often general trends, and there exists the need for a more robust rapid assessment technique for the likely performance of wet-stored materials in concrete. Establishing a reliable rapid assessment test would allow for a quick evaluation of the currently available material to determine the most suitable areas and the beneficiation processes best suited for recovery.

16. References

Alberici, S., de Beer, J. & Staats, M., 2017. *Fly ash and Blast Furnace Slag for Cement Manufacturing,* London: Department for Business, Energy & Industrial Strategy.

Atritor Ltd, 2018. *Atritor Dryer-Pulveriser.* [Online]
Available at: http://www.atritor.com/en/products/atritor
[Accessed 11 October 2016].

Atritor Ltd, 2018. *Microniser.* [Online]
Available at: http://www.atritor.com/literature/en/microniser_en.pdf
[Accessed 11 October 2016].

Aydin, S., Karatay, C. & Baradan, B., 2010. The effect of grinding process on mechanical properties and alkali-silica reaction resistance of fly ash incorporated mortars. *Powder Technology,* 197(1-2), pp. 68-72.

Baker, L., Bittner, J., Gupta, A. & Gasiorowski, S., 2014. *Triboelectrostatic beneficiation of landfilled ash.* Essen, Germany, Eurocoal Ash.

Ballirano, P. & Melis, E., 2009. Thermal behaviour and kinetics of dehydration in air of bassanite, calcium sulphate hemihydrate (CaSO4.0.5H2O), from X-ray powder diffraction. *European Journal of Mineralogy,* 21(5), pp. 985-993.

Bittner, J., Gasiorowski, S. & Hrach, F., 2009. *Fly Ash Carbon Separation and Ammonia Removal at TAmpa Electric Big Bend.* Lexington, World of Coal Ash.

Borde, I. & Levy, A., 2006. 16: Pneumatic and Flash Drying. In: A. Mujumdar, ed. *Handbook of Industrial Drying.* Abingdon: Taylor & Francis Group, LLC, pp. 397 - 410.

BSI, 2000. *BS EN 12390-4 Part 4: Compressive strength - Specification for testing machines,* London: British Standards Institution.

BSI, 2005. *BS EN 196-1 Methods of testing cement Part 1: Determination of strength,* London: British Standards Institution.

BSI, 2009. *BS EN 12350-2 Part 2: Testing fresh concrete. Slump - test,* London: British Standards Institution.

BSI, 2009. *BS EN 12350-6 Part 6: Testing fresh concrete. Density,* London: British Standards Institute.

BSI, 2009. *BS EN 12390-2 Part 2 Making and curing specimens for strength tests,* London: British Standards Institution.

BSI, 2009. *BS EN 12390-3 Part 3: Compressive strength of test specimens,* London: British Standards Institution.

BSI, 2011. *BS EN 197-1 Cement Part 1: Composition, specification and conformity criteria for concrete,* London: BSI Standards Publication.

BSI, 2012. *BS 1881-210 Part 131: Determination of the potential carbonation resistance of concrete. Accelerated carbonation method,* London: British Standards Institution.

BSI, 2012. *BS EN 12390-1 Testing hardened concrete Part 1 : Shape, dimensions and other requirements for specimens and moulds,* London: British Standards Institution.

BSI, 2012. *BS EN 450-1 Fly Ash for concrete, Part 1: Definition, specifications and conformity criteria,* London: British Standards Institution.

BSI, 2012. *BS EN 934-2,* London: British Standards Institute.

BSI, 2013. *BS 1881-125:2013 Cement and concrete technology, Concretes, Sampling methods, Mixing, Laboratory testing, Specimen preparatrion,* London: British Standard Institute.

BSI, 2013. *BS EN 196-2 Part 2: Method of testing cement. Chemical analysis of cement,* London: British Standards Institution.

BSI, 2015. *BS EN 12390-11 Part 11: Testing hardened concrete. Determination of the chloride resistance of concrete, unidirectional diffusion,* London: British Standards Institution.

BSI, 2017. *BS EN 451-1 Part 1: Method of testing fly ash. Determination of free calcium oxide content,* London: British Standards Institution.

BSI, 2017. *BS EN 451-2 Part 2: Determination of fineness by wet-sieving,* London: British Standards Institution.

Cammarota, A., Chirone, R., Solimene, R. & Urciulol, M., 2008. Beneficiation of pulverized coal combustion fly ash in fluidised bed reactors. *Experimental Thermal and Fluid Science,* Volume 32, pp. 1324-1333.

Cangialosi, F. et al., 2005. *Combustion Reactivity of Unburned Carbon in Coal Combustion Fly Ashes.* Lexington, World of Coal Ash.

Cangialosi, F. et al., 2005. *Characterisitcs of Fly Ashes and Processing Conditions Affecting Carbon-Ash Separation under Pneumatic Transport, Triboelectric Processing.* Lexington, Kentucky, World of Coal Ash.

Carroll, R., 2015. *Coal combustion Products in the United Kingdom and the Potential of Stockpile Ash.* Nashville, TN, World of Coal Ash.

Cheerarot, R. & Jaturapitakkul, C., 2004. A study of disposed fly ash from landfill tro replace Portland cement. *Waste Management,* 24(7), pp. 701-709.

Fedorka, W., Knowles, J. & Castleman, J., 2013. *Staged Turbulent Air Reactor (STAR) Beneficiation Process - Commerical Update.* Lexington, World of Coal Ash.

Fedorka, W., Knowles, J. & Castleman, J., 2015. *Reclaiming and Recycling Coal Fly Ash for Beneficial Reuse with the STAR Process.* Nashville, Tennessee, World of Coal Ash (WOCA).

Feng, X. & Clark, B., 2011. *Evaluation of the Physical and Chemical Properties of Fly Ash Products for Use in Portland Cement Concrete.* Denver, Colorado, World of Coal Ash, pp. May 9-11.

Foldvari, M., 2011. *Handbook of thermogravimetric system of minerals and its use in geological practice,* Budapest: Geological Institute of Hungary.

Gao, Y., Shim, H., Hurt, R. & Suuberg, E., 1997. Effects of Carbon on Air Entrainment in Fly Ash Concrete: The Role of Soot and Carbon Black. *Energy & Fuels,* Volume 11, pp. 457-462.

Georgakopoulos, A. et al., 2002. Leachability of Major and Trace Elements of Fly Ash from Ptolemais Power Station, Northen Greece. *Energy Sources,* 24(2), pp. 103-113.

Gitari, M. et al., 2009. *Chemical Weathering In A Dry Ash Dump: An Insight From Physicochemical and Mineralogical Analysis Of Drilled Cores.* Lexington, Kentucky, USA, World of Coal Ash (WOCA).

Hachmann, L. et al., 1998. Surfactant Adsorptivity of Solid Products from Pulverized-Coal Combustion under Controlled Conditions. *Symposim (International) on Combustion,* 27(2), pp. 2965-2971.

Helmuth, R., 1987. *Fly Ash in Cement and Concrete.* First ed. Skokie, Illinios, U.S.A: Portland Cement Association.

Hosokawa Micron Powder Systems, 1998. Homing in on the Best Size Reduction Method. *Engineering Practice*, November.

Infodrive India, 2018. *Fly Ash Exporters, Suppliers & Manufacturing Companies in India.* [Online]
Available at: https://www.infodriveindia.com/indian-exporters/fly-ash-exporters.aspx
[Accessed 24 April 2018].

Insider Media Limited, 2013. *Rocktron Group Enters Administration.* [Online]
Available at: https://www.insidermedia.com/insider/northwest/102773-south-wales-failure-forces-rocktron-administration-and-redundancies
[Accessed 20 January 2018].

Jaturapitakkul, C., Kiattikomol, K., Sata, V. & Leekeeratikul, T., 2004. Use of ground coarse fly ash as a replacement of condensed silica fume in producing high-strength concrete. *Cement and Concrete Research,* 34(4), pp. 549-555.

Kiattikomol, K., Jaturapitakkul, C., Songpiriyakij, S. & Chutubtim, ,. S., 2001. A study of ground coarse fly ashes with different finenesses from various sources as pozzolanic materials. *Cement and Concrete Composites,* Volume 23, pp. 335-343.

Kudra, T. & Mujumdar, A., 2006. Special Drying Techniques and Novel Dryers. In: A. Mujumdar, ed. *Handbook of Industrial Drying.* Boca Raton, Florida: CRC Press, pp. 454 - 514.

McCarthy, M. et al., 2013. Characterising long-term wet-stored fly ash following carbon and particle size separation. *Fuel,* Volume 111, pp. 430-441.

McCarthy, M., Sadiqul Islam, G., Csetenyi, L. & Jones, M., 2012. Colorimetric evaluation of admixture adsorption by fly ash for use in air-entrained concrete. *Materials and Structures,* p. 45.

McCarthy, M., Sadiqul Islam, G., Csetenyi, L. & Jones, M., 2013. *Evaluating Test Methods for Rapidly Assessing Fly Ash Reactivity for Use in Concrete.* Lexington, World of Coal Ash.

McCarthy, M., Tittle, P. & Dhir, R., 1999. Characterization of conditioned pulverized fuel ash for use as a cement component in concrete. *Magazine of Concrete Research,* 51(3), pp. 191-206.

McCarthy, M., Tittle, P. & Dhir, R., 2000. Influences of conditioned pulverized-fuel ash as a cement component on the properties of concrete. *Magazine of Concrete Research,* 52(5), pp. 329-343.

McCarthy, M., Zheng, L., Dhir, R. & Tella, G., 2018. Dry-processing of long-term wet-stored fly ash for use as an addition in concrete. *Cement and Concrete Composites,* Volume 92, pp. 205-215.

Menendez, J., 2014. *Electrical charge distribution on carbon surfaces as a function of the pH and point of zero charge. An approximate solution,* Madrid: Digital.CSIC.

Metso Corporation, 2018. 3. Size Control. In: *Basics in Minerals Processing.* Helsinki: Metso Corporation, p. 3:25.

Morales, J., Watts, A. & McConville, J., 2012. Chapter 4: Mechanical Particle-Size Reduction Techniques. In: R. Williams, A. Watts & D. Miller, eds. *Formulating Poorly Water Soluble Drugs.* New York: Springer, pp. 165-214.

Mucsi, G., 2016. Mechanical activation of power station fly ash by grinding - a review. *Journal of Silicate Based and Composite Materials,* 68(2), pp. 56-61.

NT Build, 1999. *Concrete, mortar and cement-based repair materials: Chloride migration coefficient from non-steady-state migration experiments ,* s.l.: Nordtest.

P. Eze, C. et al., 2013. Chemical, mineralogical and morphological changes in weather coal fly ash: A case study of a brine impacted wet ash dump. *Journal of Environmental Management,* Volume 129, pp. 479-792.

Paya, J., Monzo, J., Borrachero, M. & Peris-Mora, E., 1995. Mechanical Treatment of Fly Ahse. Part I: Physico-Chemical Characterisation of Ground Fly Ashes. *Cement and Concrete Research,* 25(7), pp. 1469-1479.

Paya, J. et al., 1996. Mechanical Treatment of Fly Ashes Part II: Particle morphologies in ground fly ashes (GFA) and workability of GFA-cement mortars. *Cement and Concrete Research,* 26(2), pp. 225-235.

Peng, G., Chan, S. & Anson, M., 2001. Chemical kinetics of C-S-H decomposition in hardened cement paste subjected to elevated temperatures up to 800°C. *Advances in Cement Research,* 13(2), pp. 47-52.

Ramezanianpour, A. A., 2014. Chapter 2 - Fly Ash. In: *Cement Replacement Materials - Properties, Durability, Sustainability.* Berlin: Springer-Verlag Berlin Heidelberg, pp. 47-156.

Roy, W. & Berger, P., 2011. Geochemical Controls of Coal Fly Ash Leachate pH. *Coal Combustion and Gasification Products,* Volume 3, pp. 63-66.

Saravacos, G. & Kostaropoulos, A., 2016. Mechanical Processing Equiptment. In: G. Saravacos & A. Kostaropoulos, eds. *Handbook of Food Processing Equiptment.* Cham, Switzerland: Springer, pp. 149 - 232.

Schramke, J., 1992. Neutralization of alkaline coal fly ash leachates by CO2(g). *Applied Geochemistry,* 7(5), pp. 481-492.

Sear, L., 2001. The production and properties of fly ash. In: L. Sear, ed. *The properties and use of coal fly ash.* London: Thomas Telford, p. 10.

Sear, L. K. A., 2001. Chapter 1: The production and properties of fly ash. In: L. Sear, ed. *The properties and use of coal fly ash.* London: Thomas Telford Publishing, pp. 1-29.

Shaprio, M. & Galperin, V., 2005. Air classification of solid particles: a review. *Chemical Engineering and Processing,* Volume 44, pp. 279-285.

Soong, Y. et al., 2002. Dry beneficiation of high loss-on-ignition fly ash. *Separation and Purification Technology,* Volume 26, pp. 177-184.

Spears, D., 1997. Natural weathering of pulverized fuel ash and porewater evolution. *Applied Geochemistry,* 12(4), pp. 367-376.

Sun, H. et al., 2013. Jet milling grinding of Portland cement, limestone, and fly ash: Impact on particle size, hydration rate, and strength. *Cement & Concrete Composites,* Volume 44, pp. 41-49.

Taylor, P. et al., 2006. *Identifying Incompatible Combinations of Concrete Materials: Volume II - Test Protocol,* Skokie, IL: US Department of Transportation, Fedral Highway Administration.

The Associated Press, 2017. *Coal ash: 'Why in the world would be importing it?'.* [Online]
Available at: https://wtop.com/virginia/2017/03/coal-ash-why-in-the-world-would-we-be-importing-it/

U.K. Qualtity Ash Association, 2016. *UKQAA Ash Availability Report,* Wolverhampton, U.K.: U.K. Quality Ash Association.

Valix, M., Cheung, W. & McKay, G., 2004. Preparation of activated carbon using low temperature carbonisation and physical activation of high ash raw bagasse for acid dye adsorption. *Chemosphere,* pp. 493 - 501.

Zevenbergen, C. B. J., Piet van Reeuwijk, L. S. A., Hjelmar, O. & Conmans, R., 1999. Clay Formation and Metal Fixation during Weathering of Coal Fly Ash. *Enironmental Scieence and Technology,* Volume 33, pp. 3405-3409.

Zhang, L. et al., 2012. Electrostatic beneficiation of fly ash in a free-falling system. *Particuology,* Volume 10, pp. 154-160.

17. Appendix A Tables

Table 1 - Typical bulk oxide composition of fly ash (Feng & Clark, 2011)

	Portland cement % by mass	Fly ash % by mass
CaO	64.01	0.37 - 27.68
SiO_2	20.13	27.88 - 59.4
Al_2O_3	5.78	5.23 - 33.99
Fe_2O_3	2.35	1.21 - 29.63
MgO	1.19	0.42 - 8.79
SO_3	3.53	0.04 - 4.71
Na_2O	0.11	0.20 - 6.90
K_2O	0.77	0.64 - 6.68
TiO_2	0.37	0.24 - 1.73
LOI	1.63	0.21 - 28.37

17.1. Experimental Details

Table 2 - Oxide composition of laboratory Hanson Portland Cement

Property	Composition, %
SiO_2	18.6
Al_2O_2	4
Fe_2O_3	3.2
CaO	59.1
MgO	2.3
SO_3	3.9
K_2O	0.7
Na_2O	0.3
TiO_2	0.3

Table 3 - Selective properties of laboratory aggregates used in concrete

Material	Passing 600 µm sieve, %	Particle density, kg/m^3	Absorption, %
10-20 mm gravel	0.1	2610	1.3
4-10 mm gravel	0.1	2600	1.4
Sand pre-May 2016	60	2630	0.8
Sand May 2016 - present	44	2610	1.1

Table 4 - Select characteristics of dry fly ash materials

Property	DFA 1	DFA 2	DFA 3	DFA 4	DFA 5	DFA 6	DFA 7	DFA 8
Fineness□, %	33.9	8.1	5.7	19.1	18.4	18.7	21.2	25.3
Water requirement, %	97	93	100	109	104	100	100	100
PSD d_{10}, µm	2.5	1.6	0.9	2.8	3.3	2.7	2.5	2.5
PSD d_{50}, µm	39.4	11.5	4.3	25.3	23.9	20.5	21.7	22.2
PSD d_{90}, µm	199.4	62.7	98.6	145.9	81.1	82.0	90.9	118.4
Quant. <10 µm particles, %	24.1	42.1	61.8	31.0	29.0	29.3	31.0	29.3
SSA B.E.T.*, m^2/g	5.4	2.4	3.0	6.3	3.3	1.2	4.2	1.8
Moisture content, %	0.1	0.1	0.5	0.5	0.0	0.1	0.2	0.0
LOI, %	8.3	3.3	5.6	14.4	13.6	3.9	6.8	4.7
Activity index 28-day, %	85	85	92	80	80	78	81	79
Activity index 90-day, %	89	99	109	87	91	93	91	91

□Retained on a 45 µm mesh sieve
*Specific surface area measured by nitrogen adsorption (B.E.T.)

Table 5 - Selective characteristics of on-site wet-stored fly ash materials

Property	SFA 1	SFA 2	SFA 3	SFA 4	SFA 5	SFA 6	SFA 7	SFA 8
Mean fineness[□], %	53.8	47.9	49.6	41.1	42.0	63.2	41.9	62.3
Minimum fineness[□], %	48.9	39.8	42.4	24.9	31.4	52.5	39.5	51.9
Maximum fineness[□], %	67.1	55.2	55.6	43.8	48.3	76.6	44.9	74.0
Water requirement, %	109	109	109	108	100	106	100	103
PSD d_{10}, μm	4.6	3.5	3.2	3.5	4.5	5.0	3.2	4.2
PSD d_{50}, μm	30.0	38.7	30.9	28.9	28.5	29.4	29.7	33.0
PSD d_{90}, μm	120.0	140.9	130.1	94.5	86.7	104.2	121.1	120.8
Quant. <10 μm particles, %	20.1	20.1	22.6	24.3	21.7	19.3	23.6	21.8
SSA B.E.T.*, m^2/g	7.7	7.3	13.5	6.4	3.9	5.4	4.8	6.5
Moisture content, %	12.7	21.1	17.7	15.7	6.0	19.8	17.6	15.7
LOI, %	9.7	8.9	10.6	15.9	5.8	3.5	7.0	5.5
Activity index 28-day, %	74	71	71	78	83	72	79	70
Activity index 90-day, %	83	86	82	81	90	82	89	80

[□]Retained on a 45 μm mesh sieve
*Specific surface area measured by nitrogen adsorption (B.E.T.)

Table 6 - Selective characteristics of on-site wet-stored lagoon materials

Property	LFA 1	LFA 3	LFA 5	LFA 6
Mean fineness[□], %	50.0	49.9	56.9	45.2
Minimum fineness[□], %	46.3	44.6	56.5	42.6
Maximum fineness[□], %	70.5	42.8	69.9	48.2
Water requirement, %	-	-	103	-
PSD d_{10}, μm	6.6	4.4	3.7	4.4
PSD d_{50}, μm	48.3	34.7	21.0	31.0
PSD d_{90}, μm	155.0	133.0	82.1	153.6
Quant. <10 μm particles, %	13.3	19.7	21.8	19.3
SSA B.E.T.*, m^2/g	9.8	11.1	13.5	9.5
Moisture content, %	30.5	34.8	23.8	18.5
LOI, %	10.7	9.8	9.4	10.7
Activity index 28-day, %	70	78	86	78
Activity index 90-day, %	81	87	95	87

[□]Retained on a 45 μm mesh sieve
*Specific surface area measured by nitrogen adsorption (B.E.T.)

Table 7 - Concrete mix proportions of 0.5 water/cement ratio, 2350 kg/m³ plastic density

Mix proportions up to May 2016, kg/m³						
Total cementitious	PC	Fly ash	Free water	Aggregates		
				20-10mm	10-5mm	Sand
345	241	103	172	793	399	640

Table 8 - Concrete mix proportions of 0.53 water/cement ratio, 2350 kg/m³ plastic density

Mix proportions May 2016 onwards, kg/m3						
Total cementitious	PC	Fly ash	Free water	Aggregates		Sand
				20-10mm	10-5mm	
350	245	105	184	791	395	639

Table 9 - Summary of test methods used during the project

Material / Property	Method	Test Arrangement
Fineness	BS EN 451-2	Wet-sieving for 1 minute through a 45 µm mesh sieve at 75 kPa.
Loss-on-Ignition, LOI	BS EN 196-2	Ignition of sample carried out at 950 ± 25 °C
Water requirement	BS EN 450-1 Annex B	30 % fly ash mortar flow compared to a PC reference mortar
Activity index	BS EN 196-1	25 % fly ash mortar strength tested at 28 and 90 days compared with a PC reference
Specific surface area of particles	B.E.T.	Surface area determined by nitrogen adsorption
Particle size distribution	Laser particle size analysis	Particle size distribution determined by laser diffraction
Mineralogy	X-ray diffraction	Monochromatic x-rays with a Cu Kα source directed at sample and reflected x-rays
Bulk oxides composition	X-ray fluorescence	x-ray fluorescence spectrometer with Rh Kα source
Hydration products	Thermogravimetric analysis	Determination of compounds present by mass loss at various temperatures
Morphology	Scanning electron microscopy	Scanning electron microscope with 15 kV accelerating voltage with a Link System Si (Li)
Consistence (Slump)	BS EN 12350-2 2009	Reduction in height after removal of cone taken as slump value
Compressive Strength	BS EN 12350-3 2009	Cube compressive strengths tested to 90 days

Table 10 - 45 µm sieve retention results for SFA 1

45 µm sieve retention test results for SFA 1, %							Maximum	Mean	Minimum	Maximum
48.9	49.1	49.8	58.1	58.2	58.8	67.1	18.1	53.8	48.9	67.1

Table 11 - Mineralogy of dry fly ash materials

Composition, %	DFA 1	DFA 2	DFA 3	DFA 4	DFA 5	DFA 6	DFA 7	DFA 8
Quartz	10.3	6.2	5.1	6.9	1.6	3.0	5.2	9.8
Mullite	10.2	6.0	4.7	3.4	6.4	10.6	6.5	8.8
Hematite	2.1	1.4	2.0	0.6	2.8	0.9	1.2	2.3
Magnetite	0.2	0.1	0.1	0.1	0.0	0.2	0.1	0.3
Bassanite	0.0	0.0	0.2	0.0	0.2	0.0	0.0	0.0
Other	77.2	86.3	87.8	89.0	89.1	85.4	86.9	78.9
Glass (Other -LOI)	68.9	83.0	82.2	74.7	75.5	81.4	80.2	74.2

17.2. Laboratory wet-storage

Table 12 - Summary of materials and moistening combinations used for laboratory wet-storage

Initial Moisture content, %	DFA 1	DFA 3	DFA 4	DFA 5	DFA 6	DFA 8
10	✓	✓	✓	✓	✓	✓
15				✓		
20			✓	✓		

Table 13 - Gradient of agglomeration of laboratory wet-stored materials on a logarithmic scale with storage duration

Gradient on log scale	Moisture content		
	10 %	15 %	20 %
DFA 1 LS	2.70	-	-
DFA 3 LS	4.44	-	-
DFA 4 LS	4.59	-	4.01
DFA 5 LS	2.25	4.00	4.44
DFA 6 LS	2.99	-	-
DFA 8 LS	3.13	-	-

Table 14 - Bulk oxide composition of DFA 4 laboratory wet-stored at 20% moisture content up to 24 months

Composition, %	DFA 4	DFA 4 LS-1D 20%	DFA 4 LS-7D 20%	DFA 4 LS-1M 20%	DFA 4 LS-3M 20%	DFA 4 LS-6M 20%	DFA 4 LS-24M 20%
SiO_2	48.8	51.7	47.8	50.9	47.1	49.3	48.8
Al_2O_3	17.9	18.1	18.1	18.0	17.6	17.4	18.3
Fe_2O_3	6.5	6.6	6.2	6.5	6.3	9.1	6.3
CaO	2.5	2.9	2.9	3.2	2.9	2.5	2.4
MgO	1.5	1.6	1.5	1.7	1.7	1.5	1.7
TiO_2	0.9	0.8	0.9	0.8	0.9	0.8	0.9
P_2O_5	0.4	0.4	0.4	0.4	0.5	0.4	0.4
K_2O	2.0	1.9	2.1	1.8	2.0	1.8	2.1
Na_2O	1.1	1.0	1.0	0.9	1.0	0.9	0.9
SO_3	2.9	3.7	3.3	4.7	3.2	3.9	2.0
$\Sigma\ Al_2O_{3\,+}SiO_2 + Fe_2O_3$	73.3	76.4	72.1	75.4	71.1	75.8	73.4
Na_2O_{eq}	2.4	2.2	2.4	2.1	2.3	2.1	2.3

Table 15 - Mineralogy of DFA 4 laboratory wet-stored at 10% moisture content up to 24 months

Composition, %	DFA 4	DFA 4 LS-1D 10%*	DFA 4 LS-7D 10%	DFA 4 LS-1M 10%	DFA 4 LS-3M 10%	DFA 4 LS-6M 10%	DFA 4 LS-24M 10%
Quartz	10.9	10.8	11.0	11.1	15.3	16.2	11.3
Mullite	5.3	5.2	4.1	5.4	8.2	7.0	5.6
Hematite	1.1	1.3	1.3	1.4	2.1	1.7	1.5
Magnetite	0.0	0.0	0.1	0.2	0.0	0.2	0.0
Bassanite	0.7	2.2	0.9	1.1	0.0	1.9	0.8
Others	82.0	80.5	82.6	81.0	74.4	73.0	80.8
LOI	14.4	15.5	15.3	15.8	15.8	15.2	14.5
Amorphous Glass	67.6	65.0	67.3	65.1	58.6	57.8	66.3

*code: DFA 4 LS-1D 10 % - DFA 4 laboratory wet-stored for 1 day at 10 % initial moisture content

17.3. On-site, wet-storage

Table 16 - Summary of on-site wet-stored material characteristics

Property	SFA 1	SFA 2	SFA 3	SFA 4	SFA 5	SFA 6	SFA 7	SFA 8
Fineness[□], %	53.8	47.9	49.6	41.1	42.0	63.2	41.9	62.3
Water Requirement, %	109	109	109	108	108	106	102	103
PSD d_{10}, µm	4.6	3.5	3.2	3.5	3.3	5.0	3.2	4.2
PSD d_{50}, µm	30.0	38.7	30.9	28.9	21.7	29.4	29.7	33.0
PSD d_{90}, µm	120.0	140.9	130.1	94.5	96.3	104.2	121.1	120.8
Quant. <10 µm particles, %	20.1	20.1	22.6	24.3	23.8	19.3	23.6	21.8
SSA B.E.T.*, m^2/g	7.7	7.3	13.5	6.4	3.9	5.4	4.8	6.5
Moisture Content, %	12.7	21.1	17.7	15.7	6.0	19.8	17.6	15.7
LOI, %	9.7	8.9	10.6	15.9	5.7	3.5	6.9	5.5
Foam index, ml	0.08	0.06	0.18	0.26	0.16	0.04	0.04	0.04
Activity Index 28-day, %	74	71	71	78	83	72	79	70
Activity Index 90-day, %	83	86	82	81	90	82	89	80

[□]Retained on a 45 µm mesh sieve

*Specific surface area measured by nitrogen adsorption (B.E.T.)

Table 17 - Particle size data for on-site wet-stored materials

Property	SFA 1	SFA 2	SFA 3	SFA 4	SFA 5	SFA 6	SFA 7	SFA 8
Mean fineness[□], %	53.8	47.9	49.6	41.1	42.0	63.2	41.9	62.3
Minimum fineness[□], %	48.9	39.8	42.4	24.9	31.4	52.5	39.5	51.9
Maximum fineness[□], %	67.1	55.2	55.6	43.8	42.8	76.6	44.9	74.0
Max variation, %	18.2	15.4	13.2	19.0	9.5	24.1	5.4	22.1
PSD d_{10} µm	4.6	3.5	3.2	3.5	3.3	5.0	3.2	4.2
PSD d_{50} µm	30.0	38.7	30.9	28.9	21.7	29.4	29.7	33.0
PSD d_{90} µm	120.0	140.9	130.1	94.5	96.3	104.2	121.1	120.8
Quant. <10 µm particles, %	20.1	20.1	22.6	24.3	23.8	19.3	23.6	21.8

Table 18 - Variability of laser diffraction data between three samples of SFA 2

Property	SFA 2 A	SFA 2 B	SFA 2 C
PSD d_{10} μm	3.5	5.4	3.8
PSD d_{50} μm	38.7	47.4	45.6
PSD d_{90} μm	140.9	205.7	170.4

Table 19 - Bulk oxide compositions of on-site wet-stored materials

Composition, %	SFA 1	SFA 2	SFA 3	SFA 4	SFA 5	SFA 6	SFA 7	SFA 8
SiO_2	44.3	43.7	47.4	41.2	51.2	49.6	48.2	46.5
Al_2O_3	21.8	22.9	19.5	22.7	22.7	25.2	23.6	24.5
Fe_2O_3	9.0	9.4	8.0	7.4	5.8	6.2	8.8	8.4
CaO	4.4	2.3	3.3	2.1	2.1	4.3	2.5	2.8
MgO	1.6	1.5	1.6	1.0	1.4	1.3	1.5	1.6
TiO_2	1.1	1.0	0.8	0.9	1.0	1.2	0.9	1.0
P_2O_5	0.6	0.4	0.7	0.8	0.2	0.9	0.3	0.4
K_2O	2.0	2.4	2.0	2.3	2.8	1.7	2.8	2.5
Na_2O	0.8	0.7	0.9	1.0	1.0	1.1	0.8	0.9
SO_3	1.6	1.3	2.3	1.4	1.7	1.6	0.8	1.8
$\Sigma\ Al_2O_3 + SiO_2 + Fe_2O_3$	75.1	76.0	74.9	71.3	79.7	81.1	80.5	79.4
Na_2O_{eq}	2.1	2.3	2.2	2.5	2.8	2.2	2.7	2.5

Table 20 – The mean and range of oxide compositions for the on-site wet-stored and dry materials evaluated during the project

Composition, %	SFA Average	SFA Min	SFA Max	DFA Average	DFA Min	DFA Max
SiO_2	46.5	41.2	51.2	46.9	41.3	50.1
Al_2O_3	22.9	19.5	25.2	21.9	17.9	25.3
Fe_2O_3	7.9	5.8	9.4	7.4	6.2	9.5
CaO	3.0	2.1	4.4	3.4	2.1	6.2
MgO	1.4	1.0	1.6	1.5	0.9	1.8
TiO_2	1.0	0.8	1.2	0.9	0.9	0.9
P_2O_5	0.5	0.2	0.9	0.6	0.2	0.9
Na_2O	0.9	0.7	1.1	1.1	0.6	1.7
K_2O	2.3	1.7	2.8	2.3	1.9	2.7
SO_3	1.6	0.8	2.3	1.7	0.6	2.9
$\Sigma\ Al_2O_3 + SiO_2 + Fe_2O_3$	77.3	71.3	81.1	76.2	71.3	80.1
Na_2O_{eq}	2.4	2.1	2.8	2.6	1.9	3.3

Table 21 - Mineralogy of on-site wet-stored materials

Composition, %	SFA 1	SFA 2	SFA 3	SFA 4	SFA 5	SFA 6	SFA 7	SFA 8
Quartz	4.3	7.5	8.9	1.1	11.7	11.4	8.0	4.3
Mullite	7.0	10.0	6.4	3.2	10.4	17.0	10.0	9.3
Hematite	1.7	1.7	1.1	0.5	1.4	1.9	1.5	1.4
Magnetite	0.2	0.0	0.3	0.1	0.2	0.2	0.1	0.1
Bassanite	0.1	0.2	0.5	0.3	0.0	0.0	0.0	0.0
Other	86.9	80.6	82.8	94.8	76.3	69.4	80.4	84.9
Glass (Other -LOI)	77.2	71.7	72.1	79.0	70.5	65.9	73.5	79.4

Table 22 - Concrete strength of on-site wet-stored materials using mix proportions outlined in Table 8

Concrete strength, MPa	SFA 1	SFA 2	SFA 3	SFA 4	SFA 5	SFA 6	SFA 8
3 days	18.0	18.0	-	18.5	15.5	18.5	-
7 days	23.5	24.0	22.5	25.0	21.5	24.5	23.5
28 days	33.0	31.5	32.5	34.0	30.0	33.0	32.5
56 days	39.0	36.5	34.5	38.5	34.5	38.5	37.5
90 days	41.5	39.5	38.0	42.0	36.5	40.5	40.0

17.4. Laboratory processing

17.4.1. Pre-screening

Table 23 - Yields obtained for on-site wet-stored materials after screening at 600 μm

Fly Ash	Initial, g	<600μm, g	Yield <600μm, %
SFA 1	393	169	43
SFA 2	487	322	66
SFA 3	471	238	51
SFA 4	2017	1208	60
SFA 5	501	311	62
SFA 7	538	48	89

Table 24 - Range of 45 μm sieve retention results of on-site wet-stored materials before and after screening at 600 μm

45 μm sieve retention results range	SFA 1	SFA 2	SFA 4	SFA 5	SFA 6	SFA 7	LFA 5
Unscreened	18.1	15.4	18.9	16.9	24.1	5.4	13.4
<600 μm	6.9	0.8	8.1	0.8	1.0	6.9	0.3

Table 25 - Bulk oxide compositions for on-site materials screened at 600 μm

Composition, %	SFA 1	SFA 2	SFA 4	SFA 1 <600 μm	SFA 2 <600 μm	SFA 4 <600 μm
SiO_2	44.3	43.7	41.2	42.7	47.0	42.9
Al_2O_3	21.8	22.9	22.7	20.9	25.0	23.3
Fe_2O_3	9.0	9.4	7.4	8.8	8.6	7.6
CaO	4.4	2.3	2.1	5.1	2.5	2.0
MgO	1.6	1.5	1.0	2.1	1.8	1.1
TiO_2	1.1	1.0	0.9	1.0	1.0	0.9
P_2O_5	0.6	0.4	0.8	0.6	0.4	0.9
K_2O	2.0	2.4	2.3	2.0	2.5	2.1
Na_2O	0.8	0.7	1.0	0.9	0.9	1.0
SO_3	1.6	1.3	1.4	1.9	1.0	1.0
$\Sigma\ Al_2O_{3\,+}\ SiO_2 + Fe_2O_3$	75.1	76.0	71.3	72.5	80.6	73.8
Na_2O_{eq}	2.1	2.3	2.5	2.2	2.5	2.4

Table 26 - Mineralogy of on-site wet-stored materials screened at 600 μm

Composition, %	SFA 1	SFA 2	SFA 4	SFA 1 <600 μm	SFA 2 <600 μm	SFA 4 <600 μm
Quartz	4.3	7.5	1.1	4.6	7.3	2.2
Mullite	7.0	10.0	3.2	6.5	13.9	6.8
Hematite	1.7	1.7	0.5	1.5	3.1	1.1
Magnetite	0.2	0.0	0.1	0.0	0.1	0.2
Bassanite	0.1	0.2	0.3	0.1	0.1	1.3
Other	86.9	80.6	94.9	87.3	75.5	88.3
Glass (Other -LOI)	77.2	71.7	79.0	77.5	66.3	72.0

17.4.2. Particle size separation

Table 27 - Summary of on-site materials screened at 63 µm

Property	SFA 1 <63µm	SFA 2 <63µm	SFA 3 <63µm	SFA 4 <63µm	SFA 5 <63µm	LFA 5 <63µm
Fineness[□], %	9.2	6.4	8.6	8.5	3.4	6.6
Water requirement, %	104	100	103	104	98	100
PSD d_{10} µm	4.0	2.4	5.4	4.6	4.8	3.1
PSD d_{50} µm	20.9	18.6	22.4	24.2	18.1	17.3
PSD d_{90} µm	54.2	56.7	50.8	57.0	45.2	51.3
Quant. <10 µm particles, %	21.7	30.1	16.6	18.5	24.4	31.8
SSA B.E.T.*, m^2/g	4.9	6.4	8.1	5.5	3.6	-
LOI, %	8.9	6.0	7.4	15.0	4.3	7.5
28-day activity index, %	-	-	-	-	80	89
90-day activity index, %	-	-	-	-	93	95

[□]Retained on a 45 µm mesh sieve
*Specific surface area measured by nitrogen adsorption (B.E.T.)

Table 28 - Yields obtained for select on-site wet-stored materials after screening at 63 µm

	Initial, g	<63 µm, g	Yield, %
SFA 1	1095	438	40
SFA 2	992	308	31
SFA 3	1426	239	17
SFA 4	894	424	47

Table 29 - Bulk oxide composition for on-site materials screened at 63 μm

	SFA 1	SFA 2	SFA 4	SFA 1 <63μm	SFA 2 <63μm	SFA 4 <63μm
SiO_2	44.3	43.7	41.2	46.4	49.0	42.4
Al_2O_3	21.8	22.9	22.7	23.0	26.2	23.1
Fe_2O_3	9.0	9.4	7.4	9.3	9.6	8.1
CaO	4.4	2.3	2.1	5.0	2.4	2.4
MgO	1.6	1.5	1.0	1.7	1.8	1.1
TiO_2	1.1	1.0	0.9	0.8	0.9	0.9
P_2O_5	0.6	0.4	0.8	0.6	0.4	0.9
K_2O	2.0	2.4	2.3	2.3	2.8	2.3
Na_2O	0.8	0.7	1.0	0.8	0.7	0.9
SO_3	1.6	1.3	1.4	1.6	0.5	1.3
$\Sigma\ Al_2O_{3\,+}\ SiO_2 + Fe_2O_3$	75.1	76.0	71.3	78.8	84.8	73.7
Na_2O_{eq}	2.12	2.31	2.46	2.32	2.54	2.43

Table 30 - Mineralogy of on-site wet-stored materials screened at 63 μm

	SFA 1	SFA 2	SFA 4	SFA 1 <63μm	SFA 2 <63μm	SFA 4 <63μm
Quartz	4.3	7.5	1.1	5.4	11.6	2.0
Mullite	7.0	10.0	3.2	7.3	13.4	5.6
Hematite	1.7	1.7	0.5	2.0	1.7	1.4
Magnetite	0.2	0.0	0.1	0.2	0.1	0.2
Bassanite	0.1	0.2	0.3	0.2	0.0	0.4
Other	86.7	80.6	94.9	85.0	73.1	90.4
Glass (Other -LOI)	77.2	71.7	79.0	76.1	67.1	75.4

17.4.3. Particle size reduction

Table 31 - Characteristics of on-site wet-stored materials ball milled for 120 minutes

Property	SFA 1 <600 µm	SFA 1 <600µm BM120	SFA 2 <600 µm	SFA 2 <600µm BM120	SFA 6 <600 µm	SFA 6 <600µm BM120
Fineness□, %	52.7	0.0	36.0	0.0	44.3	0.2
Water requirement, %	109	105	104	103	-	-
PSD SSA, m^2/kg	0.39	1.26	0.37	1.12	0.40	1.08
PSD d_{10}, µm	3.2	0.7	3.6	0.9	4.4	1.0
PSD d_{50}, µm	31.5	5.0	33.8	5.0	28.0	4.9
PSD d_{90}, µm	128.8	20.8	144.5	16.1	95.2	13.9
Quant. <10 µm particles, %	23.3	71.0	22.1	74.1	20.7	79.0
SSA B.E.T.*, m^2/g	9.8	6.6	7.5	5.9	5.8	4.6
LOI, %	9.8	10.2	8.9	9.2	4.4	4.6
28-day Activity index, %	74	91	80	91	72	99
90-day Activity index, %	83	106	85	121	82	121

□Retained on a 45 µm mesh sieve
*Specific surface area measured by nitrogen adsorption (B.E.T.)

Table 32 - Laser diffraction analysis data for select wet-stored materials after micronising

Property	SFA 1	SFA 1 SJM	SFA 5	SFA 5 SJM	SFA 6	SFA 6 SJM
Quant. <10 µm particles, %	20.1	38.4	23.8	41.9	19.3	31.9
PSD SSA*, m^2/kg	0.337	0.621	0.424	0.585	0.337	0.655
PSD d_{10}, µm	4.6	2.0	3.3	2.2	5.0	3.0
PSD d_{50}, µm	30.0	14.1	21.7	12.3	29.4	16.7
PSD d_{90}, µm	120.0	64.1	96.3	49.9	104.2	62.5

*Specific surface area measured by laser diffraction (PSD)

Table 33 - Change in LOI observed after ball milling for 120 minutes in 50 g batches

LOI, %	SFA 1 <600 µm	SFA 2 <600 µm	SFA 6 <600 µm
Before ball milling	9.8	8.9	4.4
After ball milling	10.2	9.2	4.6

Table 34 - Specific surface area results for selective on-site wet-stored materials after ball milling in 125 g batches for 10 to 40 minutes

B.E.T. SSA*, m^2/g	Grinding duration, minutes				
	0	10	20	30	40
SFA 1	7.7	7.7	8.1	8.6	7.3
SFA 2	7.3	7.4	6.4	5.9	6.1
SFA 4	6.4	6.5	5.6	6.4	6

*Specific surface area measured by Nitrogen Adsorption (B.E.T.)

Table 35 - Activity index results for on-site wet-stored materials after ball milling for 20 minutes at a batch size of 125 g

	SFA 1	SFA 1 BM20	SFA 2	SFA 2 BM20	SFA 3	SFA 3 BM20	SFA 4	SFA 4 BM20
28-day activity index, %	74	84	71	78	71	81	78	87
90-day activity index, %	83	101	86	97	82	100	81	101

Table 36 - Bulk oxide compositions of SFA 1 <600 µm and SFA 2 <600 µm before and after ball milling for 120 minutes in 50 g batches

Composition, %	SFA 1 <600 µm	SFA 1 <600µm BM120	SFA 2 <600 µm	SFA 2 <600µm BM120
SiO_2	42.7	46.0	47.0	49.4
Al_2O_3	20.9	21.7	25.0	24.8
Fe_2O_3	8.8	9.9	8.6	9.4
CaO	5.1	5.3	2.5	2.6
MgO	2.1	2.0	1.8	1.8
TiO_2	1.0	1.0	1.0	1.0
P_2O_5	0.6	0.6	0.4	0.3
K_2O	2.0	2.1	2.5	2.5
Na_2O	0.9	1.6	0.9	0.9
SO_3	1.9	2.3	1.0	1.3
$\Sigma\ Al_2O_{3\ +}\ SiO_2 + Fe_2O_3$	72.5	77.5	80.6	83.6
Na_2O_{eq}	2.2	2.9	2.5	2.5

Table 37 - Mineralogy of SFA 1 <600 μm and SFA 2 <600 μm before and after ball milling for 120 minutes in 50 g batches

Composition, %	SFA 1 <600 μm	SFA 1 BM120	SFA 2 <600 μm	SFA 2 BM120
Quartz	4.6	4.4	7.3	10.4
Mullite	6.5	7.3	13.9	14.7
Hematite	1.5	2.2	3.1	3.0
Magnetite	0.0	0.2	0.1	0.2
Bassanite	0.1	0.0	0.1	0.0
Other	87.3	85.9	75.5	71.7
Glass (Other -LOI)	77.5	75.7	66.6	62.5

Table 38 - Concrete cube strengths for SFA 1 and SFA 2 after ball milling in 125 g batches for 10 to 30 minutes using mix proportions outlined in Table 7

Concrete strength, MPa	SFA 1	SFA 1 BM10	SFA 1 BM20	SFA 1 BM30	SFA 2	SFA 2 BM10	SFA 2 BM20	SFA 2 BM30
3 days	19.5	20.5	20.0	17.0	19.0	20.0	20.5	19.5
7 days	28.5	26.5	23.5	25.5	24.5	24.0	27.5	25.0
28 days	38.0	39.0	37.0	38.5	37.5	36.5	39.5	39.0
56 days	44.5	44.0	43.5	44.0	42.5	46.0	47.5	45.5
90 days	48.0	44.0	48.5	48.0	45.5	45.0	47.0	49.5

Table 39 - Concrete strength of on-site wet-stored materials after ball milling for 120 minutes

Concrete strength, MPa	SFA 1 <600 μm	SFA 1 <600μm BM120	SFA 2 <600 μm	SFA 2 <600μm BM120	SFA 6 <600 μm	SFA 6 <600 μm BM120
28 days	35.5	41.5	32.5	40.0	33.5	41.0
56 days	40.5	46.0	37.0	45.0	40.5	45.5
90 days	41.5	51.0	41.5	50.5	43.5	48.5

17.4.4. Carbon removal

Table 40 - Bulk oxide compositions of SFA 5 and SFA 7 after carbon removal at 500°C/1hr

Composition, %	SFA 5	SFA 5 500°C/1hr	SFA 7	SFA 7 500°C/1hr
SiO_2	51.2	53.0	48.2	48.5
Al_2O_3	22.7	23.6	23.6	23.3
Fe_2O_3	5.8	5.8	8.8	8.7
CaO	2.1	2.0	2.5	2.6
MgO	1.4	1.4	1.5	1.5
TiO_2	1.0	1.0	0.9	0.9
P_2O_5	0.2	0.2	0.3	0.3
K_2O	2.8	2.8	2.8	2.8
Na_2O	1.0	0.7	0.8	0.9
SO_3	1.7	0.7	0.8	1.5
$\Sigma\ Al_2O_{3\,+}\ SiO_2 + Fe_2O_3$	79.7	82.4	80.5	80.4
Na_2O_{eq}	2.8	2.5	2.7	2.7

Table 41 - Mineralogy of SFA 5 and SFA 7 after carbon removal at 500°C/1hr

Composition, %	SFA 5	SFA 5 500°C/1hr	SFA 7	SFA 7 500°C/1hr
Quartz	11.7	10.6	8.0	6.3
Mullite	10.4	12.1	10.0	6.6
Hematite	1.4	0.5	1.5	1.1
Magnetite	0.2	0.0	0.1	0.1
Bassanite	0.0	0.0	0.0	0.1
Other	76.3	76.8	80.4	85.9
Glass (Other -LOI)	70.6	72.0	73.5	81.2

Table 42 - Concrete strength of on-site wet-stored materials after carbon removal at 500°C for 1 hour

Concrete strength, MPa	SFA 2	SFA 2 <600µm 500°C/1hr	SFA 5	SFA 5 <600µm 500°C/1hr	SFA 7	SFA 7 <600µm 500°C/1hr
3 days	18.0	-	17.5	18.5	17.5	19.0
7 days	24.0	23.5	24.0	25.5	24.0	25.5
28 days	31.5	33.0	34.5	37.5	33.0	36.0
56 days	34.5	38.5	42.5	-	42.5	42.0
90 days	36.5	42.5	44.5	-	44.5	45.0

17.5. Pilot-scale trial

Table 43 - Details of pilot-scale trial materials

Material	Processes used	Details
SFA 8	Screened at 500 µm	Wet-stored pilot-scale processing feed material
PFA 2	Dryer-pulveriser	Flash dried and de-agglomeration
PFA 3	Dryer-pulveriser and air classifier	Flash dried, de-agglomerated and air-classified
PFA 4	Dryer-pulveriser and microniser	Flash dried, de-agglomerated and ground in the micronisier (spiral jet mill)
PFA 5	Dryer-pulveriser and air classifier	Over-size material from air-classifier
PFA 2 LC	Dryer-pulveriser, air classifier and electrostatic separation	Low carbon output from electrostatic separation of PFA 2
PFA 2 HC	Dryer-pulveriser, air classifier and electrostatic separation	High carbon output from electrostatic separation of PFA 2
PFA 4 LC	Dryer-pulveriser, air classifier and electrostatic separation	Low carbon output from electrostatic separation of PFA 4
PFA 4 HC	Dryer-pulveriser, air classifier and electrostatic separation	High carbon output from electrostatic separation of PFA 4

Table 44 - Summary of the characteristics of pilot-scale trial materials

Property	PFA 2	PFA 3	PFA 4	PFA 5	SFA 8
LOI %	6.1	6.3	6.6	4.7	6.3
Fineness[□], %	30.6	1.5	0.6	56.0	62.3
PSD d_{10}, μm	5.6	3.7	1.8	29.2	4.2
PSD d_{50}, μm	33.2	13.8	7.1	58.0	33.0
PSD d_{90}, μm	104.4	40.3	14.2	111.0	120.8
Quant. <10 μm particles, %	19.7	36.5	71.8	0.0	21.8
SSA B.E.T.*, m^2/g	6.2	6.2	4.5	3.0	6.5
Measured carbon, %	5.0	4.9	4.6	-	4.8
Water demand, %	102	100	98	100	103
28-day Mortar strength, MPa	37.2	37.0	39.6	-	33.5
90-day Mortar strength, MPa	46.4	53.7	55.3	-	44.5
28-day Activity index, %	70	75	80	-	70
90-day Activity index, %	83	88	108	-	80

[□]Retained on a 45 μm mesh sieve
*Specific surface area measured by nitrogen adsorption (B.E.T.)

Table 45 - Summary of characteristics of pilot-scale trial materials after electrostatic separation

Property	PFA 2 LC	PFA 2 HC	PFA 4 LC	PFA 4 HC
LOI %	3.1	7.2	3.3	6.7
Fineness[□], %	30.8	42.5	4.4	5.9
PSD d_{10}, μm	2.3	2.1	4.1	7.7
PSD d_{50}, μm	9.2	8.1	24.9	41.0
PSD d_{90}, μm	19.5	17.2	89.8	111.2
<10 μm content, %	26.5	13.8	54.9	62.8
SSA B.E.T.*, m^2/g	3.8	4.4	3.4	3.9
28-day Activity index, %	75	73	80	76
90-day Activity index, %	93	82	104	99

[□]Retained on a 45 μm mesh sieve
*Specific surface area measured by nitrogen adsorption (B.E.T.)

Table 46 - LOI and carbon content of pilot-scale trial materials

Property	PFA 2	PFA 3	PFA 4	SFA 8
LOI, %	6.1	6.3	6.6	6.3
Carbon content, %	5	4.9	4.6	4.8

Table 47 - Activity index values of pilot-scale trial materials

Property	PFA 2	PFA 3	PFA 4	SFA 8	PFA 2 LC	PFA 2 HC	PFA 4 LC	PFA 4 HC
28-days Activity index, %	70	75	80	70	75	73	80	76
90-days Activity index, %	83	88	103	80	93	82	104	99

Table 48 - Bulk oxide compositions of pilot-scale trial materials

Composition, %	SFA 8	PFA 2	PFA 3	PFA 4
SiO_2	46.5	46.5	45.3	46.9
Al_2O_3	24.5	23.5	24.4	23.6
Fe_2O_3	8.4	9.1	8.3	10.0
CaO	2.8	3.0	2.5	2.6
MgO	1.6	1.6	1.5	1.5
TiO_2	1.0	1.0	1.0	1.0
P_2O_5	0.4	0.4	0.4	0.3
K_2O	2.5	2.7	2.5	2.4
Na_2O	0.9	1.0	0.8	0.7
SO_3	1.8	1.4	1.2	1.4
$\Sigma\ Al_2O_{3+}SiO_2 + Fe_2O_3$	79.4	79.1	77.9	80.6
Na_2O_{eq}	2.5	2.7	2.5	2.3

Table 49 - Mineralogy of pilot-scale trial materials

Composition, %	SFA 8	PFA 2	PFA 3	PFA 4
Quartz	4.3	5.8	4.2	5.8
Mullite	9.3	8.6	10.9	10.4
Hematite	1.4	1.6	1.8	3.0
Magnetite	0.1	0.0	0.1	0.2
Bassanite	0.0	0.0	0.5	0.0
Other	84.9	84.0	82.5	80.6
Glass (Other -LOI)	78.6	77.9	76.2	74.0

Table 50 - Concrete cube strength of pilot-scale materials, mix proportions given in Table 8

Concrete	PFA 2	PFA 3	PFA 4	SFA 8	SFA 8 Wet
7-day	22.5	23.0	22.0	23.5	23.0
28-day	31.5	31.0	34.5	32.5	31.5
56-day	37.5	37.0	39.0	37.5	37.5
90-day	39.0	41.0	43.0	40.0	40.0

Table 51 - Concrete cube strength of pilot-scale material with adjusted water/cement ratio

Concrete strength, MPa	PFA 2 0.51 w/c	PFA 3 0.51 w/c	PFA 4 0.49 w/c	SFA 8 0.53 w/c
3-days	19.5	20.0	22.0	16.0
7-days	25.5	25.5	29.0	23.0
28-days	35.0	37.0	42.5	32.5
56-days	40.5	40.5	46.5	37.0
90-days	42.5	44.5	50.5	40.5

18. Appendix B Figures

18.1. Materials
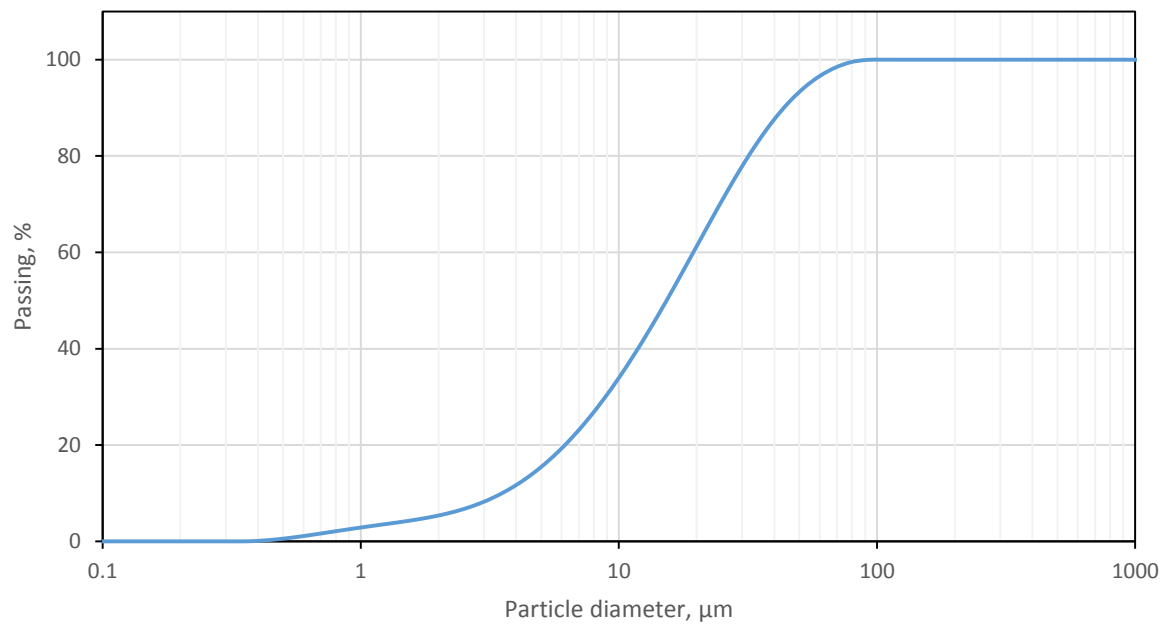
Figure 1 - Particle size distribution of Portland cement
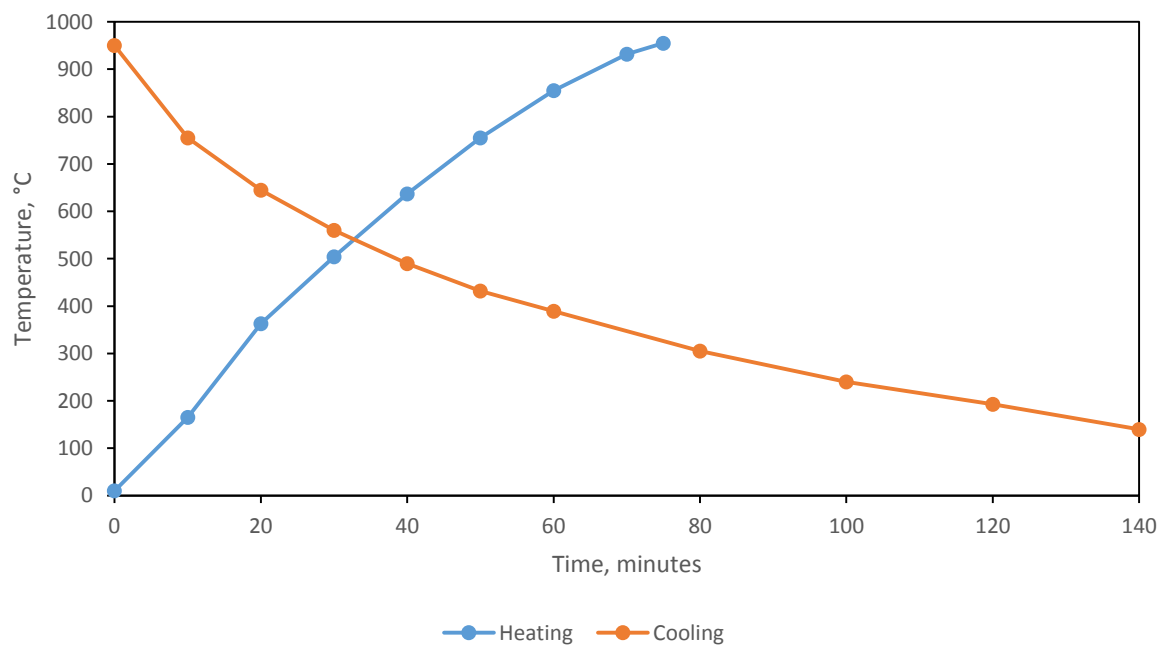
Figure 2 - Time taken for the laboratory furnace to heat to 950°C and cool back to <200°C

18.2. Wet-storage effects
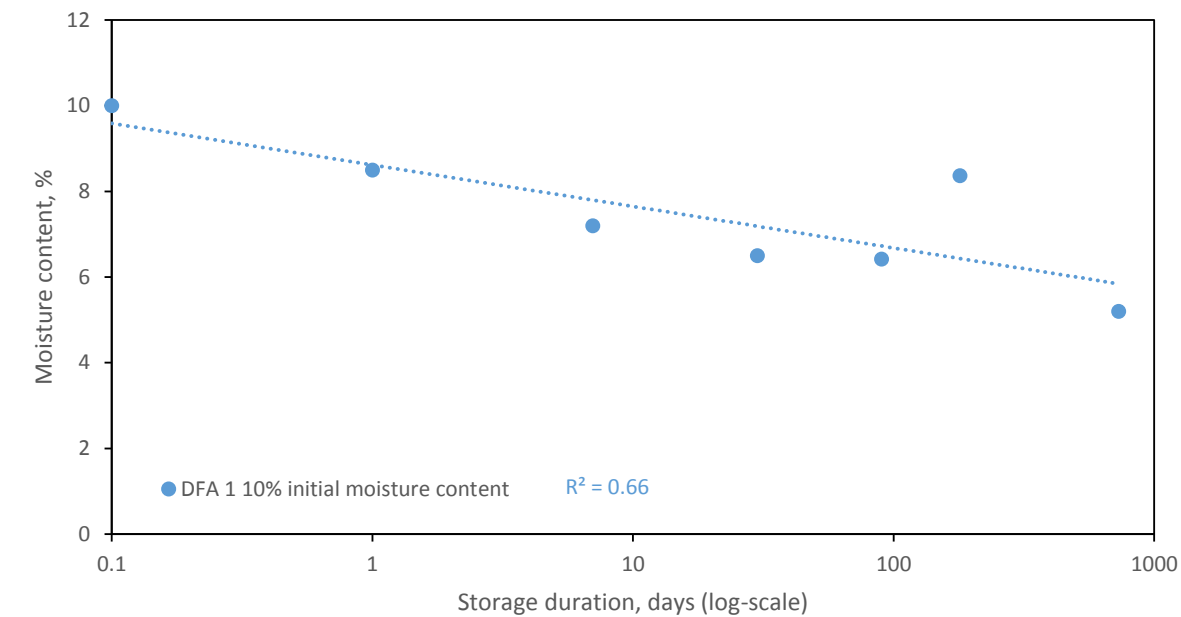
Figure 3 - Relationship between storage duration and moisture content for DFA 1 laboratory wet-stored at 10% moisture
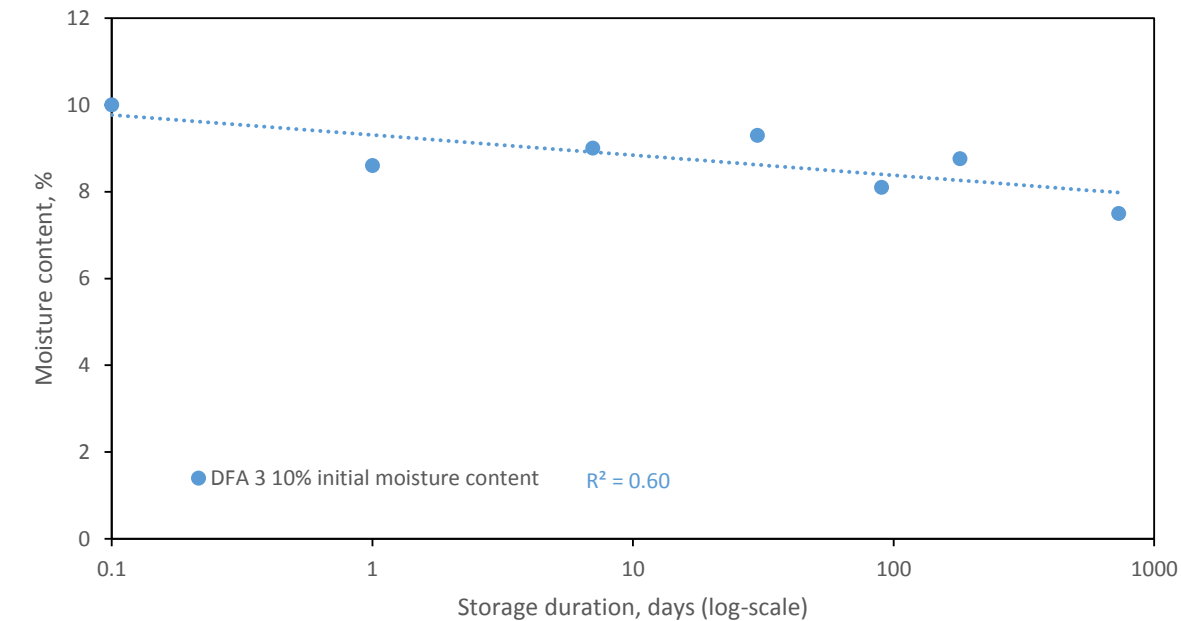
Figure 4 - Relationship between storage duration and moisture content for DFA 3 laboratory wet-stored at 10% moisture
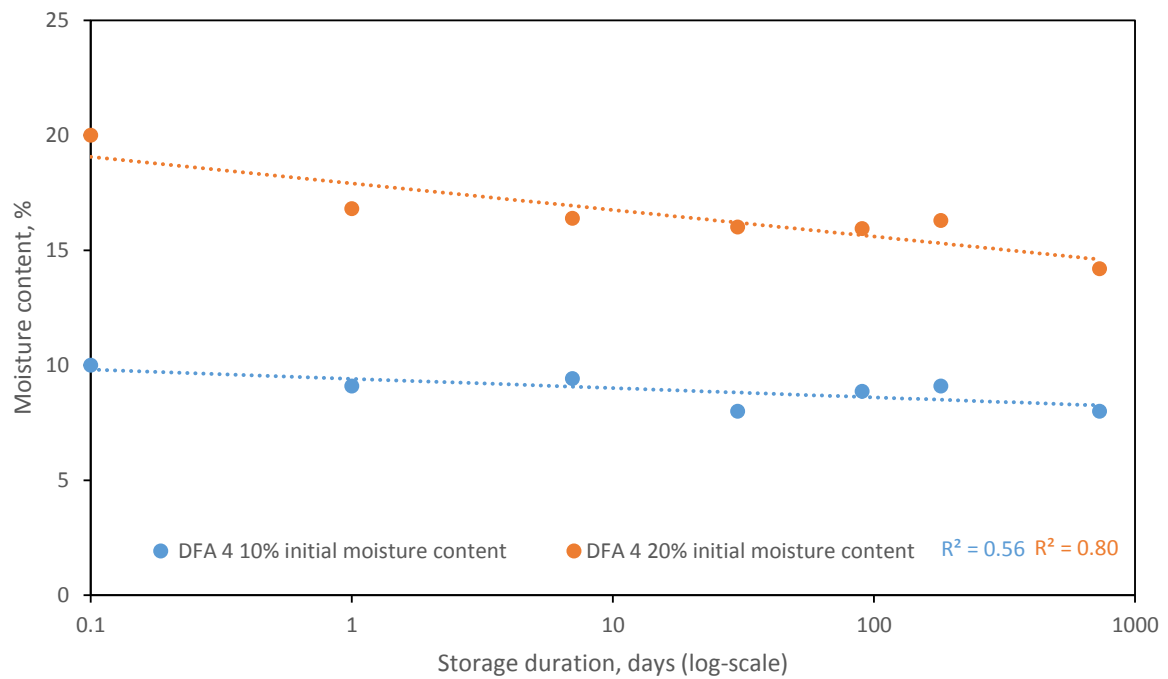
Figure 5 - Relationship between storage duration and moisture content for DFA 4 laboratory wet-stored at 10 and 20% moisture
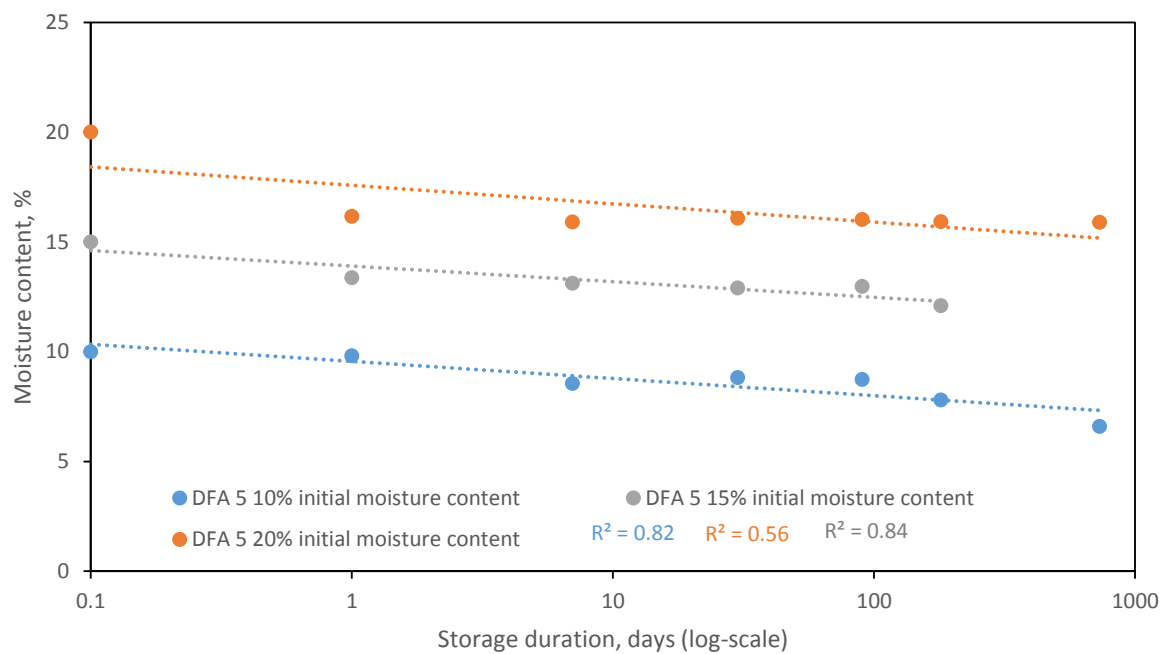
Figure 6 - Relationship between storage duration and moisture content for DFA 5 laboratory wet-stored at 10, 15 and 20% moisture

120
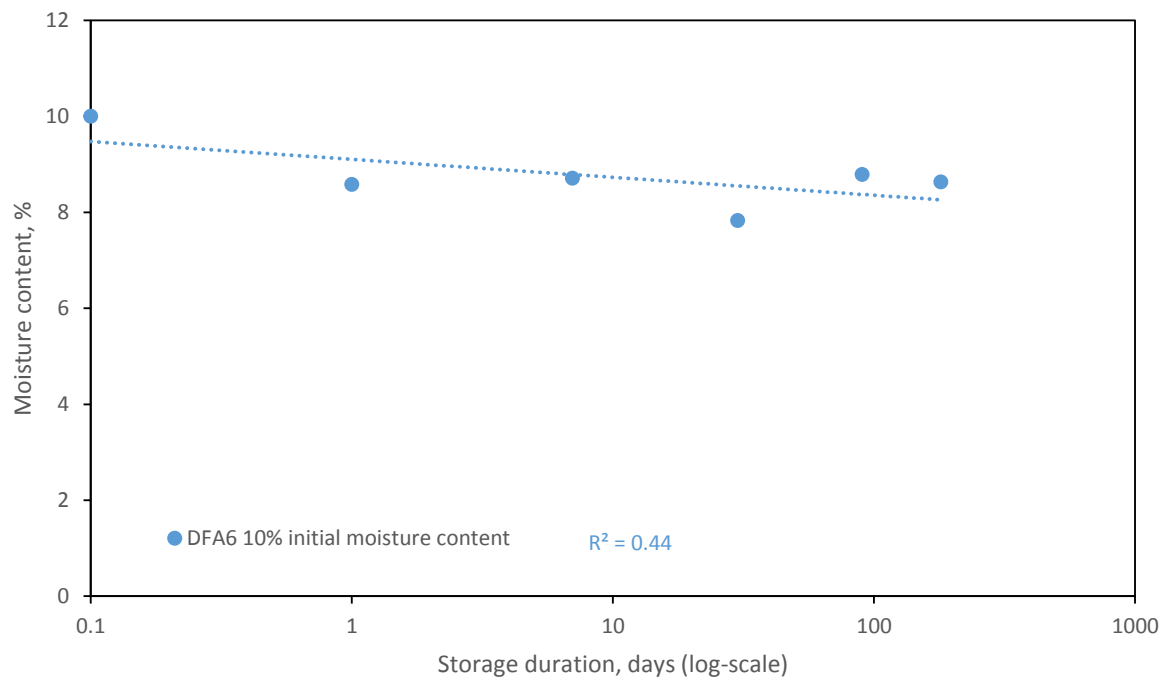
Figure 7 - Relationship between moisture content and storage duration for DFA 6 laboratory wet-stored at 10% moisture
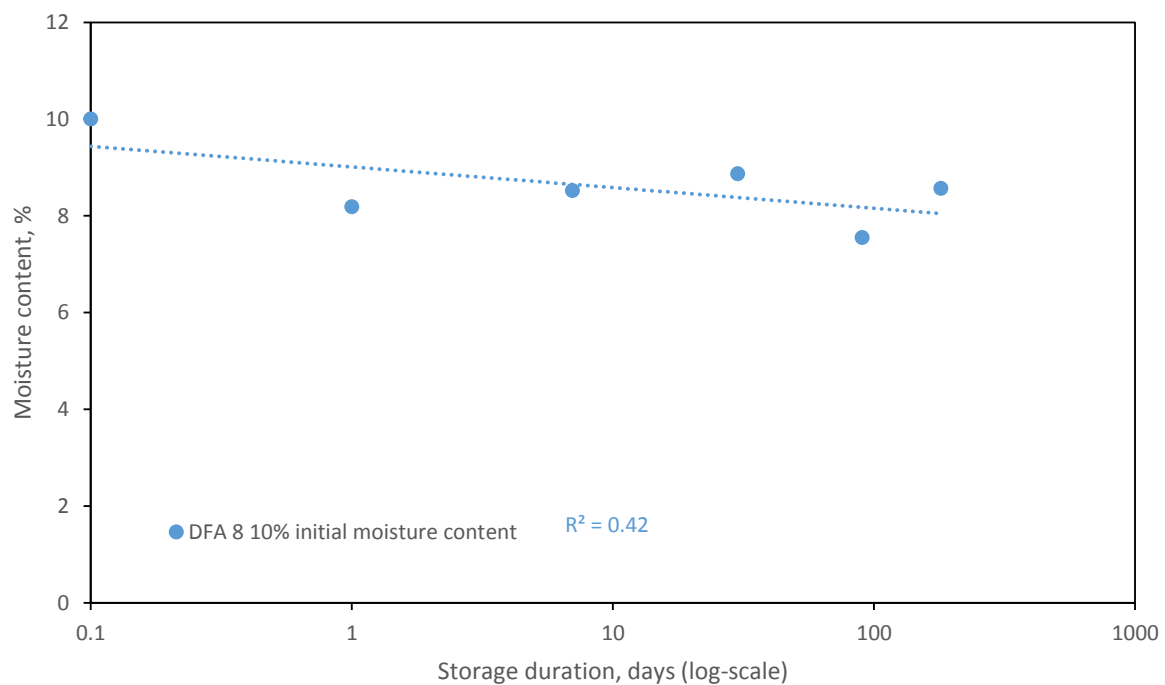
Figure 8 - Relationship between moisture content and storage duration for DFA 8 laboratory wet-stored at 10% moisture

121

In Figure 9 to 14 the plotted points represent the mean fineness, with the error bars representing the maximum and minimum fineness result recorded for each material.
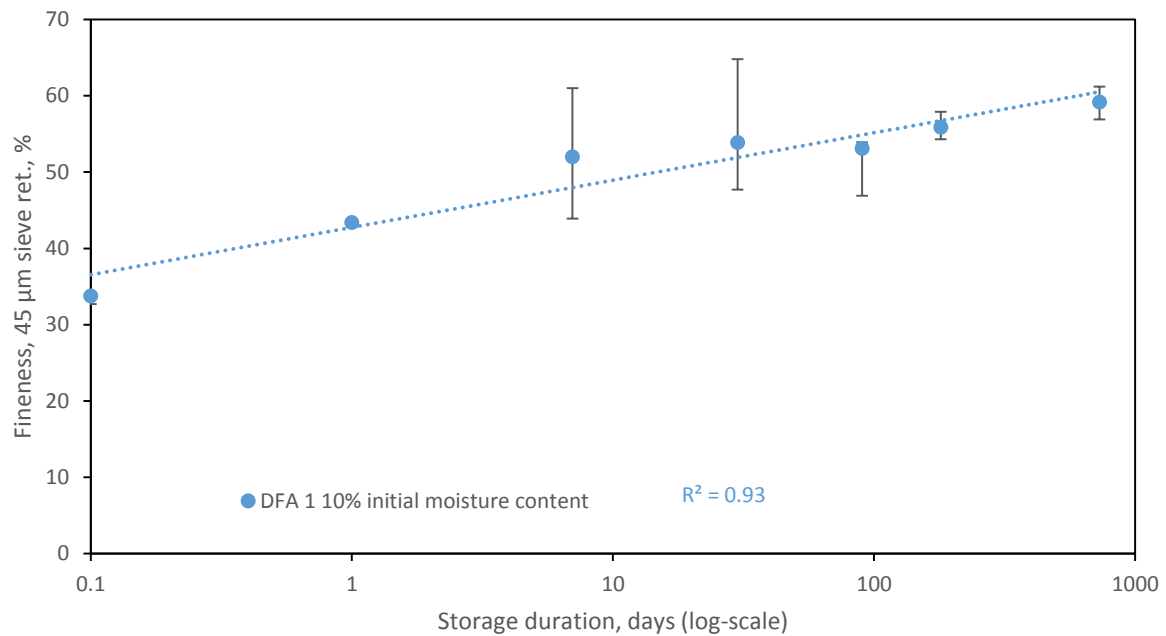
Figure 9 - Relationship between fineness and storage duration for DFA 1 laboratory wet-stored at 10% moisture
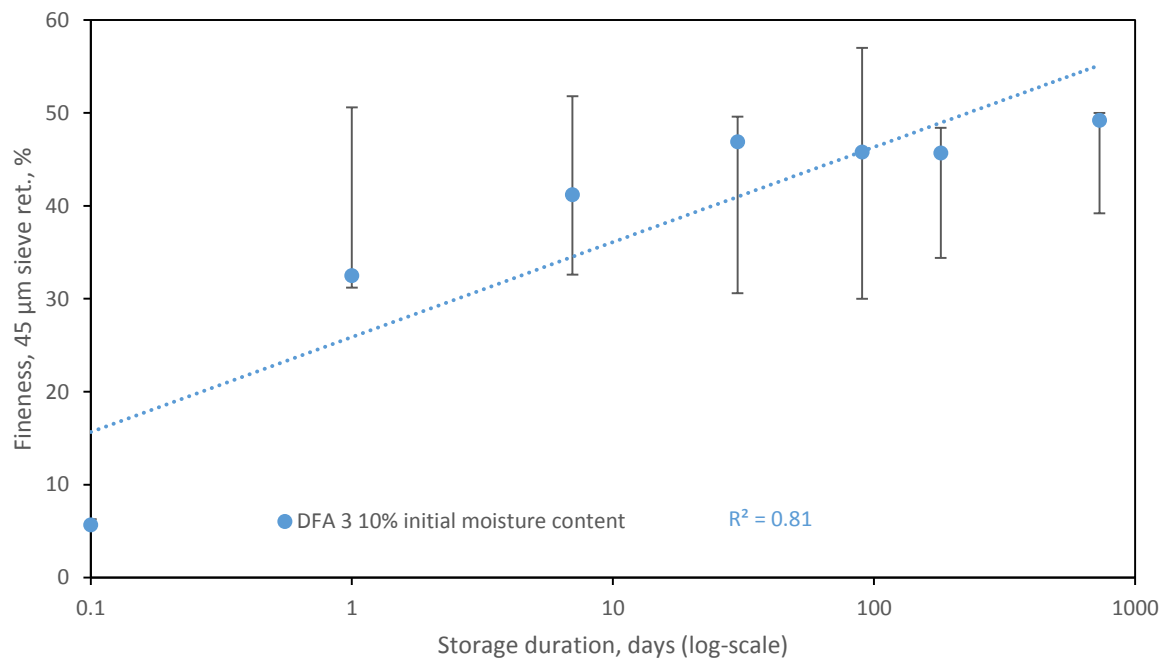
Figure 10 - Relationship between fineness and storage duration for DFA 3 laboratory wet-stored at 10% moisture
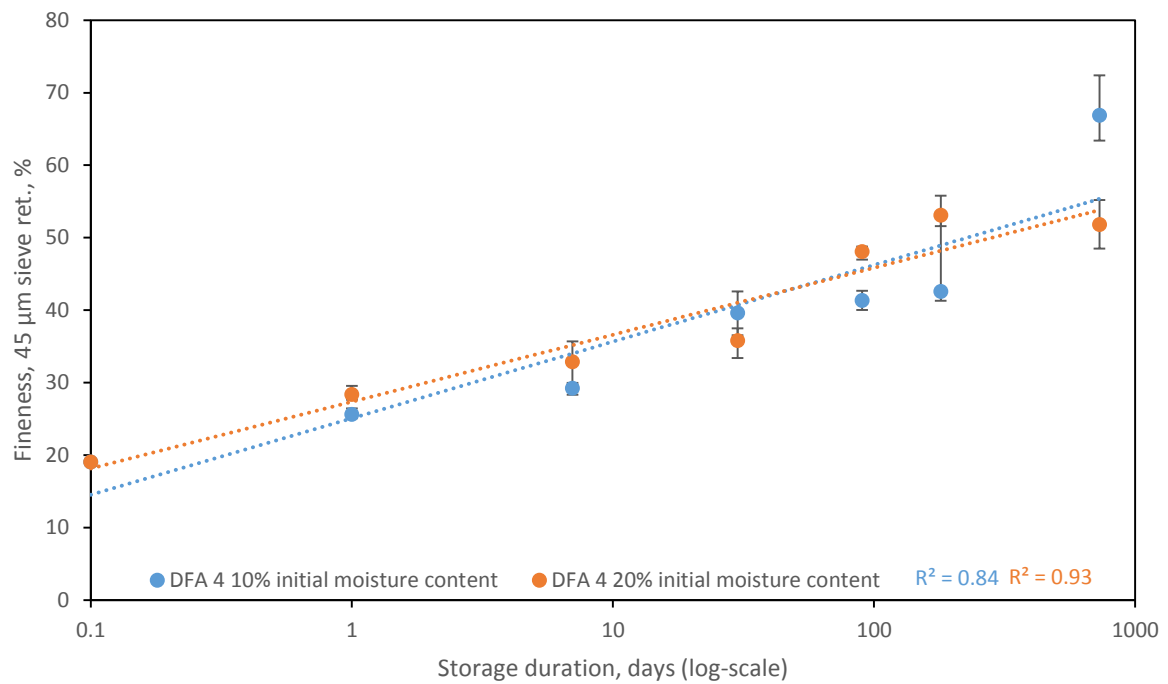
Figure 11 - Relationship between fineness and storage duration for DFA 4 laboratory wet-stored at 10 and 20% moisture
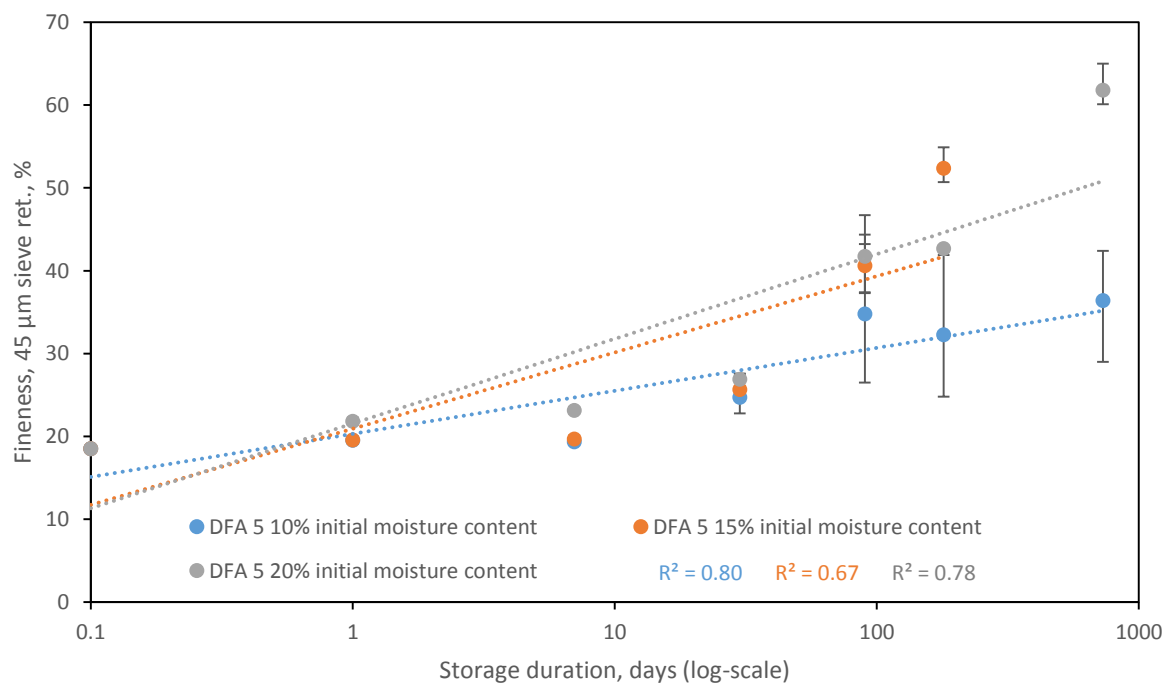
Figure 12 - Relationship between fineness and storage duration for DFA 5 laboratory wet-stored at 10, 15 and 20% moisture
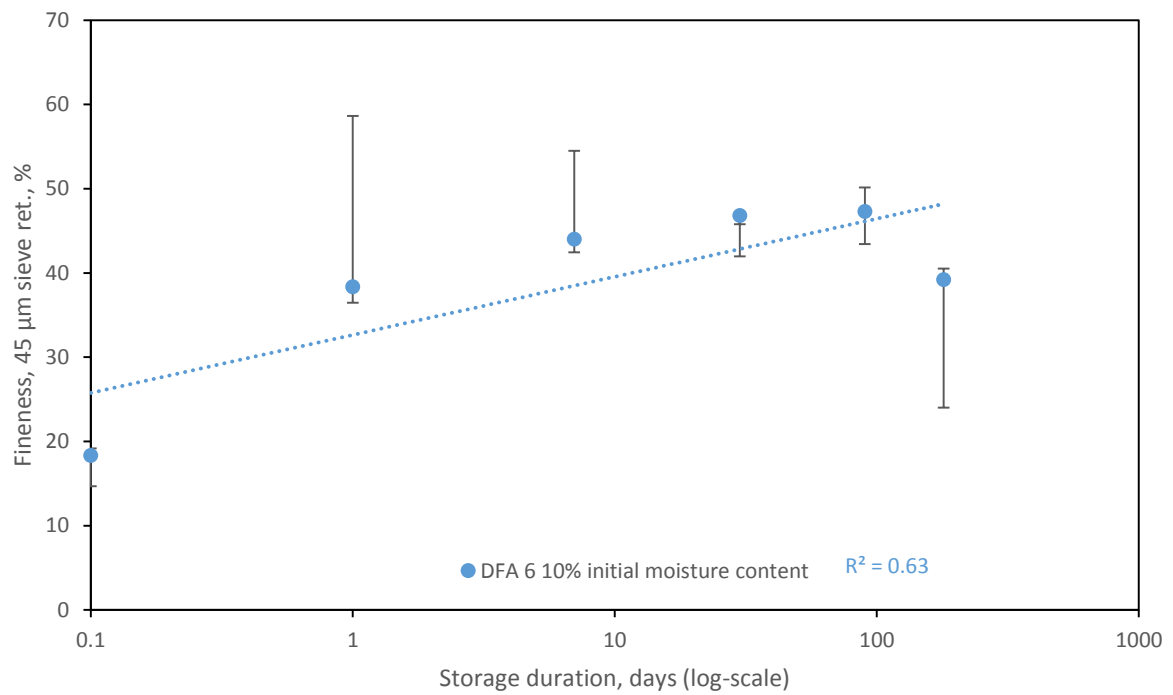
Figure 13 - Relationship between fineness and storage duration for DFA 6 laboratory wet-stored at 10% moisture
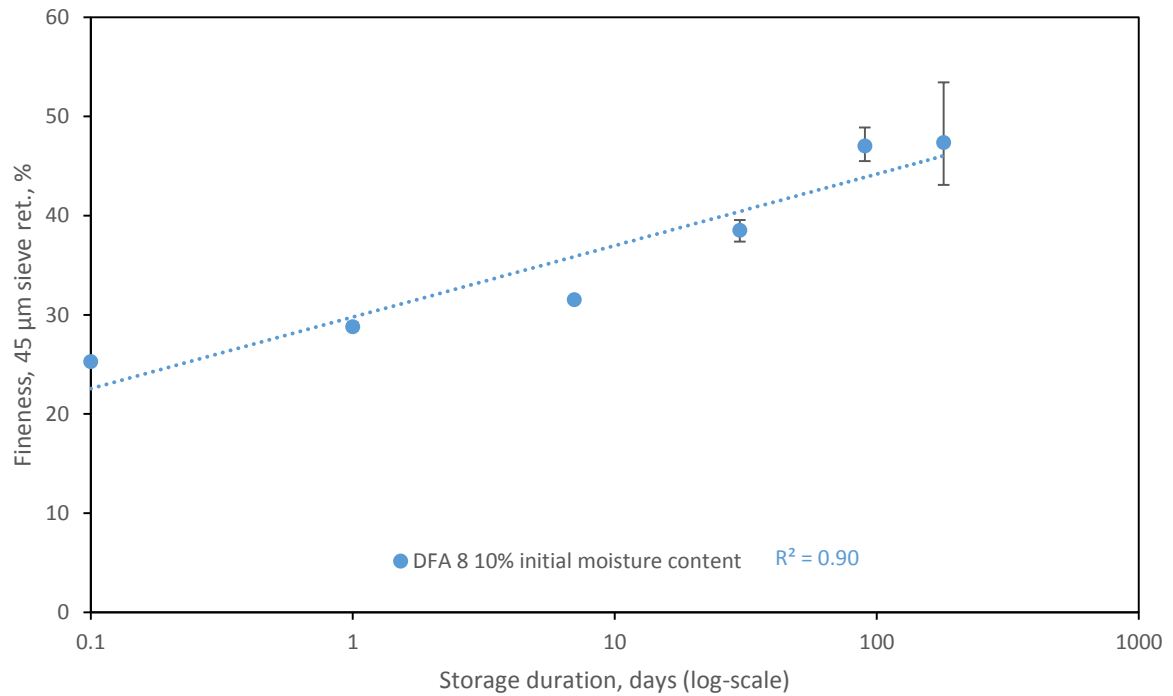
Figure 14 - Relationship between fineness and storage duration for DFA 8 laboratory wet-stored at 10% moisture

124
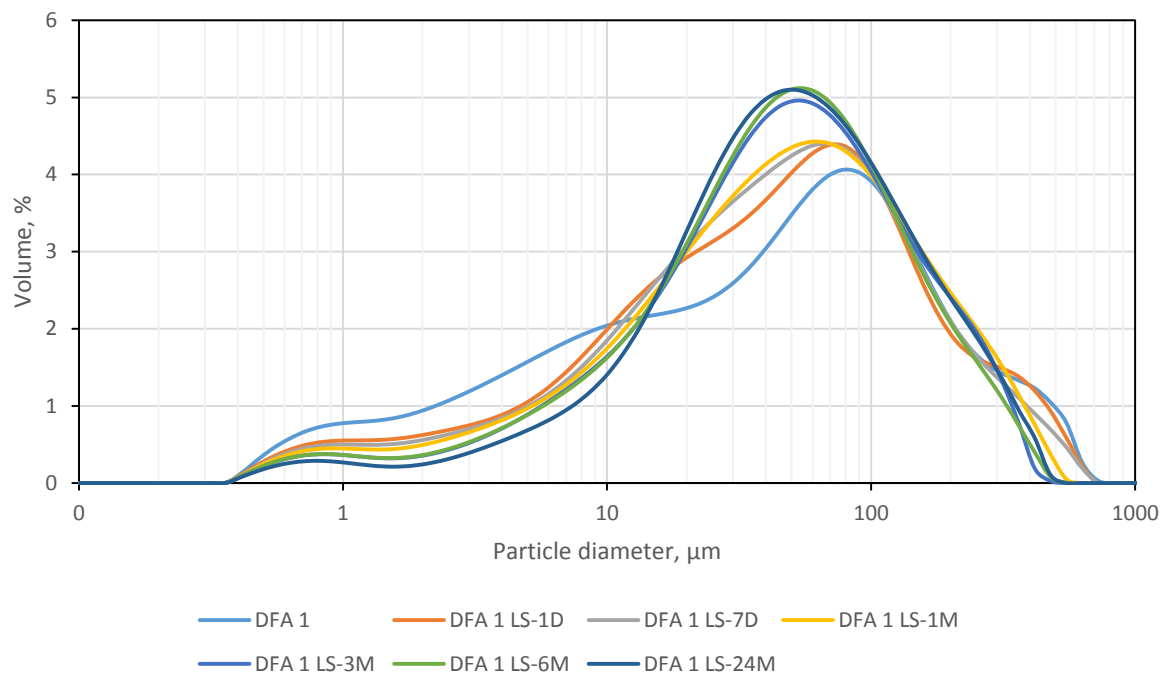
Figure 15 - Particle size distribution curves for DFA 1 laboratory wet-stored at 10% up to 24 months
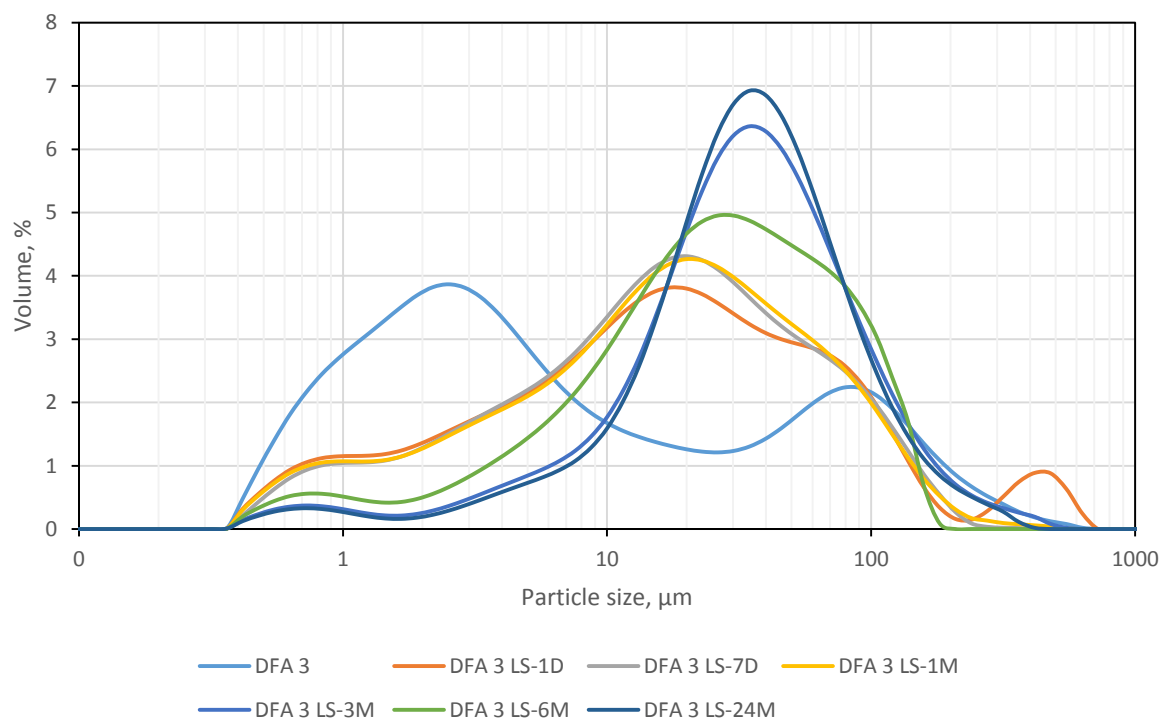
Figure 16 - Particle size distribution curves for DFA 3 laboratory wet-stored at 10% up to 24 months
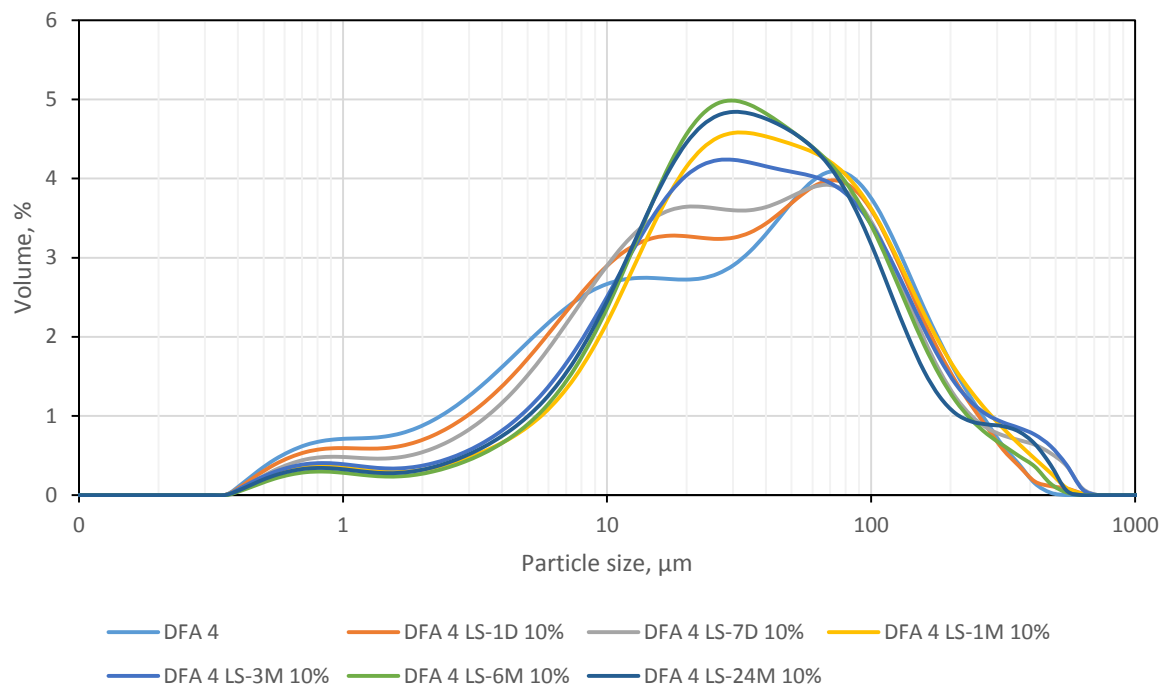
Figure 17 - Particle size distribution curves for DFA 4 laboratory wet-stored at 10% up to 24 months
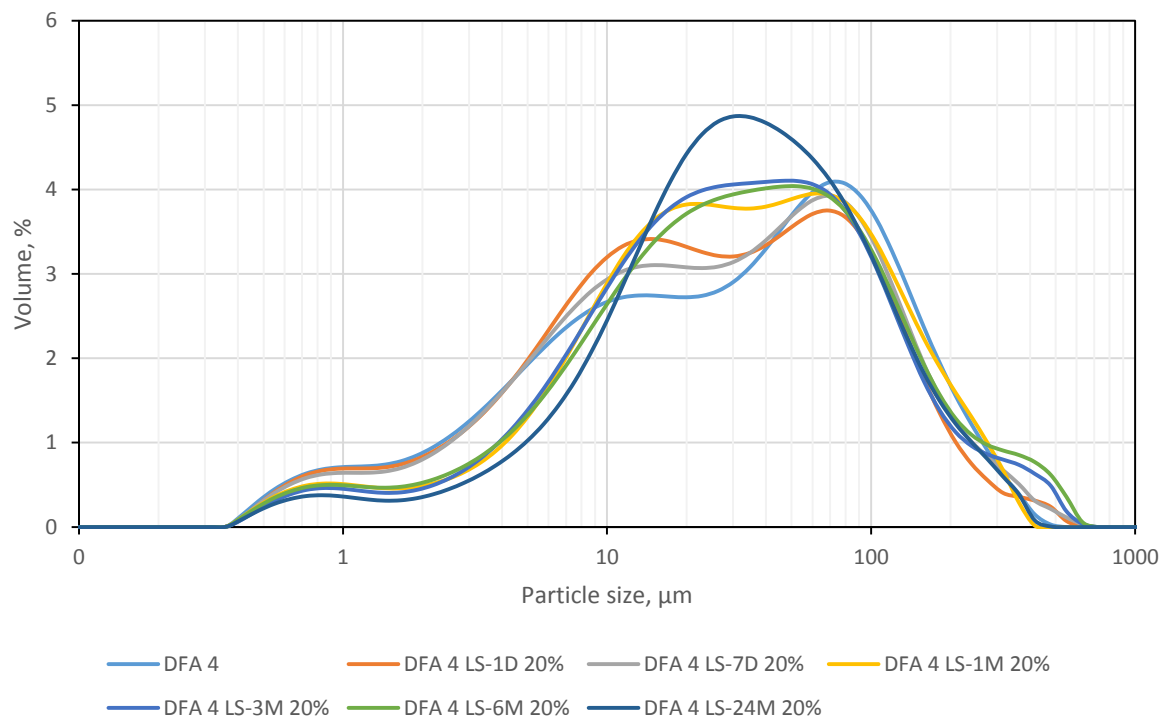
Figure 18 - Particle size distribution curves for DFA 4 laboratory wet-stored at 20% up to 24 months

126
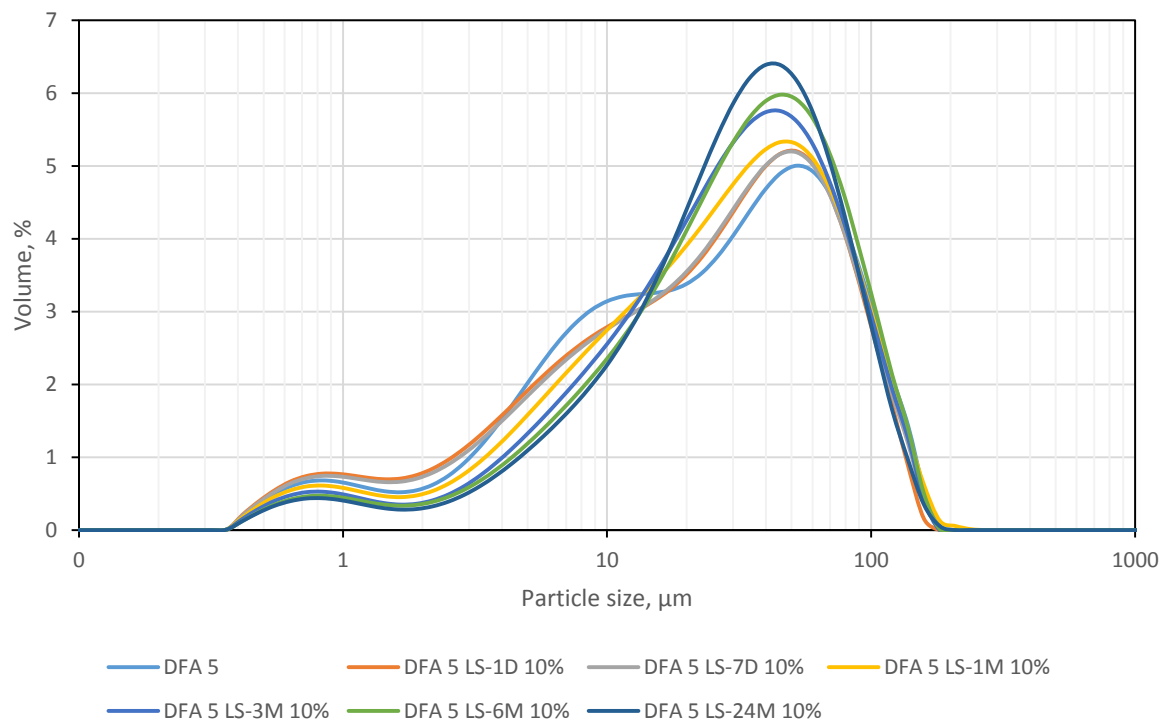
Figure 19 - Particle size distribution curves for DFA 5 laboratory wet-stored at 10% up to 24 months
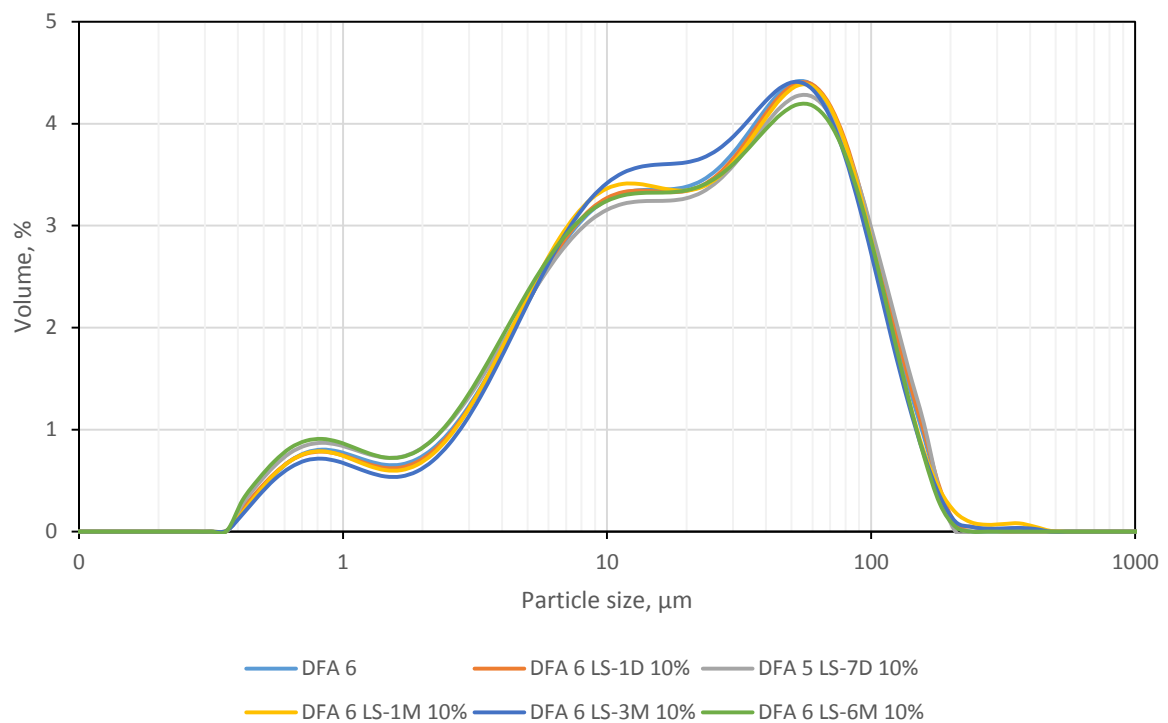
Figure 20 - Particle size distribution curves for DFA 6 laboratory wet-stored at 10% up to 24 months
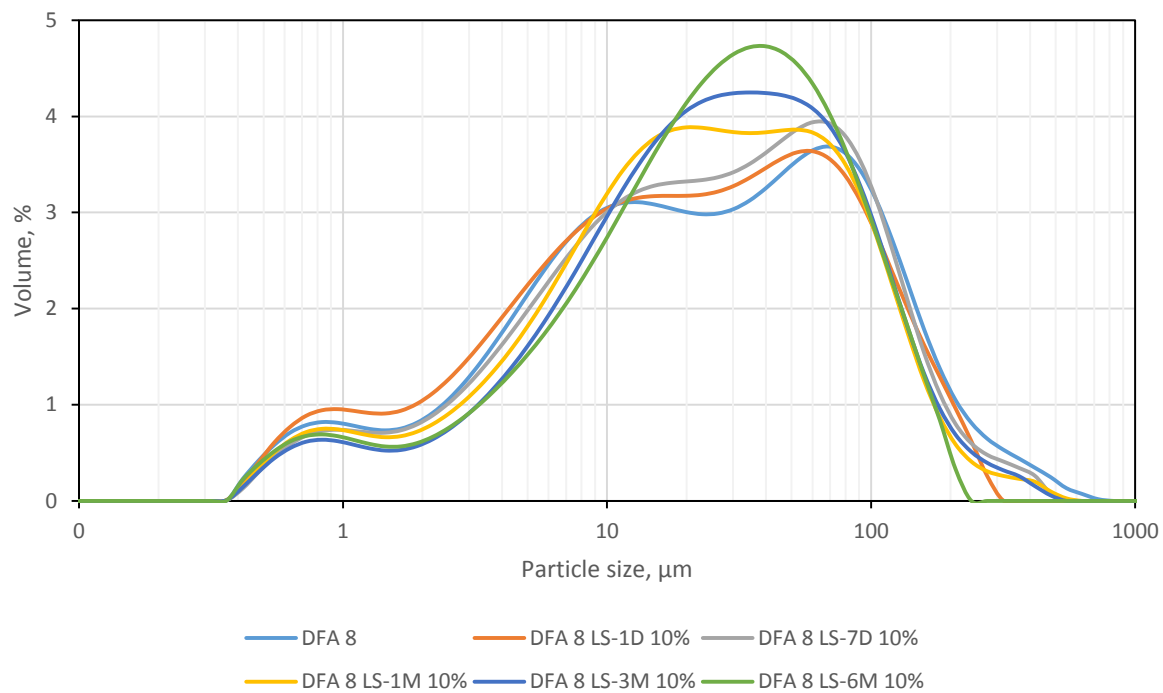
Figure 21 - Particle size distribution curves for DFA 8 laboratory wet-stored at 10% up to 24 months
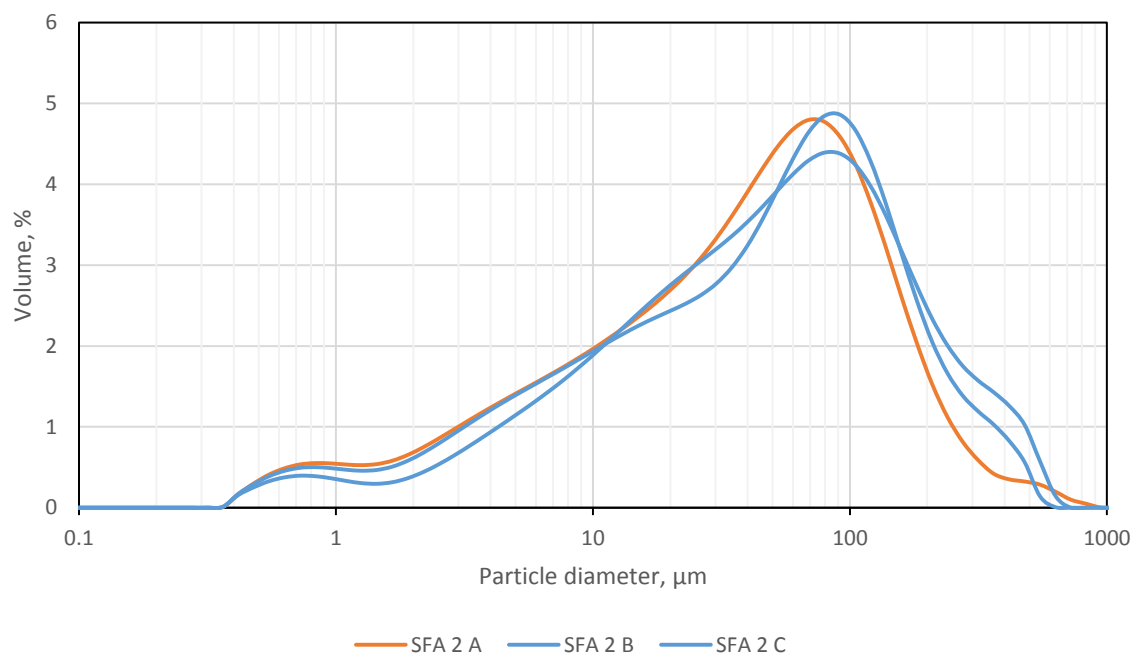
Figure 22 - Comparison of the particle size distributions of three samples of SFA 2
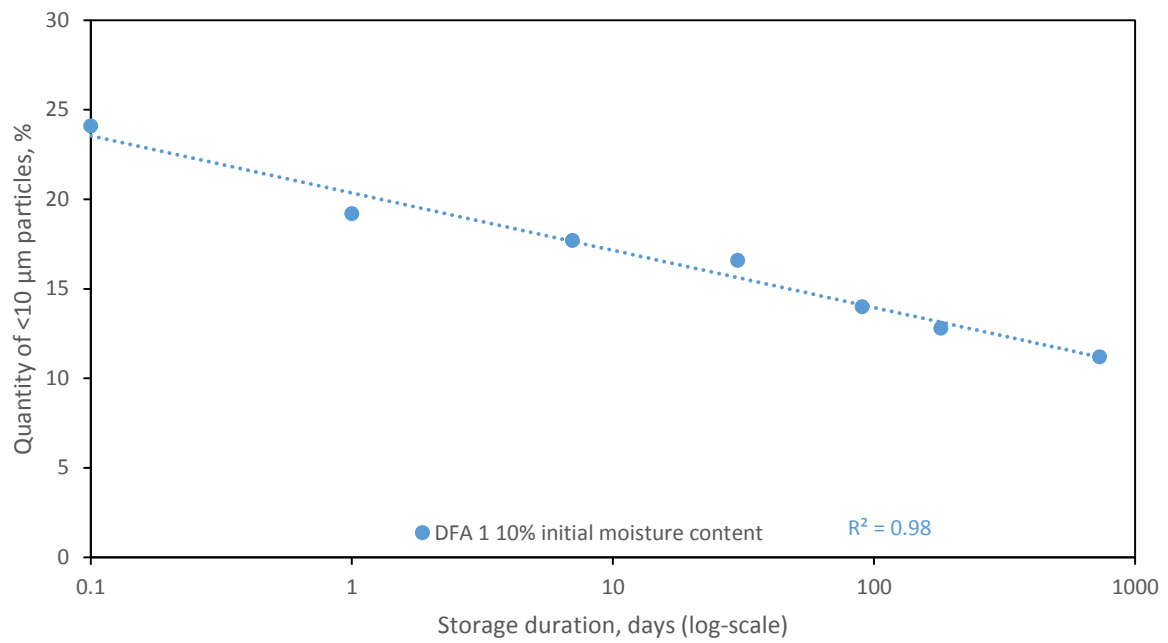
Figure 23 - Relationship between quantity of <10 μm particles and storage duration for DFA 1 laboratory wet-stored at 10% moisture
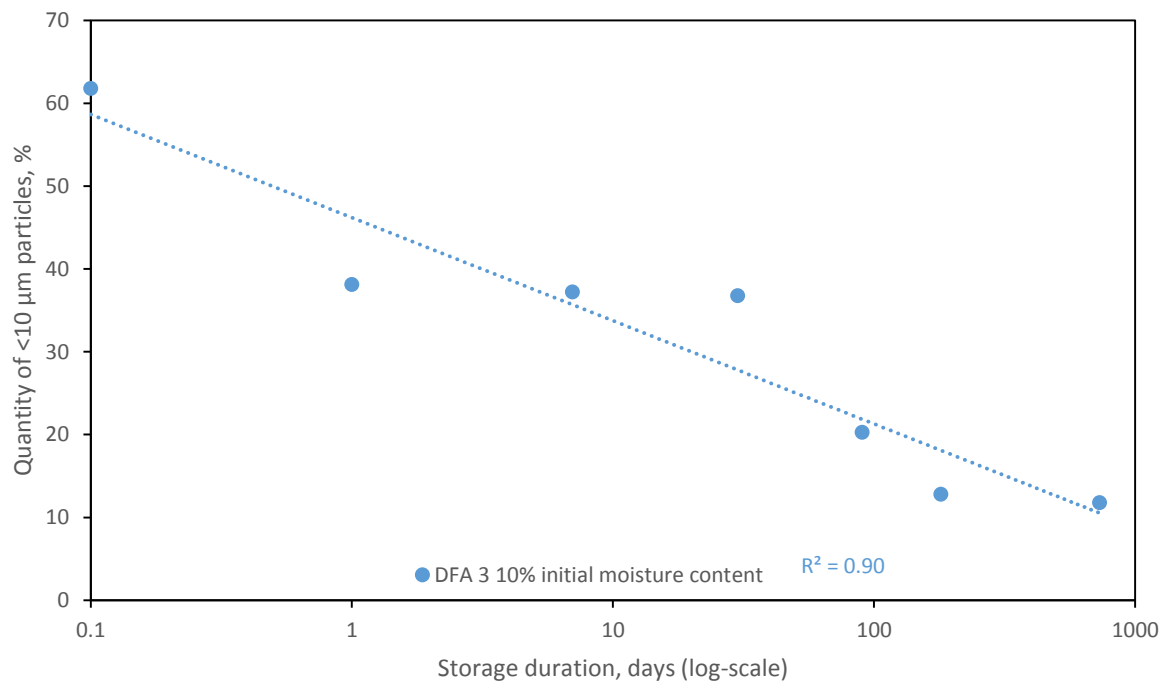
Figure 24 - Relationship between quantity of <10 μm particles and storage duration for DFA 3 laboratory wet-stored at 10% moisture
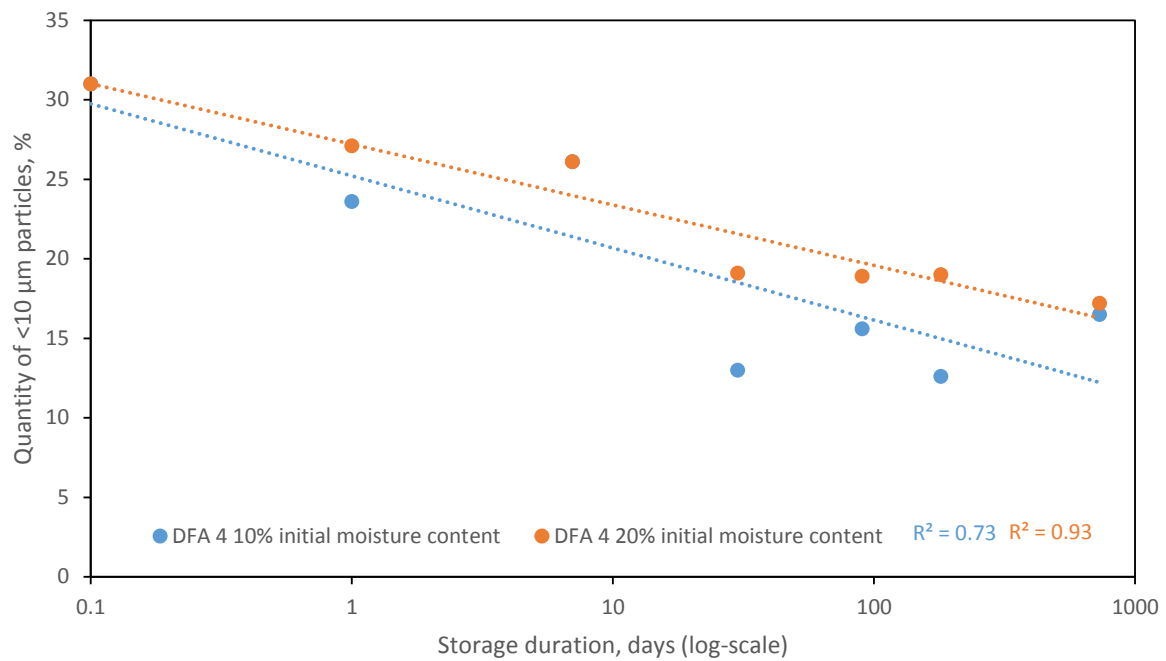
Figure 25 - Relationship between quantity of <10 μm particles and storage duration for DFA 4 laboratory wet-stored at 10% and 20% moisture
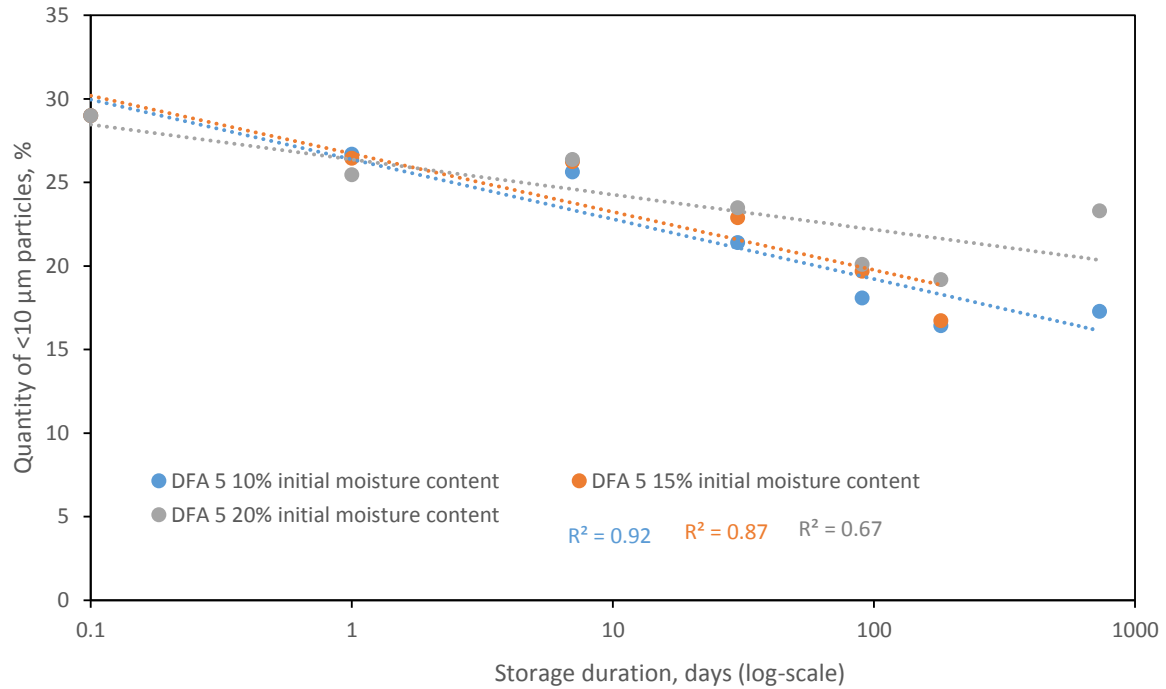
Figure 26 - Relationship between quantity of <10 μm particles and storage duration for DFA 5 laboratory wet-stored at 10%, 15% and 20% moisture
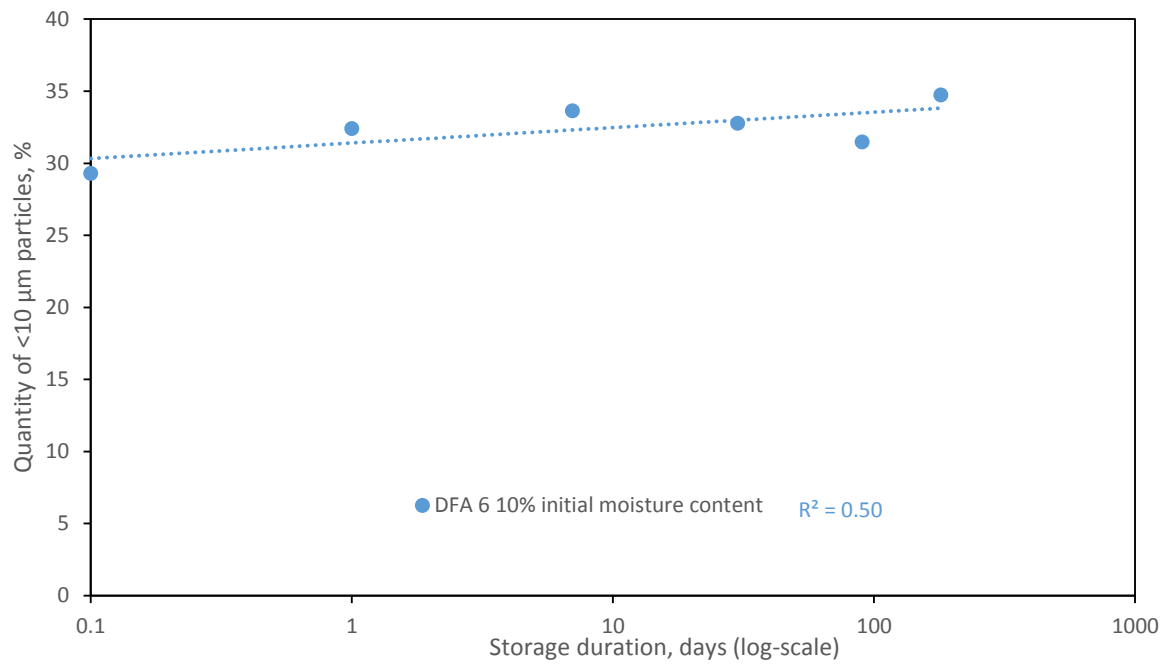
Figure 27 - Relationship between quantity of <10 µm particles and storage duration for DFA 6 laboratory wet-stored at 10% moisture
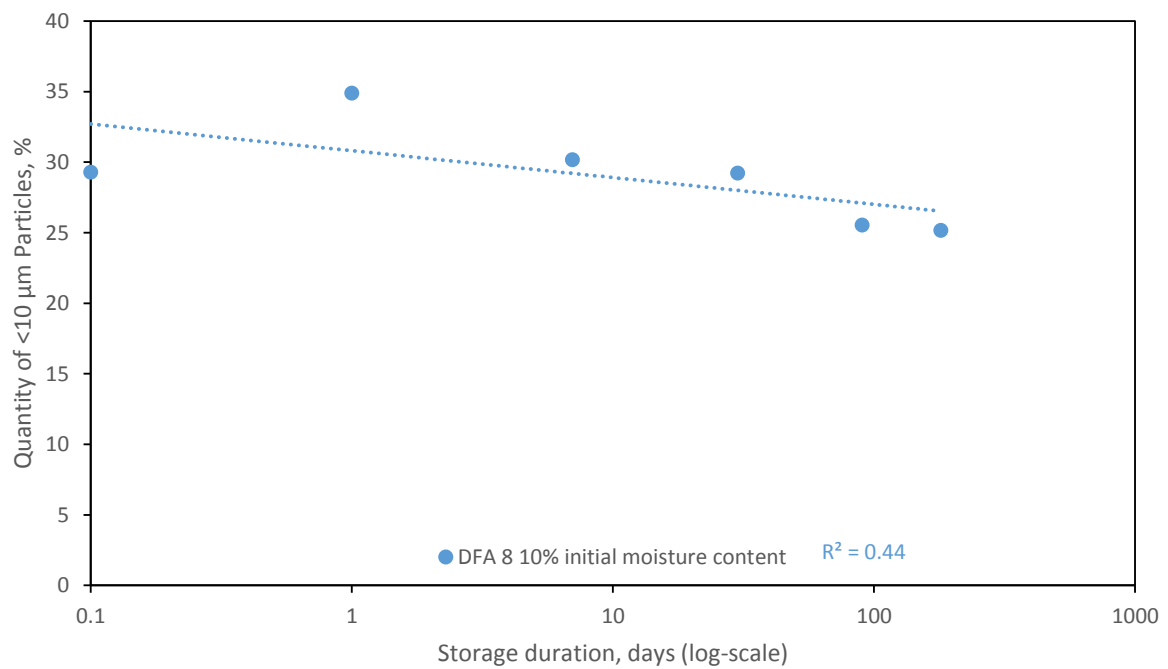
Figure 28 - Relationship between quantity of <10 µm particles and storage duration for DFA 8 laboratory wet-stored at 10% moisture
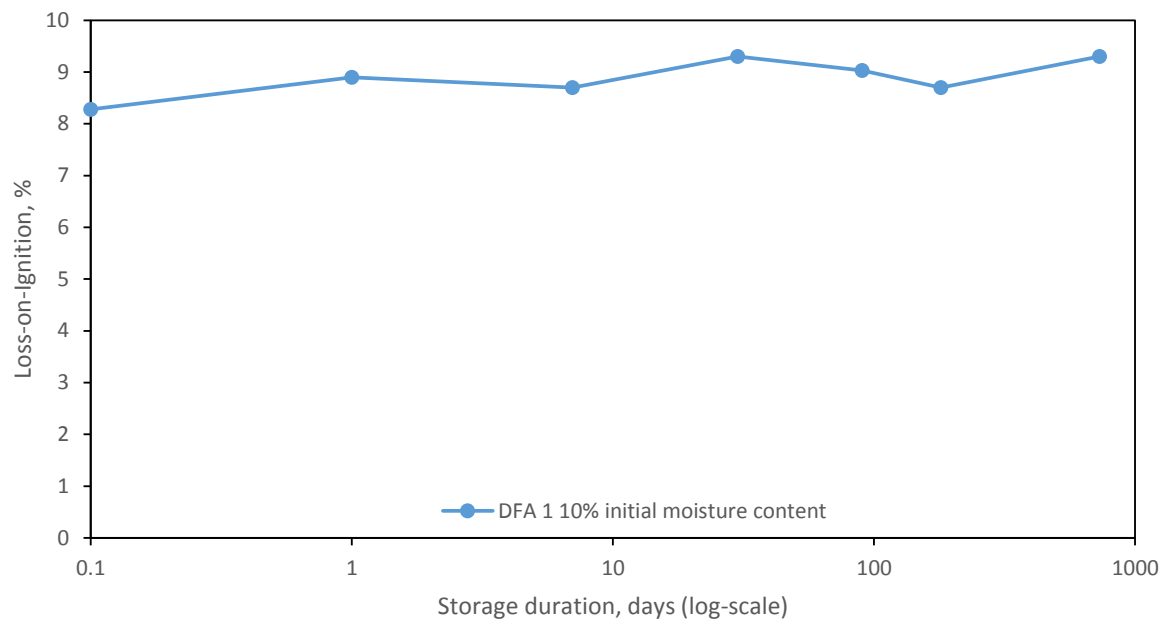
Figure 29 - Relationship between Loss-on-Ignition and storage duration for DFA 1 laboratory wet-stored at 10% moisture
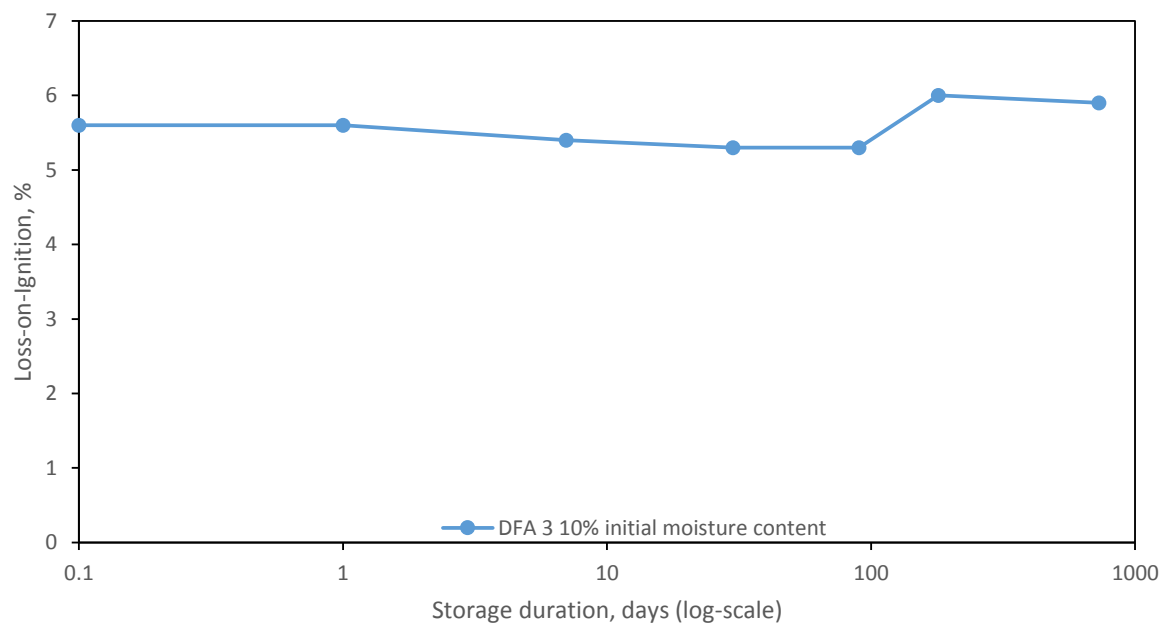
Figure 30 - Relationship between Loss-on-Ignition and storage duration for DFA 3 laboratory wet-stored at 10% moisture
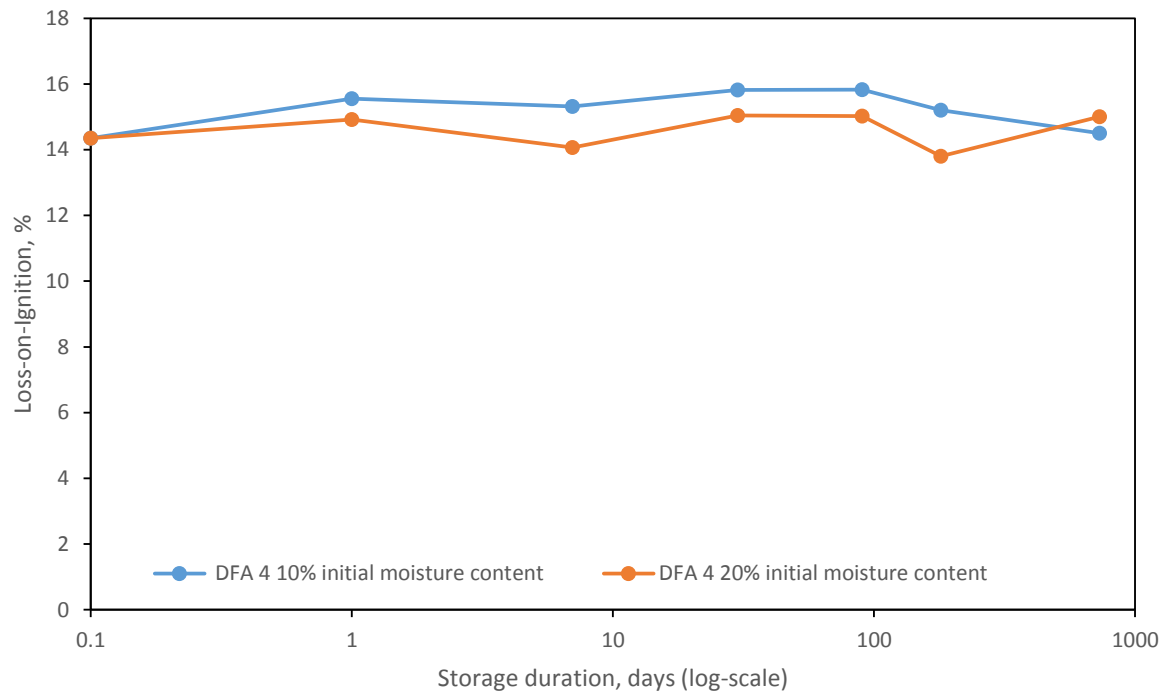
Figure 31 - Relationship between Loss-on-Ignition and storage duration for DFA 4 laboratory wet-stored at 10% and 20% moisture
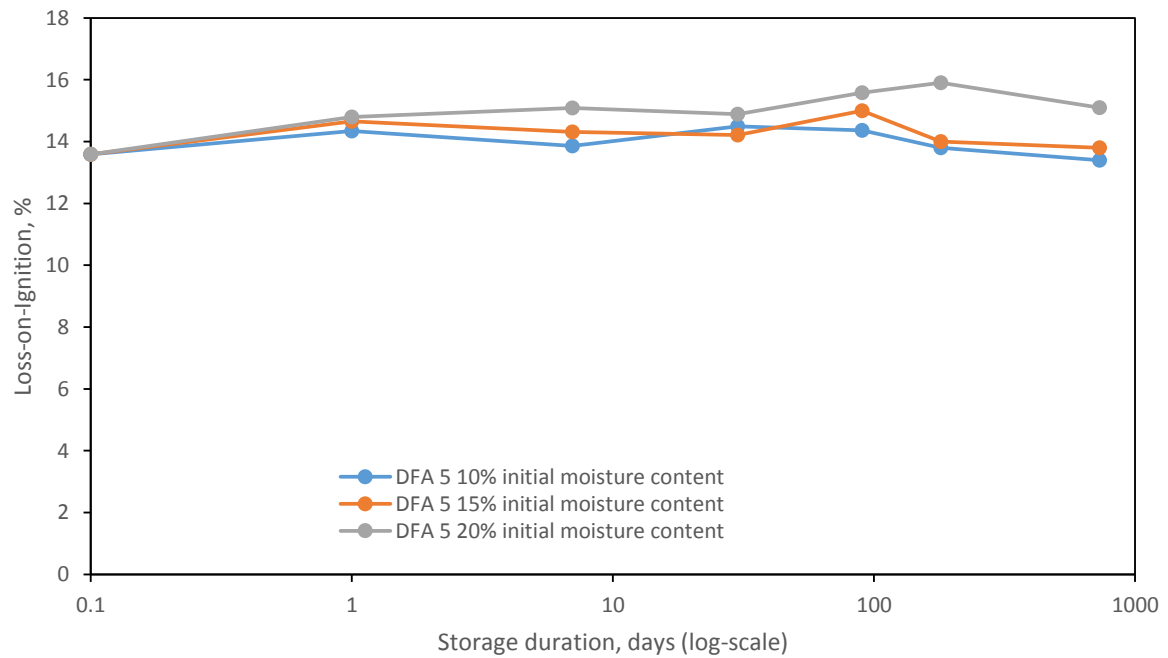
Figure 32 - Relationship between Loss-on-Ignition and storage duration for DFA 5 laboratory wet-stored at 10%, 15% and 20% moisture
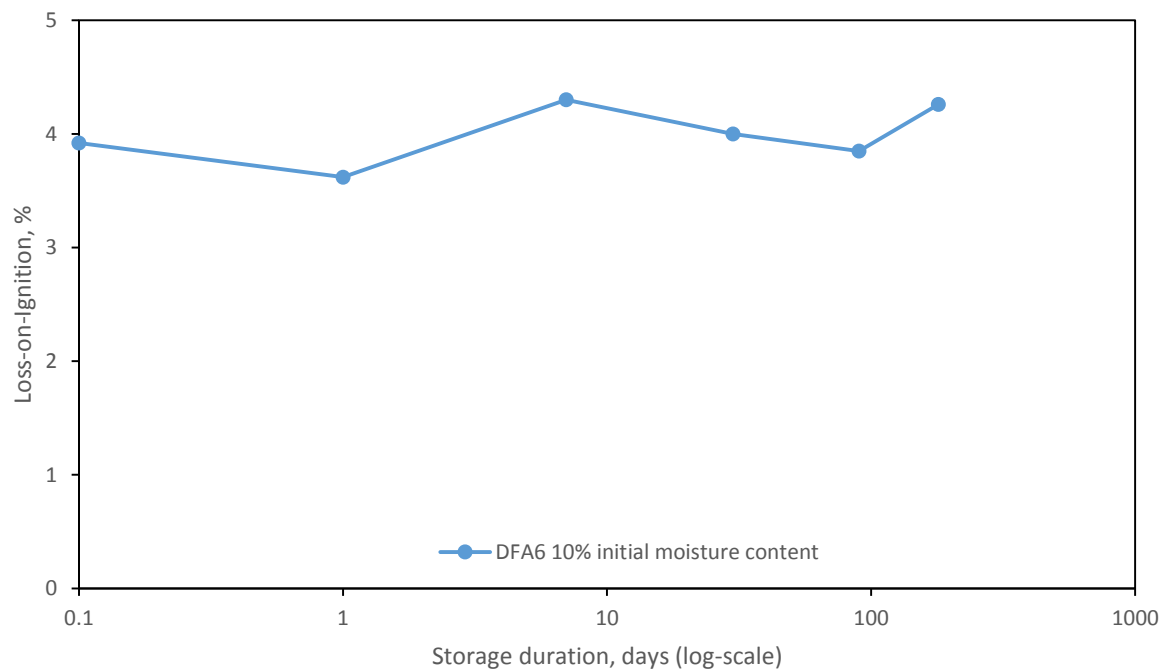
Figure 33 - Relationship between Loss-on-Ignition and storage duration for DFA 6 laboratory wet-stored at 10% moisture
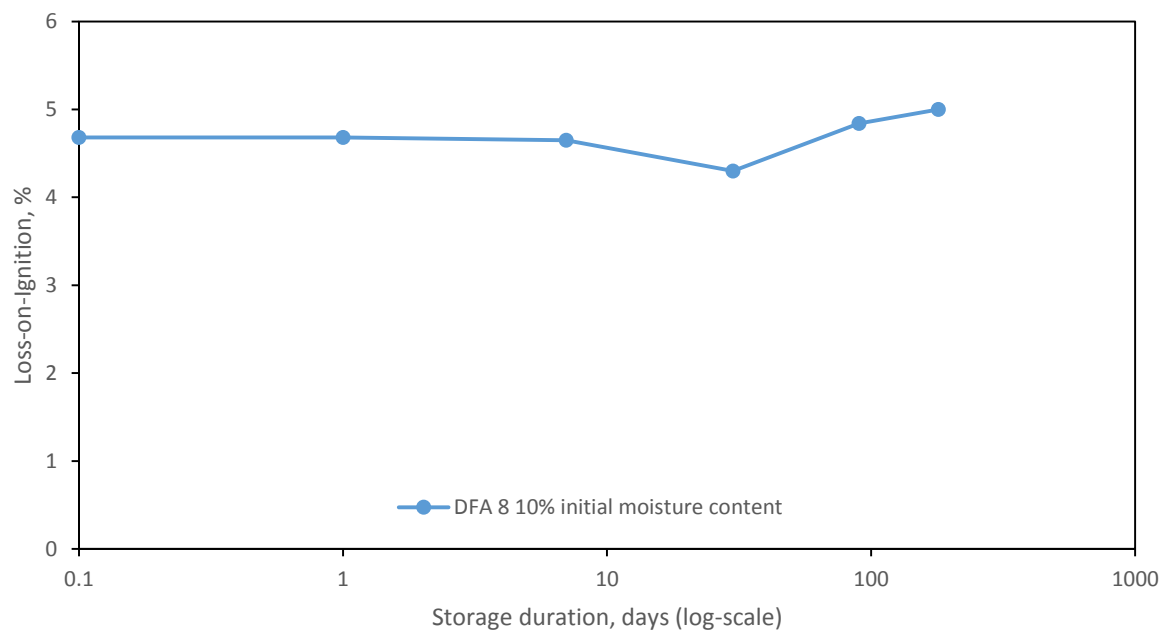
Figure 34 - Relationship between Loss-on-Ignition and storage duration for DFA 8 laboratory wet-stored at 10% moisture
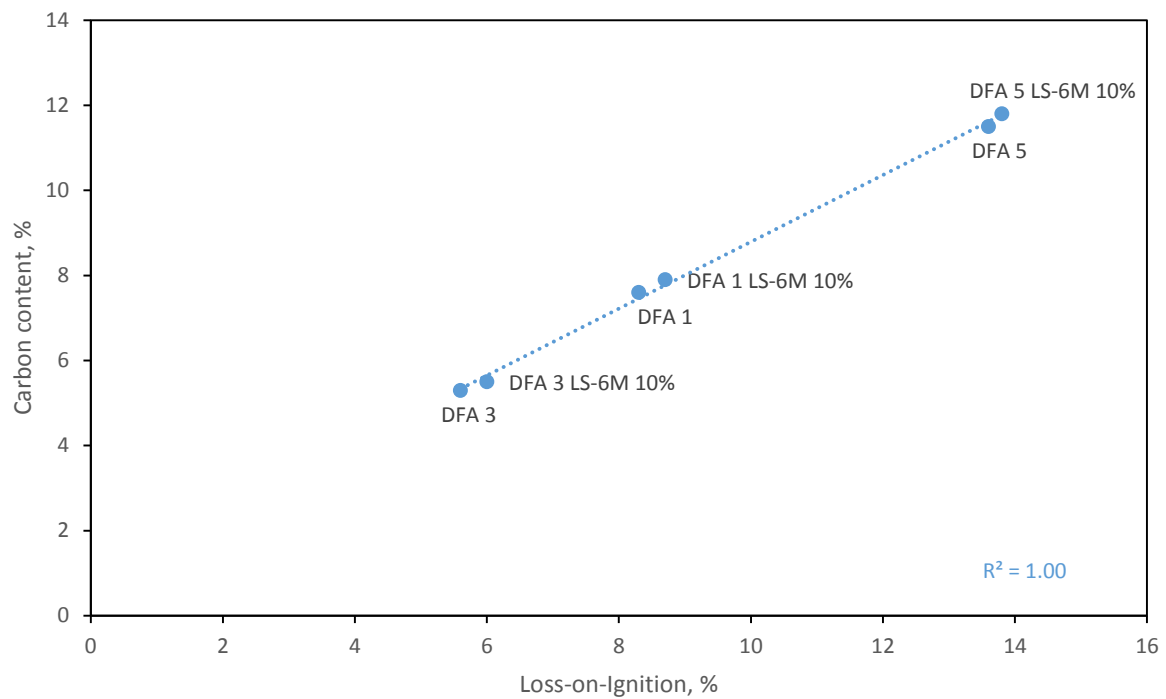
Figure 35 - Relationship between Loss-on-Ignition and carbon content of laboratory wet-stored materials
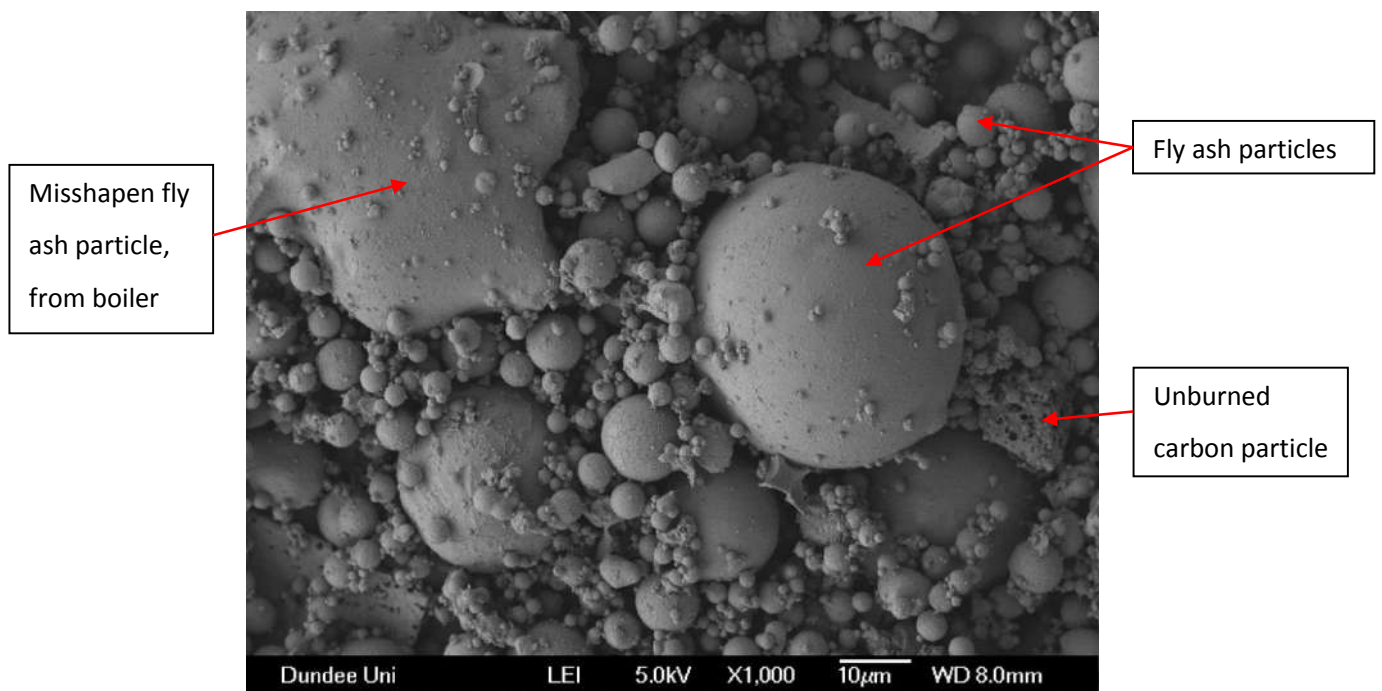
Figure 36 - Scanning Electron Microscopy image of DFA 1 (x1000)
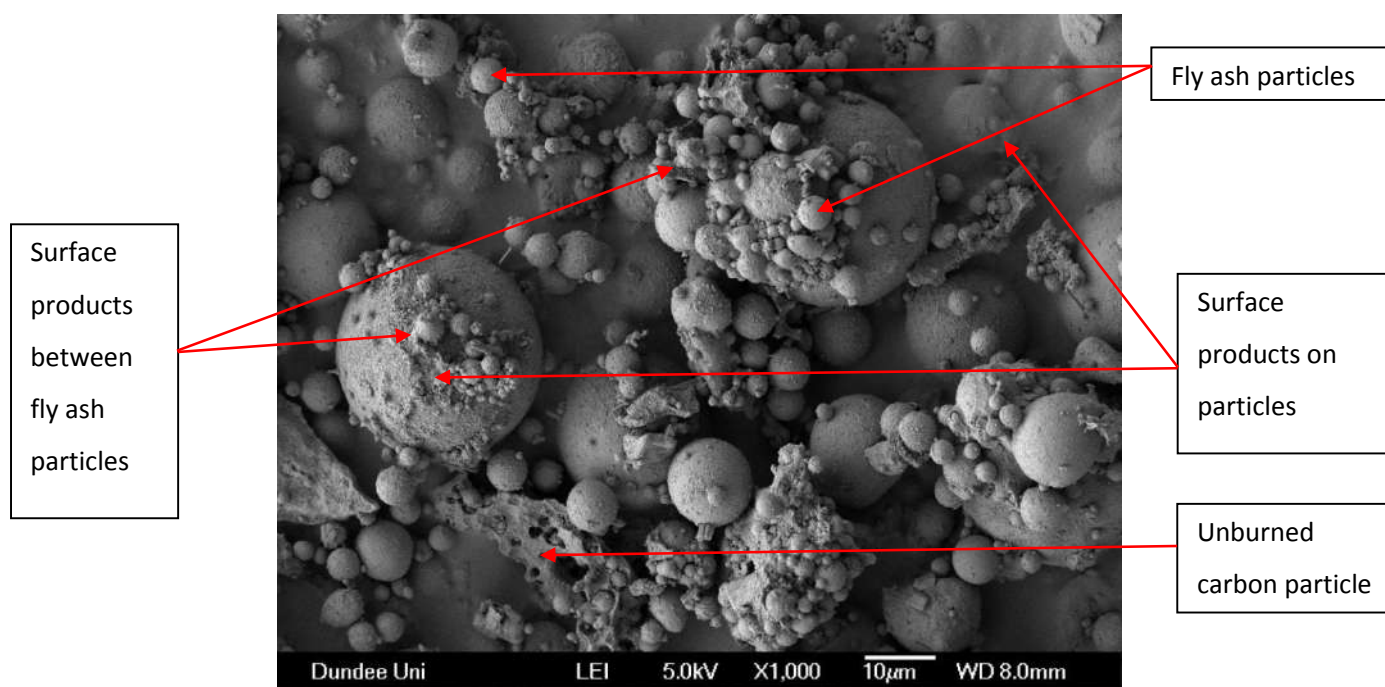
Figure 37 - Scanning Electron Microscopy image of DFA 1 laboratory wet-stored for 6 months at 10% moisture (x1000)
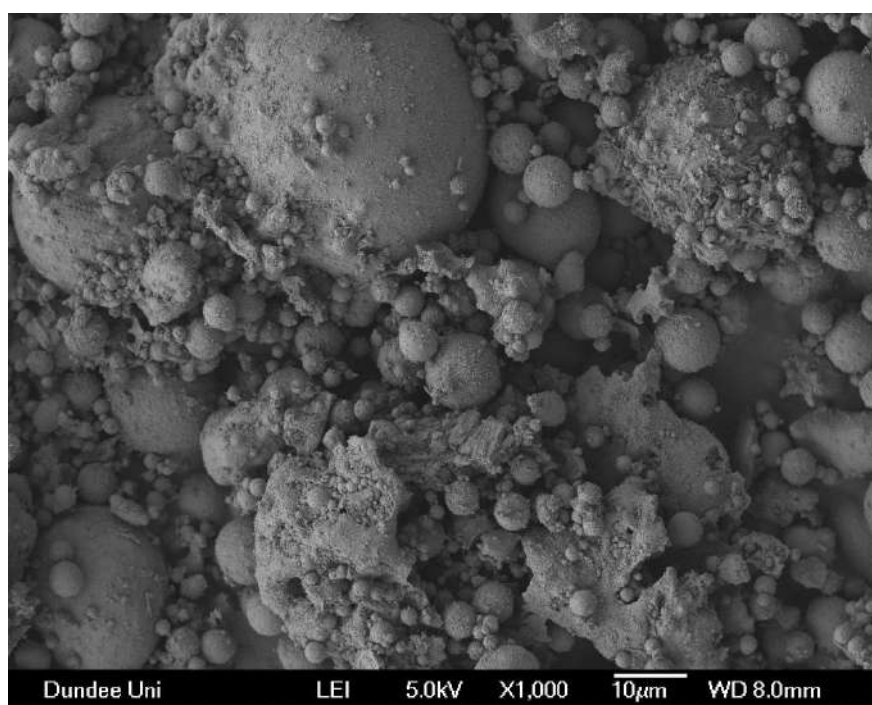
Figure 38 - Scanning Electron Microscopy image of SFA 1 (x1000)
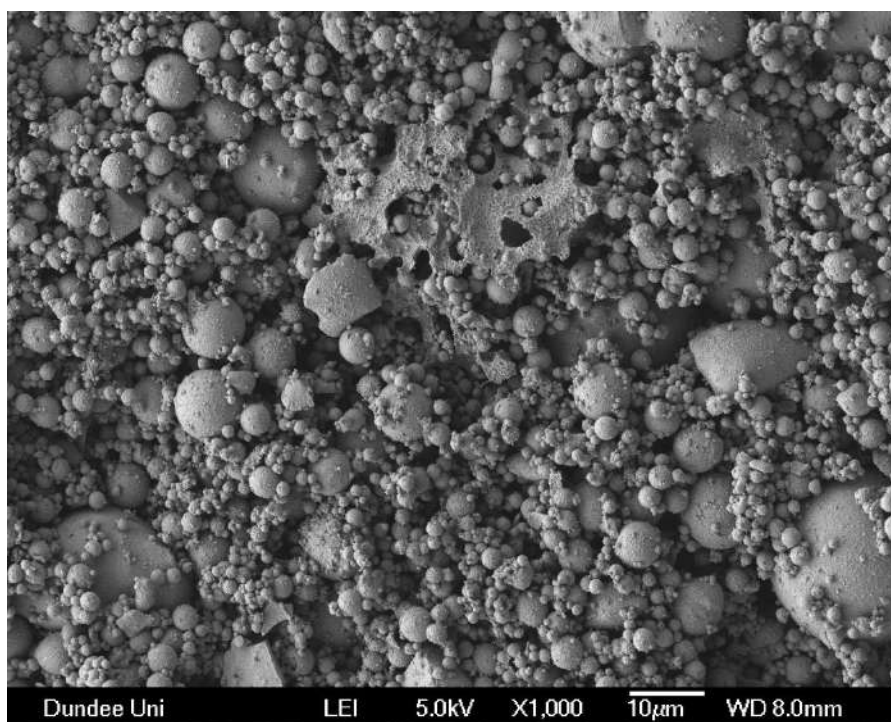
Figure 39 - Scanning Electron Microscopy image of DFA 3 (x1000)
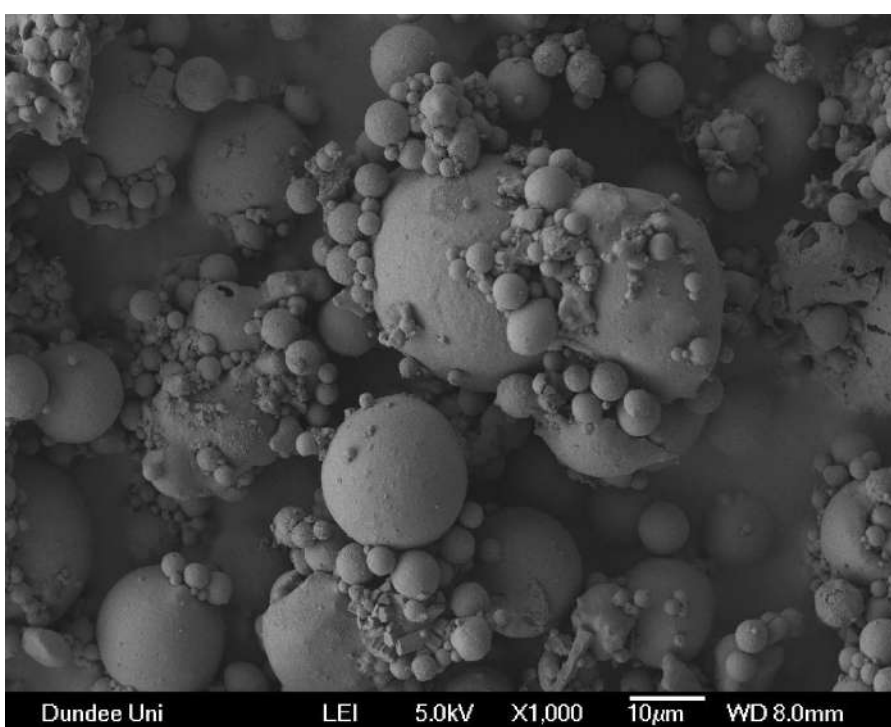
Figure 40 - Scanning Electron Microscopy image of DFA 3 laboratory wet-storage for 6 months at 10% moisture (x1000)
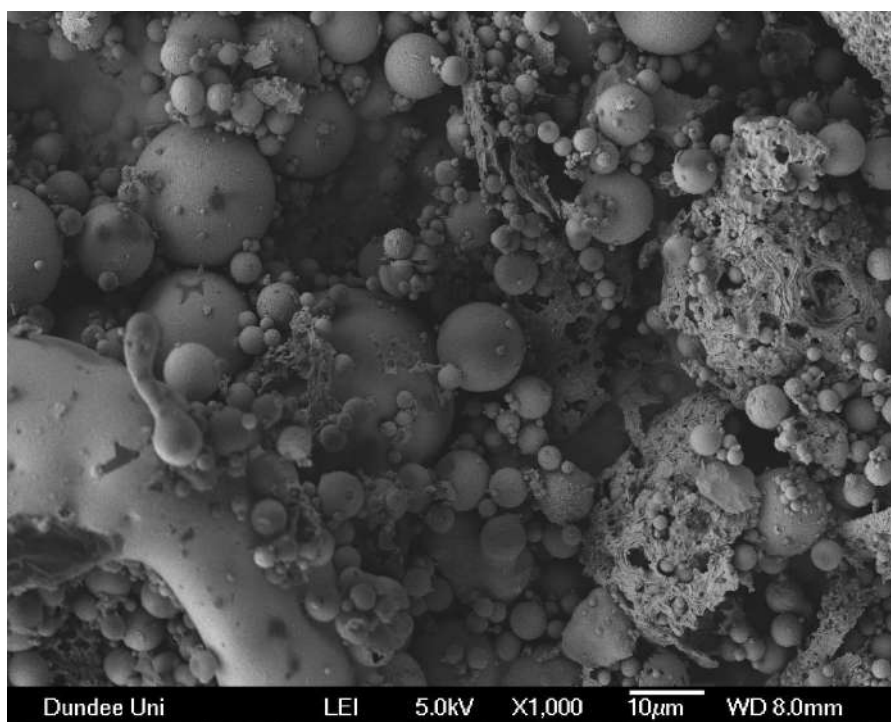
Figure 41 - Scanning Electron Microscopy image of DFA 5 (x1000)
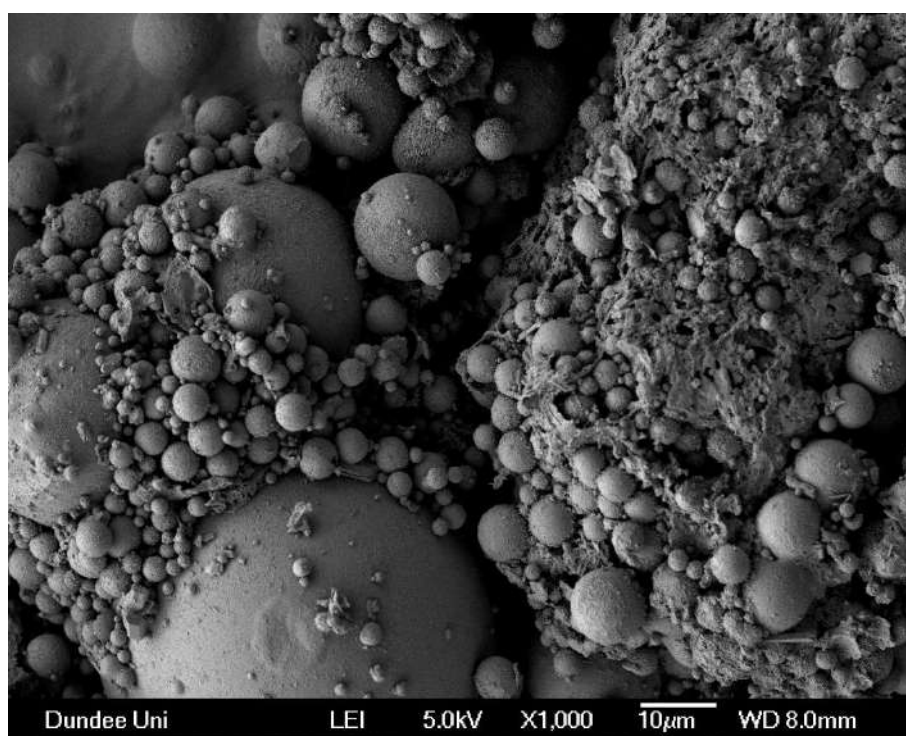
Figure 42 - Scanning Electron Microscopy image of DFA 5 laboratory wet-stored for 6 months at 10% moisture (x1000)

138
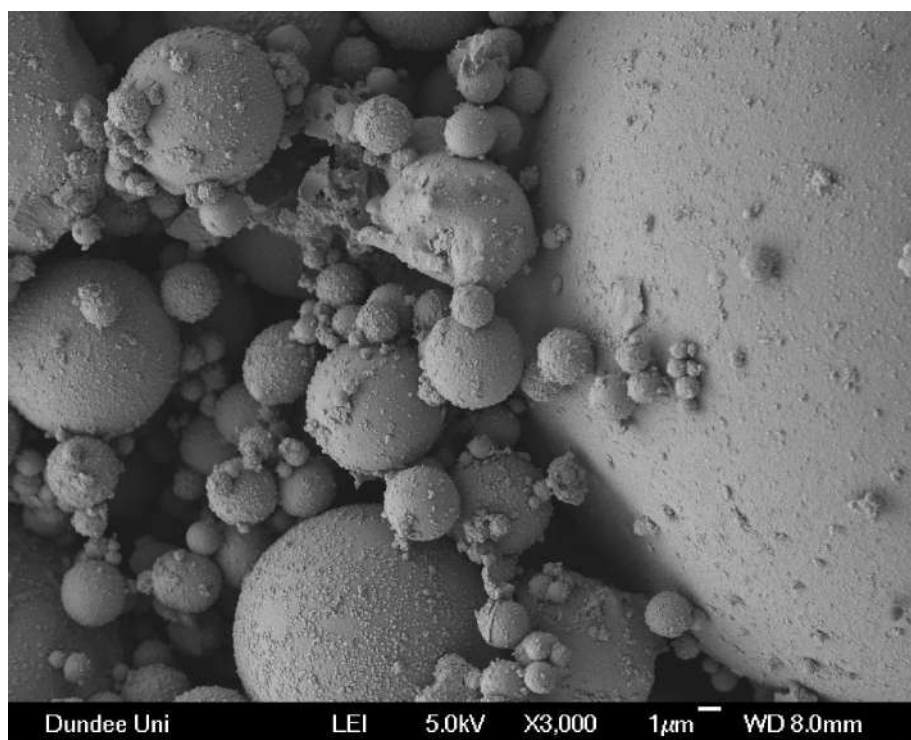
Figure 43 - Scanning Electron Microscopy image of DFA 1 (x3000)
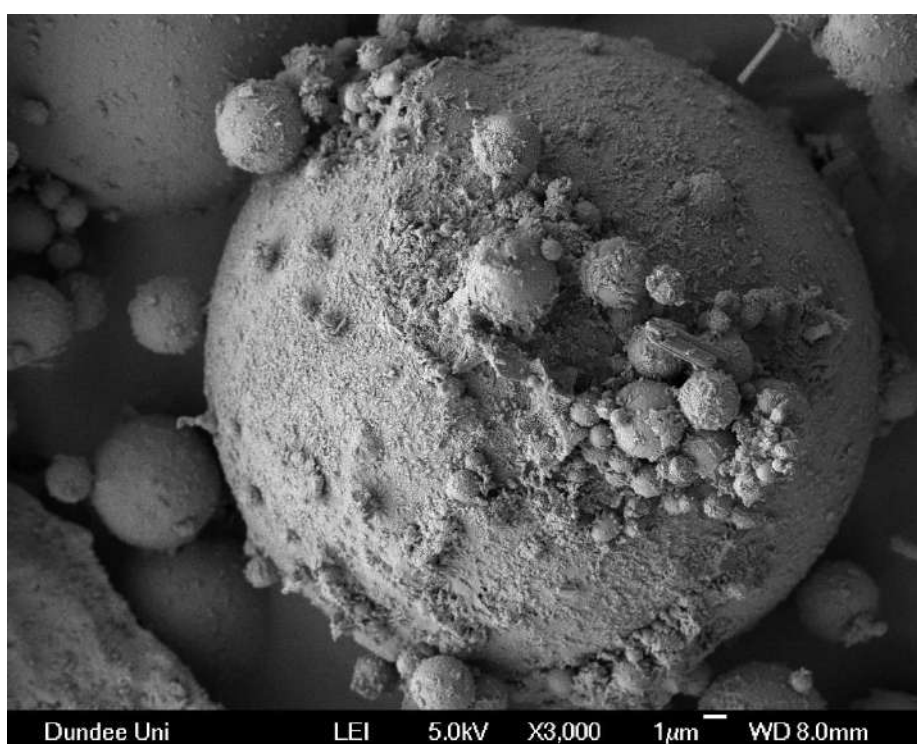
Figure 44 - Scanning Electron Microscopy image of DFA 1 laboratory wet-stored for 6 months at 10% moisture (x3000)
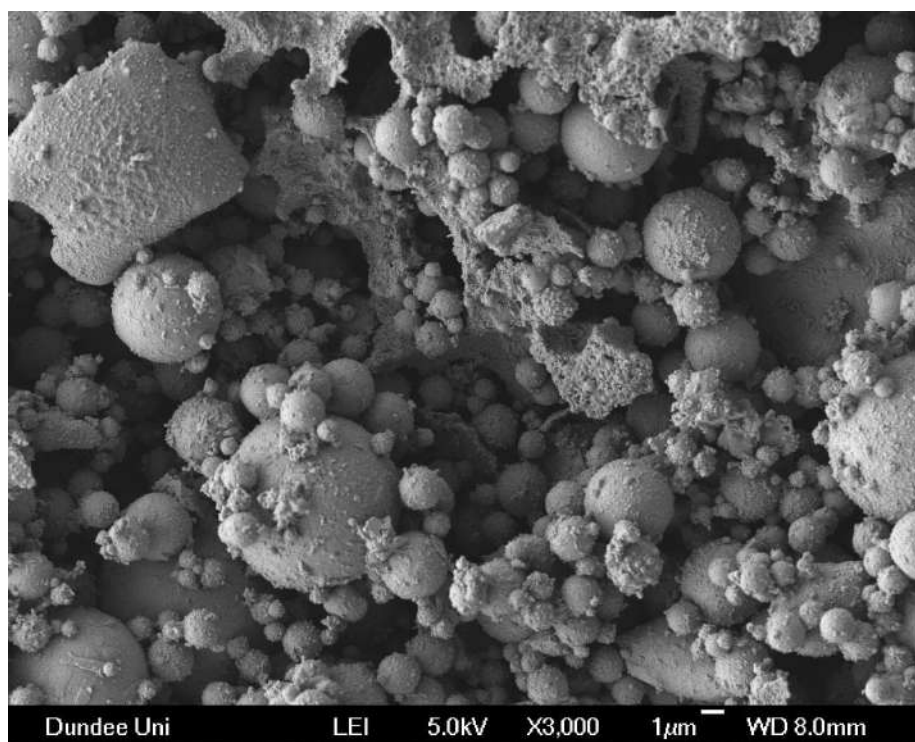
Figure 45 - Scanning Electron Microscopy image of DFA 3 (x3000)
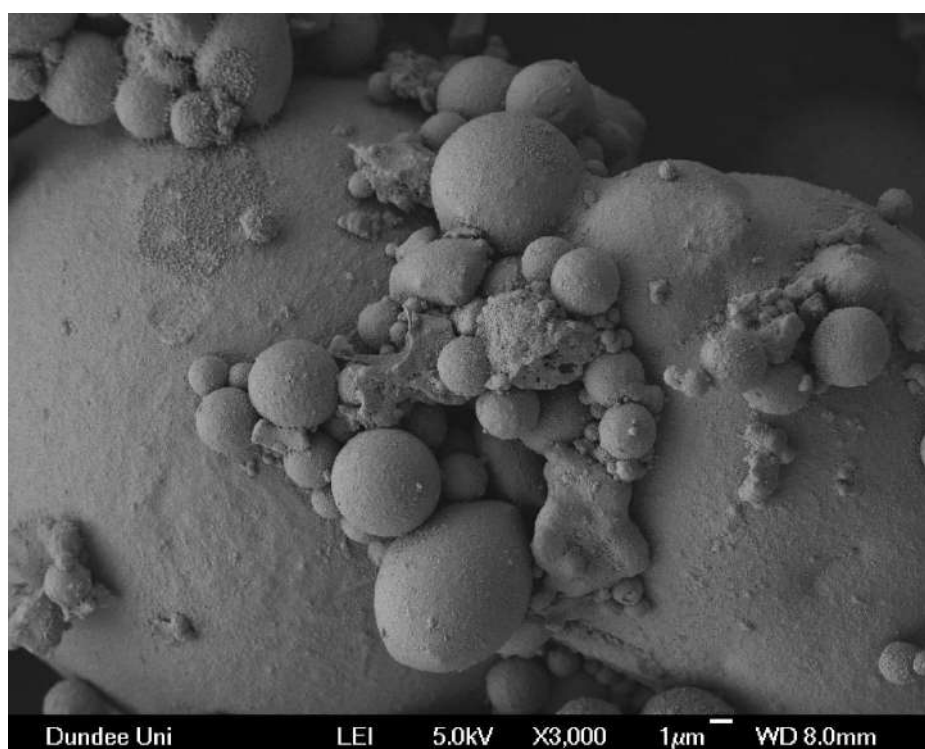
Figure 46 - Scanning Electron Microscopy image of DFA 3 laboratory wet-stored for 6 months at 10% moisture (x3000)

140
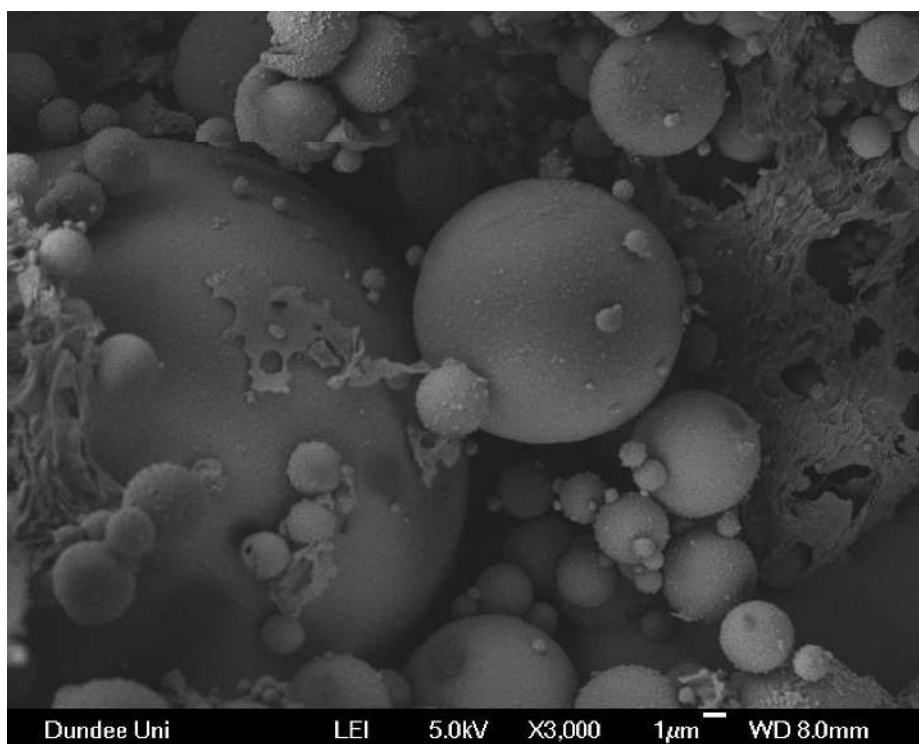
Figure 47 - Scanning Electron Microscopy image of DFA 5 (x3000)
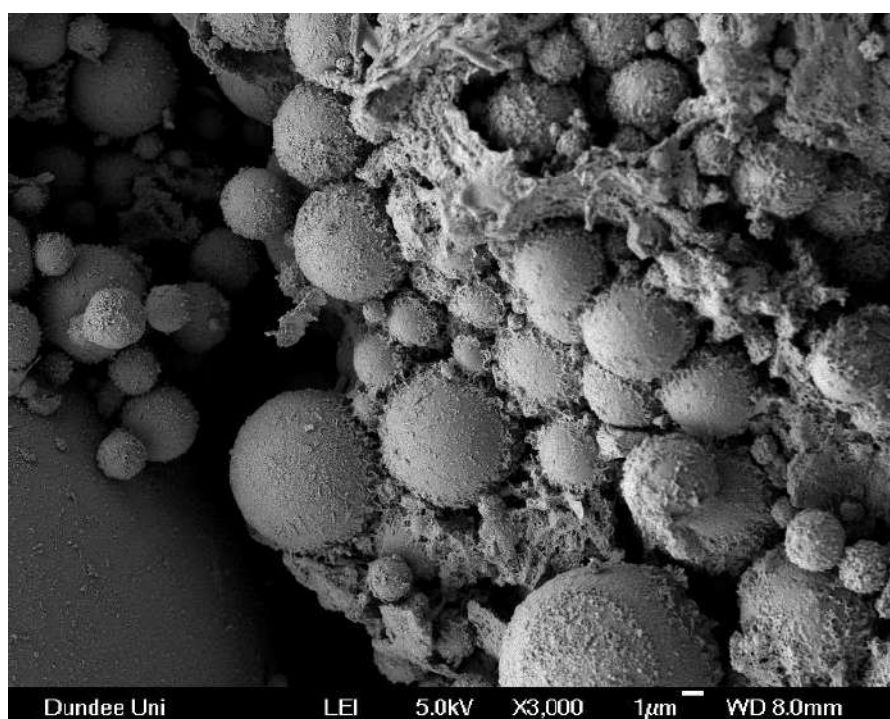
Figure 48 - Scanning Electron Microscopy image of DFA 5 laboratory wet-stored for 6 months at 10% moisture (x3000)

141
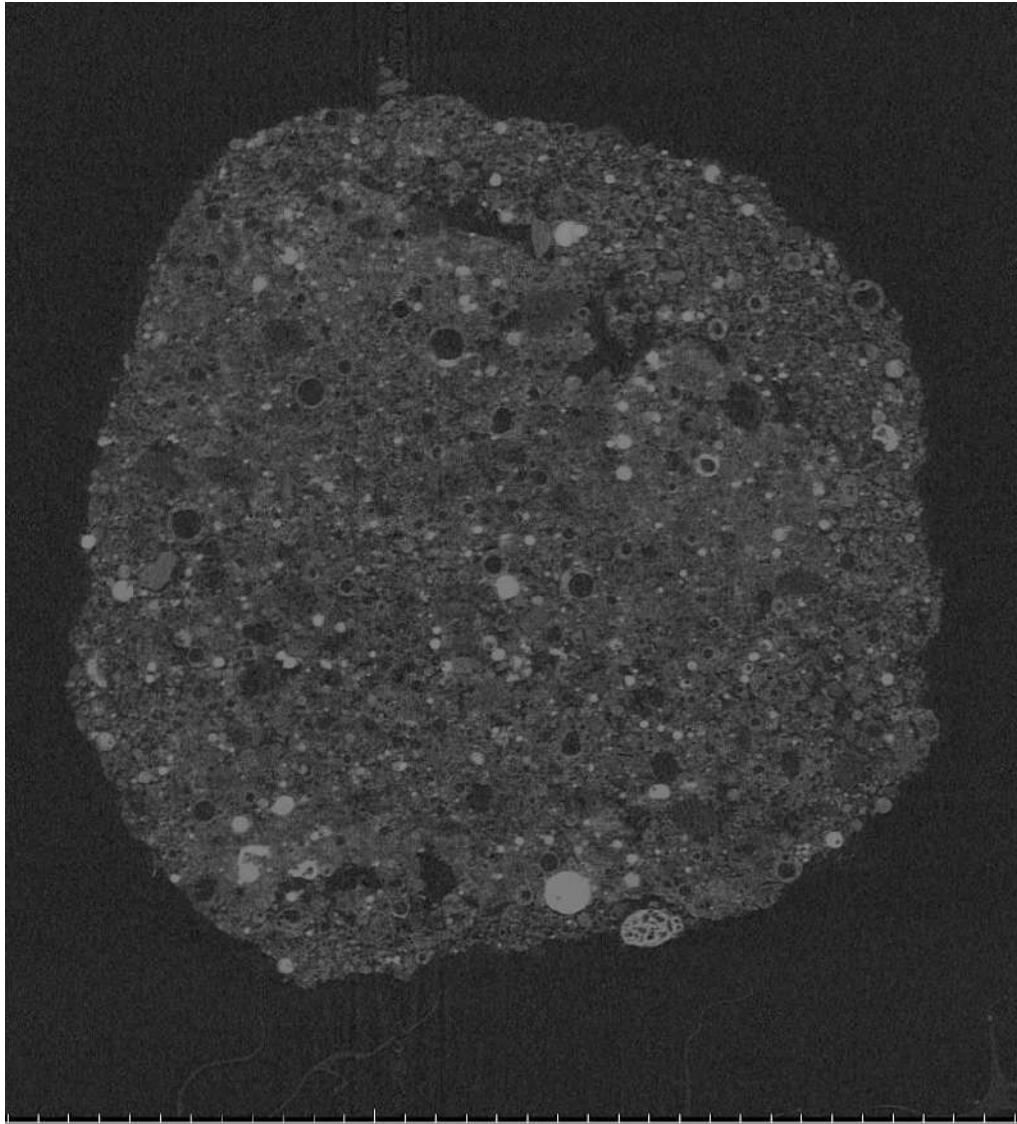
Figure 49 – Cross-section of Ø4mm agglomerate of DFA 5 LS-24M 10% using CT scanner

White regions represent solid fly ash particles

Grey regions represent fly ash particles and surface products between particles

Circular black regions with white/grey outlines are hollow fly ash cenospheres

Irregular black regions represent voids between fly ash particles
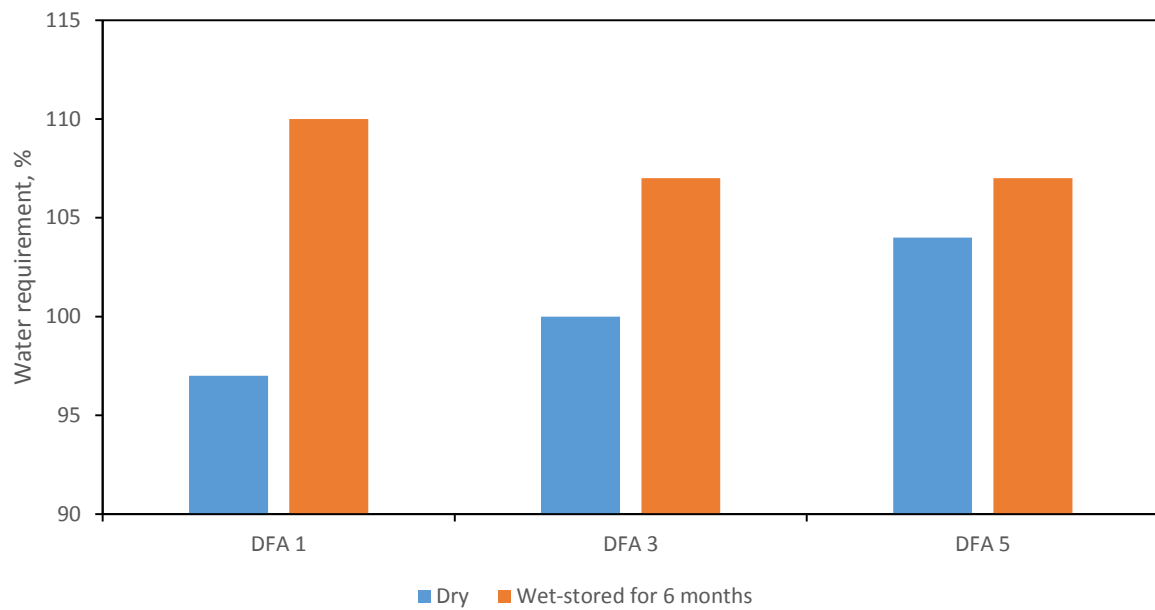
Figure 50 - Change in water requirement in selective dry materials after laboratory wet-storage for 6 months at 10% moisture
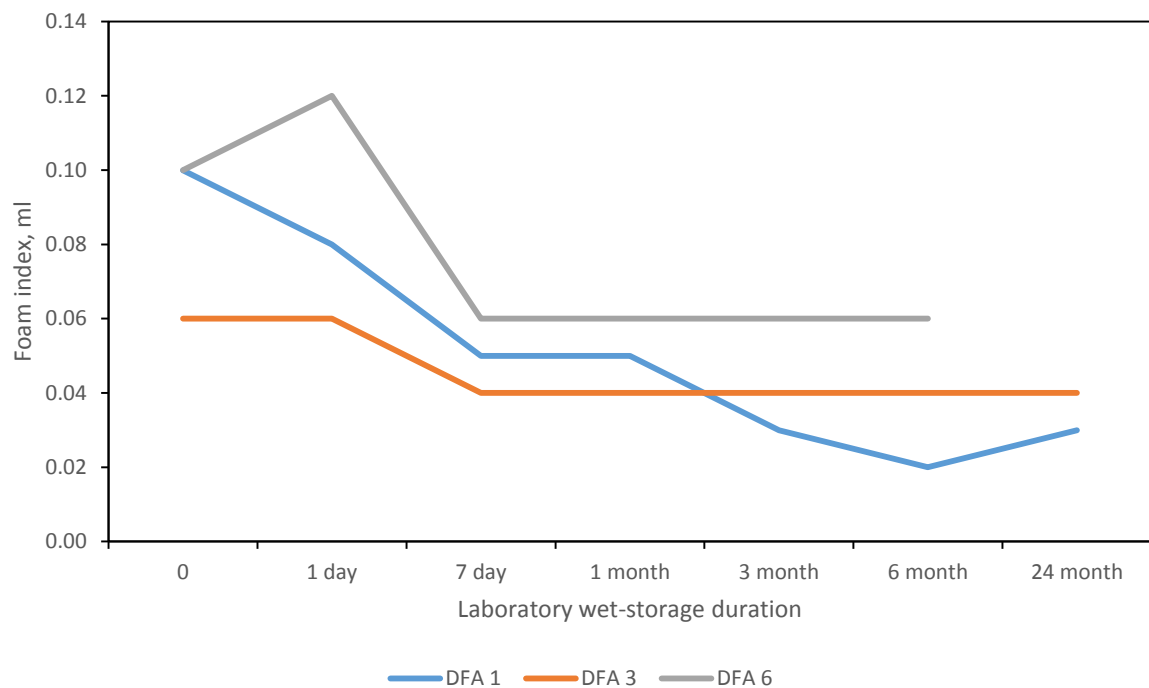
Figure 51 - Change in foam index with storage duration for laboratory wet-stored materials

143
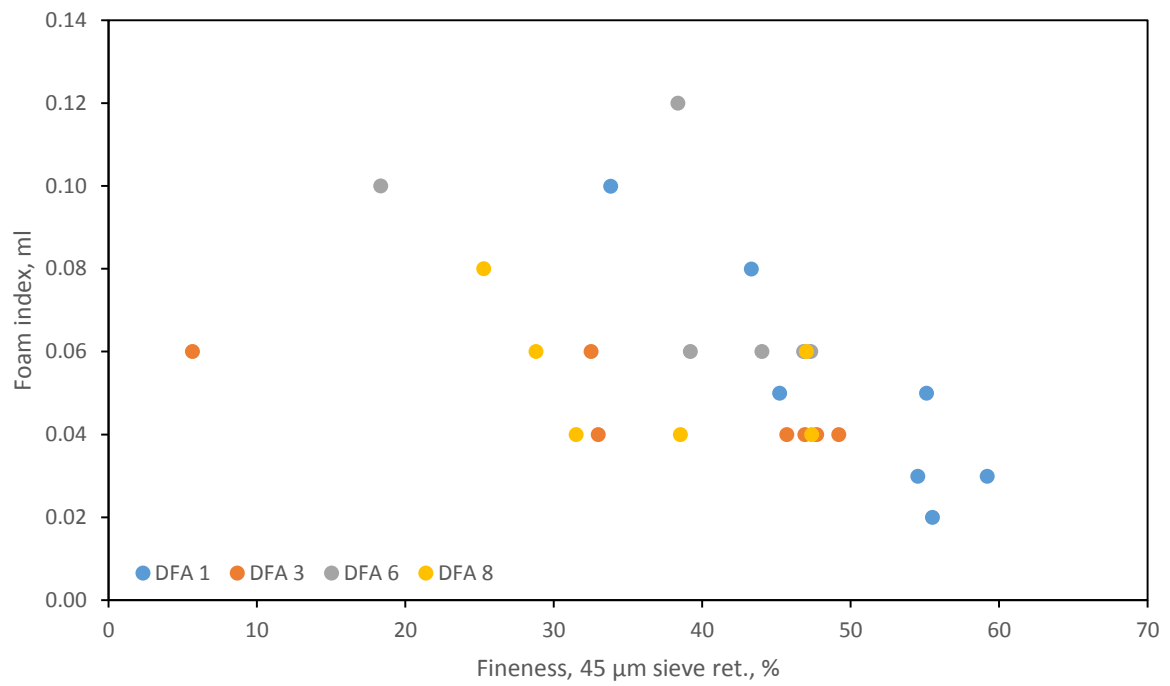
Figure 52 - Relationship between 45 µm sieve retention and foam index for various laboratory wet-stored materials
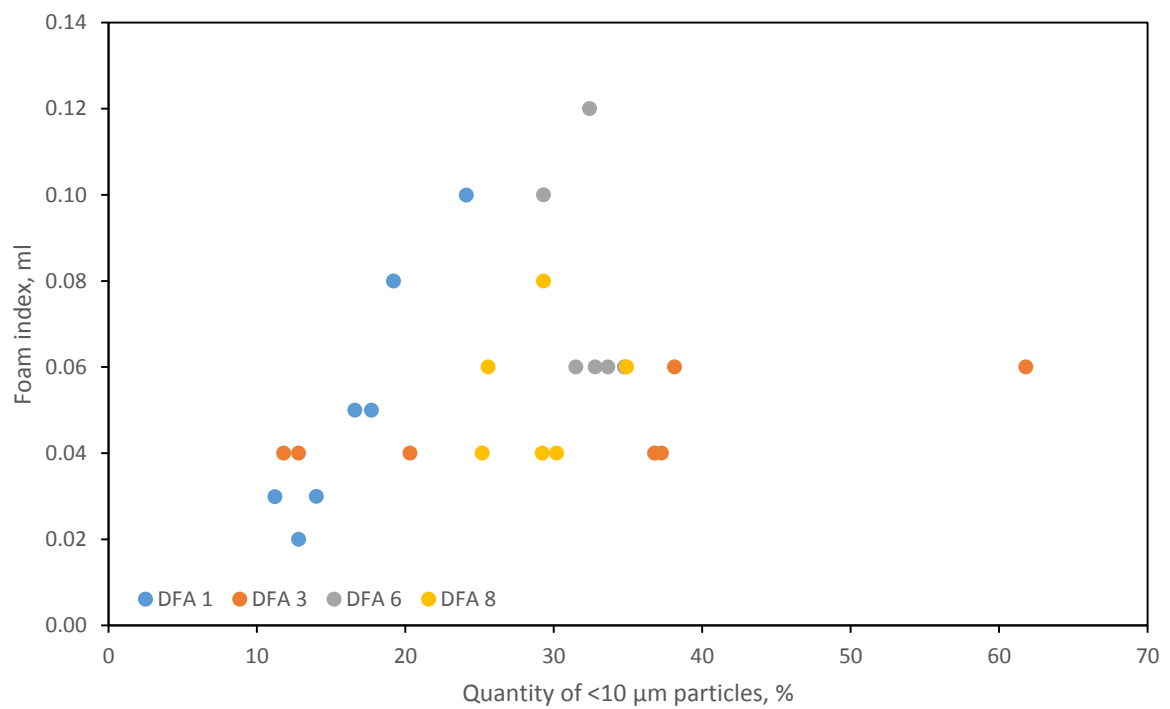
Figure 53 - Relationship between quantity of <10 µm particles and foam index for various laboratory wet-stored materials

144
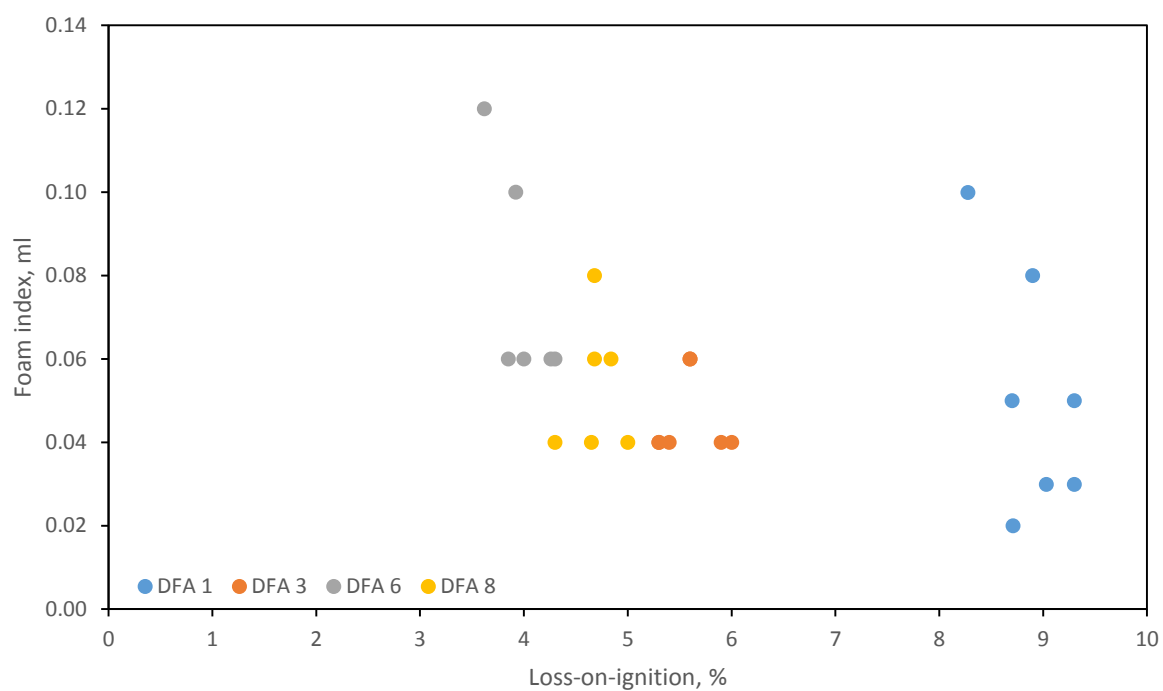
Figure 54 - Relationship between loss-on-ignition and foam index for various laboratory wet-stored materials
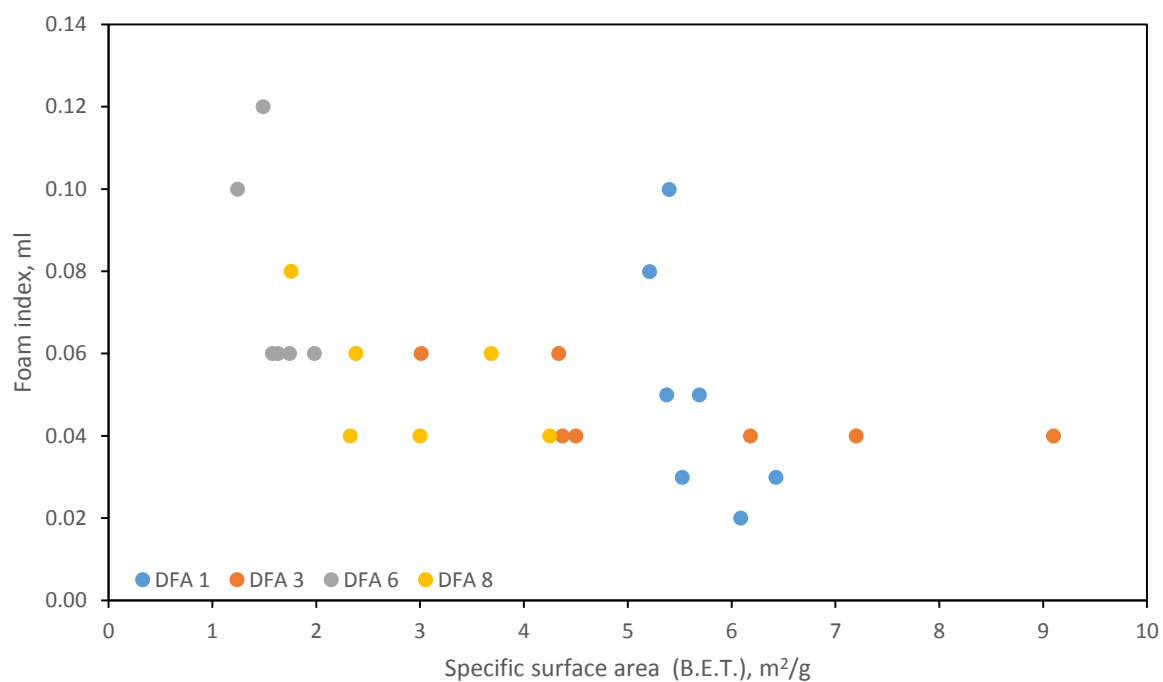
Figure 55 - Relationship between specific surface area (B.E.T.) and foam index for various laboratory wet-stored materials

145
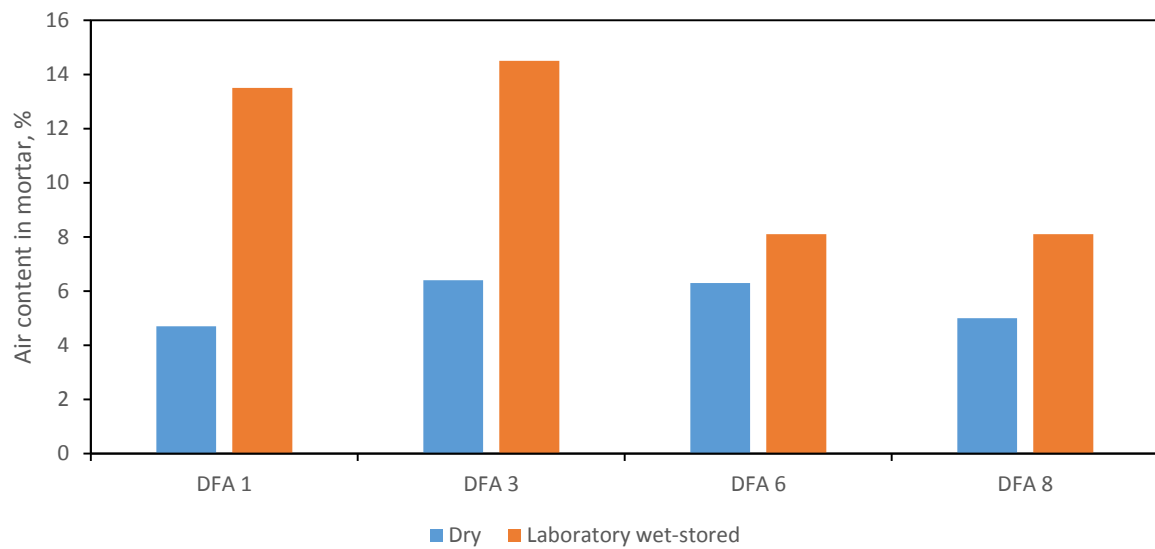
Figure 56 - Comparison between air contents achieved in mortar between dry and laboratory wet-stored materials after   6 months wet-storage for the same AEA dose
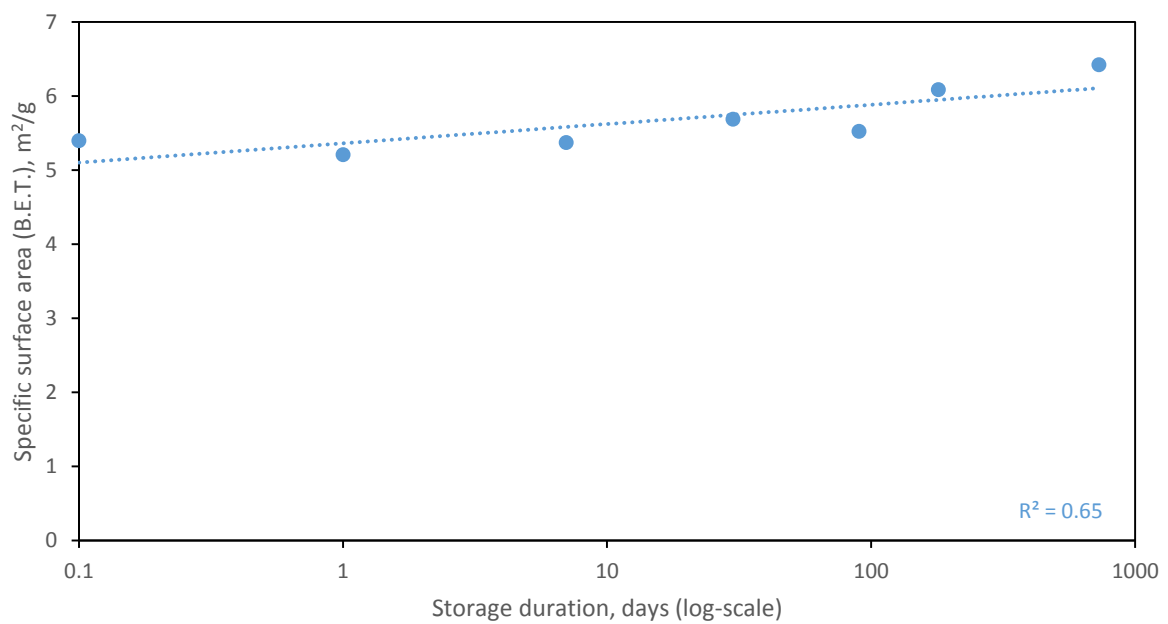
Figure 57 - Relationship between specific surface area (B.E.T.) and storage duration for DFA 1 laboratory wet-stored at 10% moisture
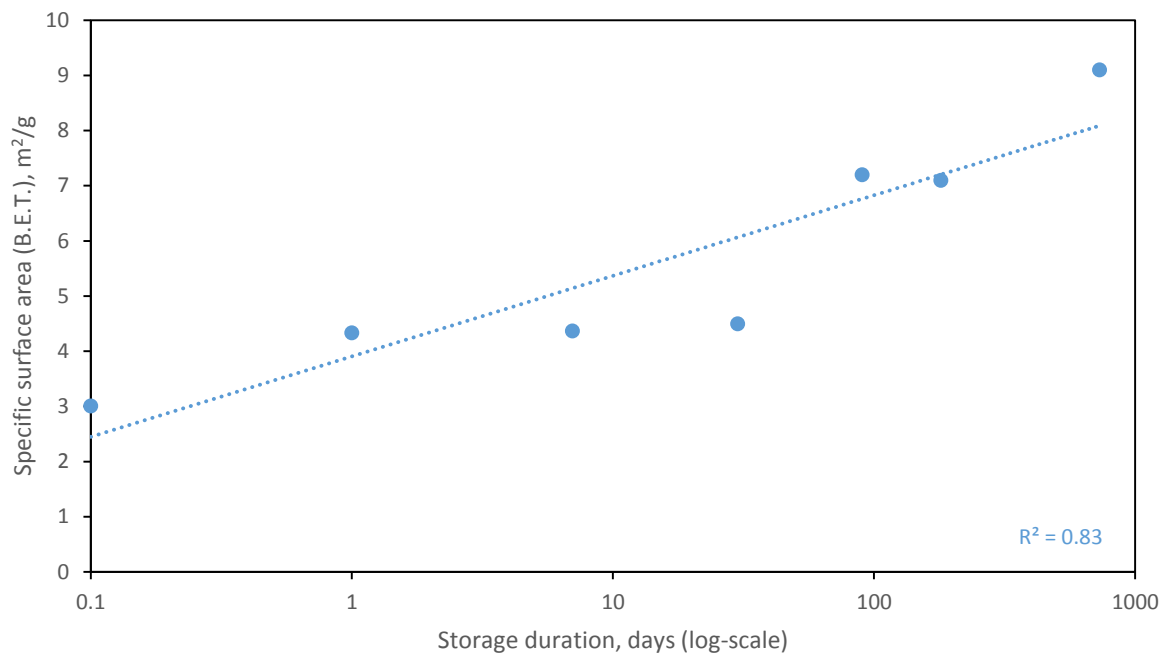
Figure 58 - Relationship between specific surface area (B.E.T.) and storage duration for DFA 3 laboratory wet-stored at 10% moisture
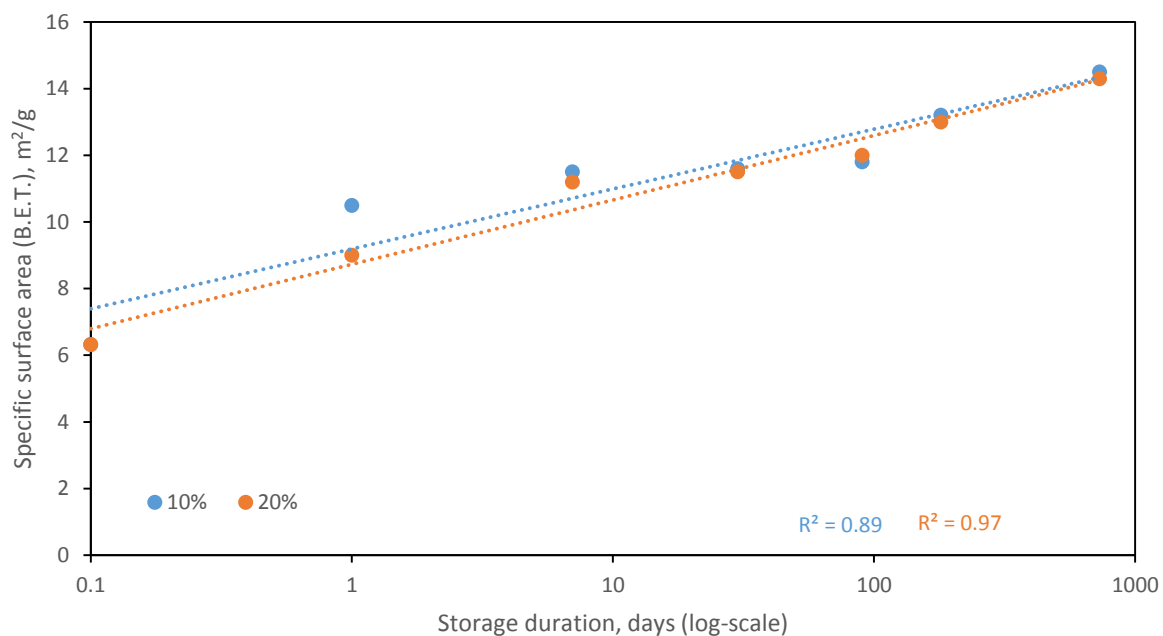
Figure 59 - Relationship between specific surface area (B.E.T.) and storage duration for DFA 4 laboratory wet-stored at 10% and 20% moisture

147
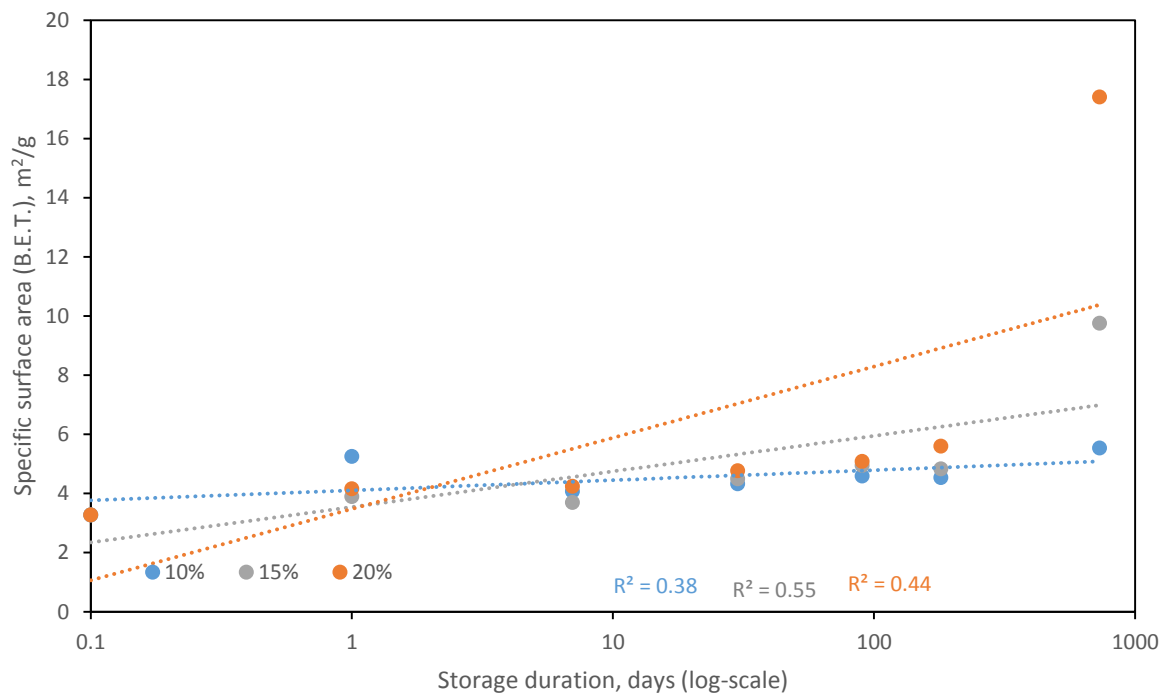
Figure 60 - Relationship between specific surface area (B.E.T.) and storage duration for DFA 5 laboratory wet-stored at 10%, 15% and 20% moisture
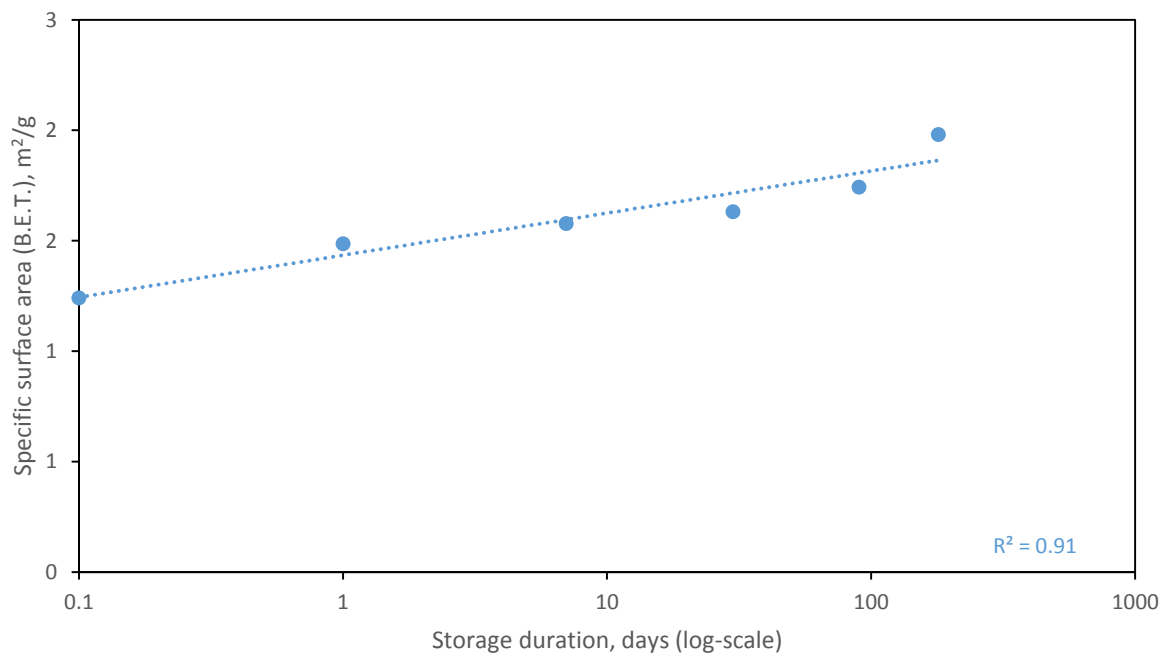
Figure 61 - Relationship between specific surface area (B.E.T.) and storage duration for DFA 6 laboratory wet-stored at 10% moisture
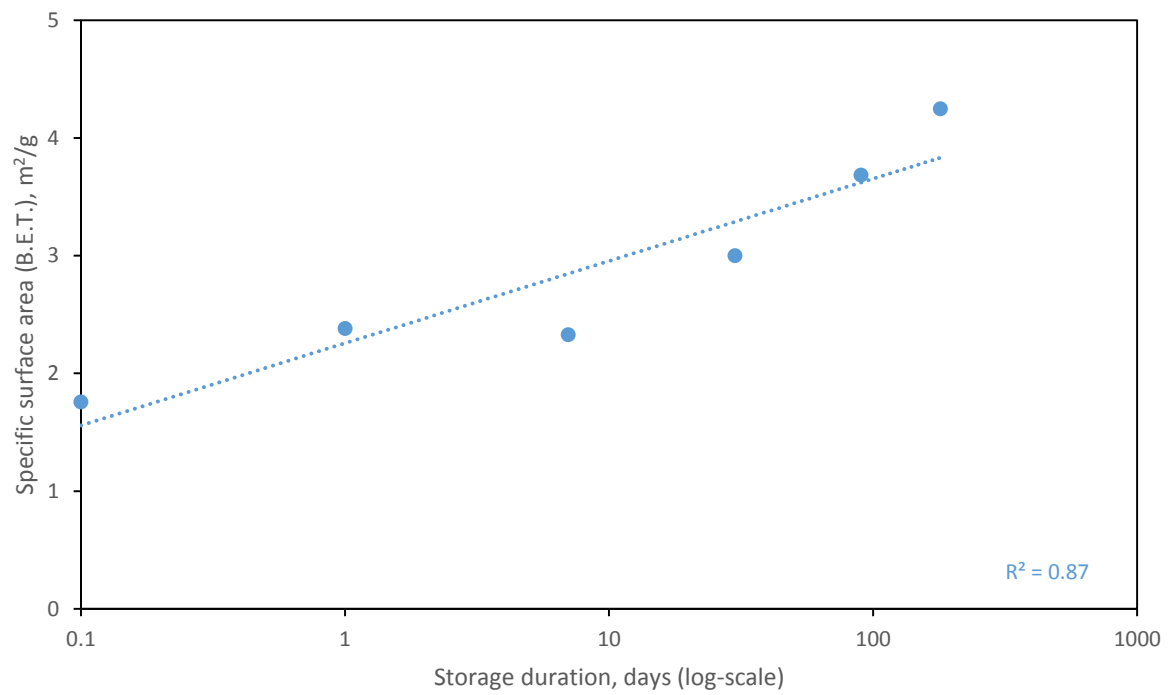
Figure 62 - Relationship between specific surface area (B.E.T.) and storage duration for DFA 8 laboratory wet-stored at 10% moisture
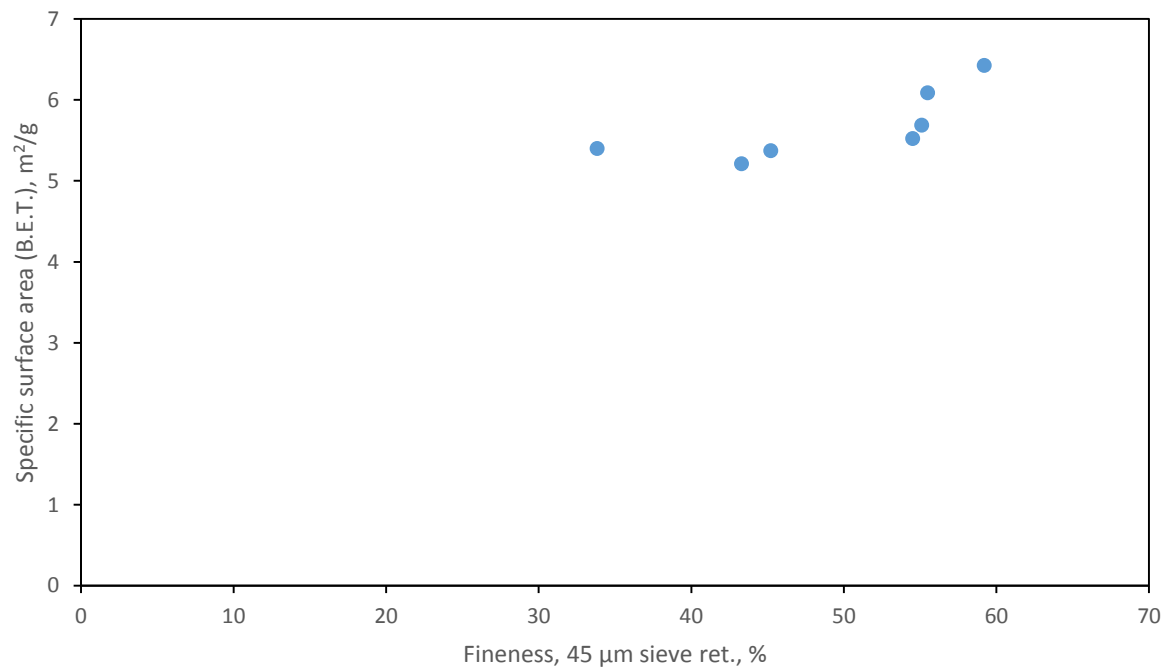
Figure 63 - Relationship between specific surface area (B.E.T.) and fineness for DFA 1 laboratory wet-stored at 10% moisture

149
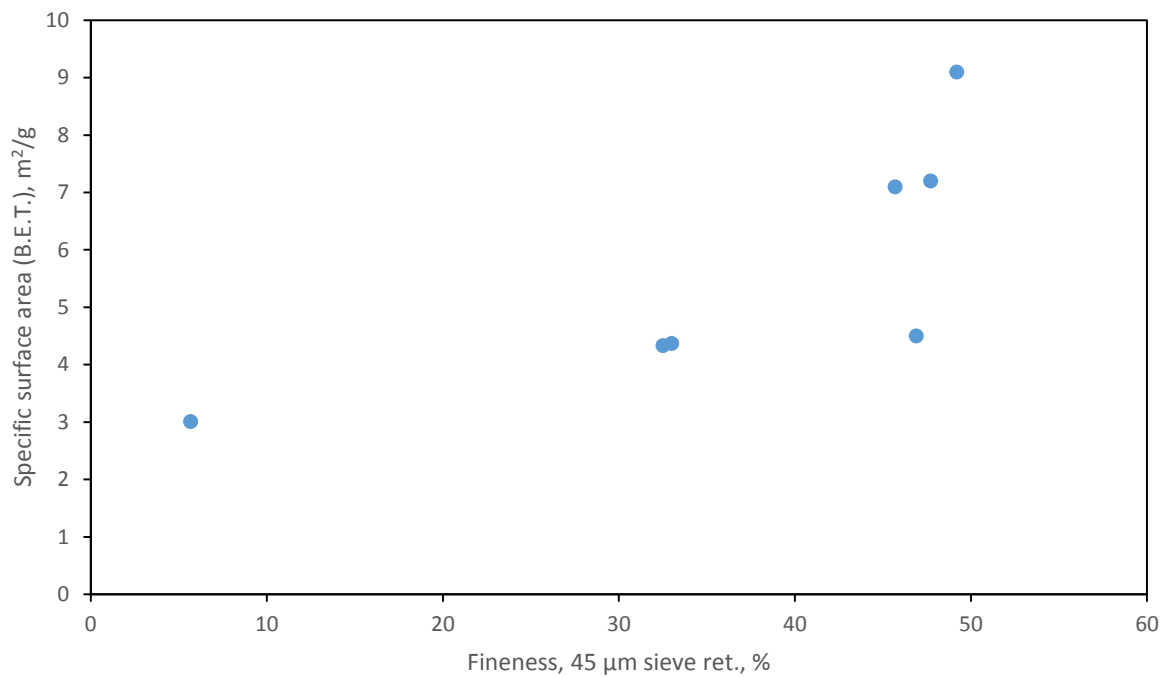
Figure 64 - Relationship between specific surface area (B.E.T.) and fineness for DFA 3 laboratory wet-stored at 10% moisture
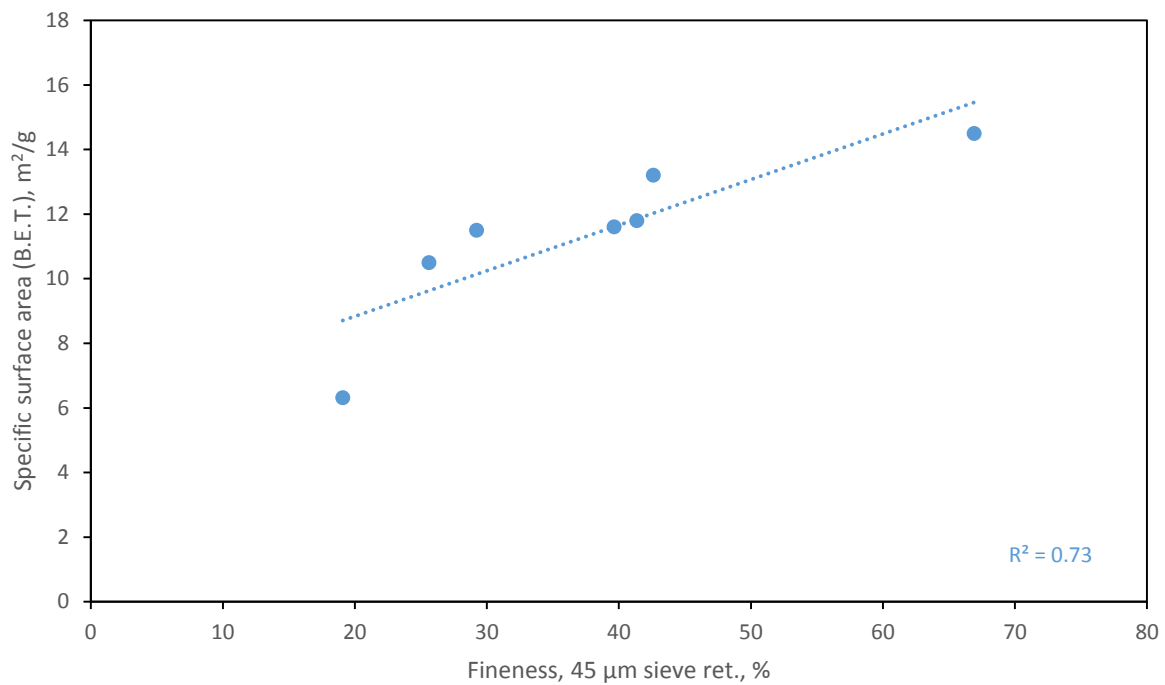
Figure 65 - Relationship between specific surface area (B.E.T.) and fineness for DFA 4 laboratory wet-stored at 10% moisture
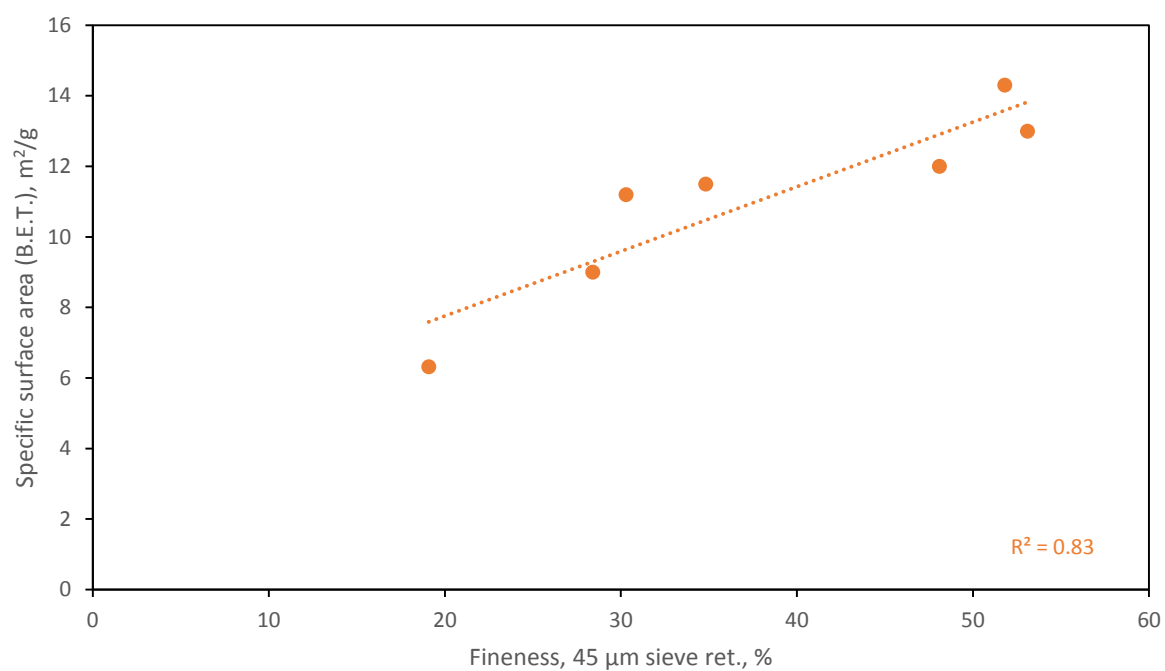
Figure 66 - Relationship between specific surface area (B.E.T.) and fineness for DFA 4 laboratory wet-stored at 20% moisture
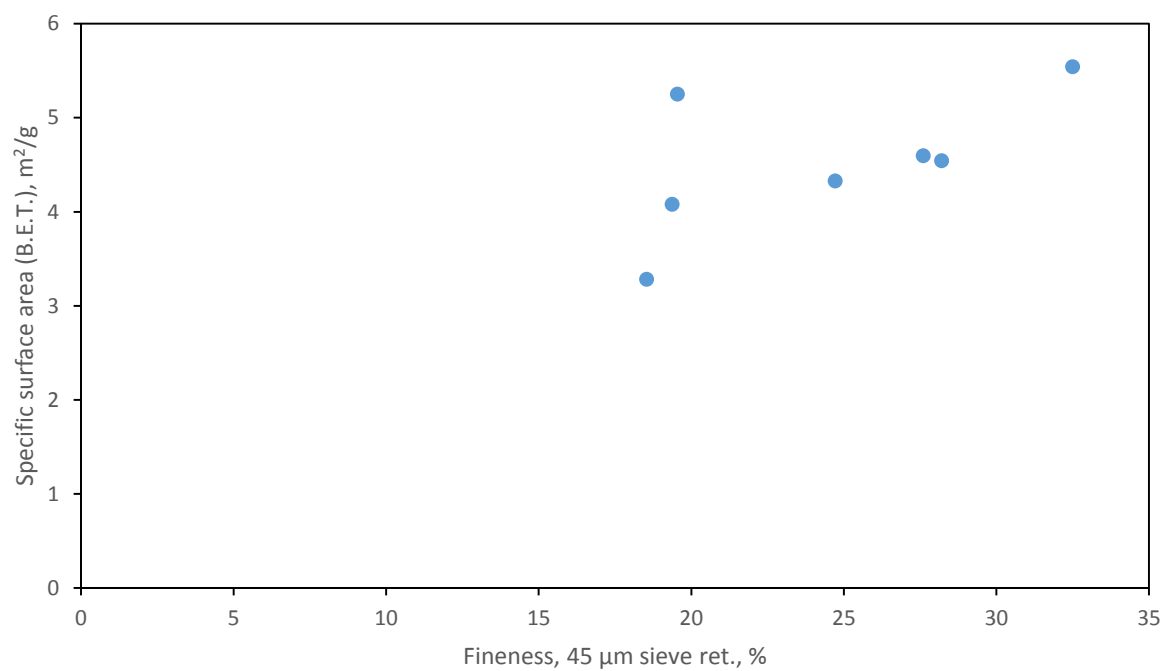
Figure 67 - Relationship between specific surface area (B.E.T.) and fineness for DFA 5 laboratory wet-stored at 10% moisture
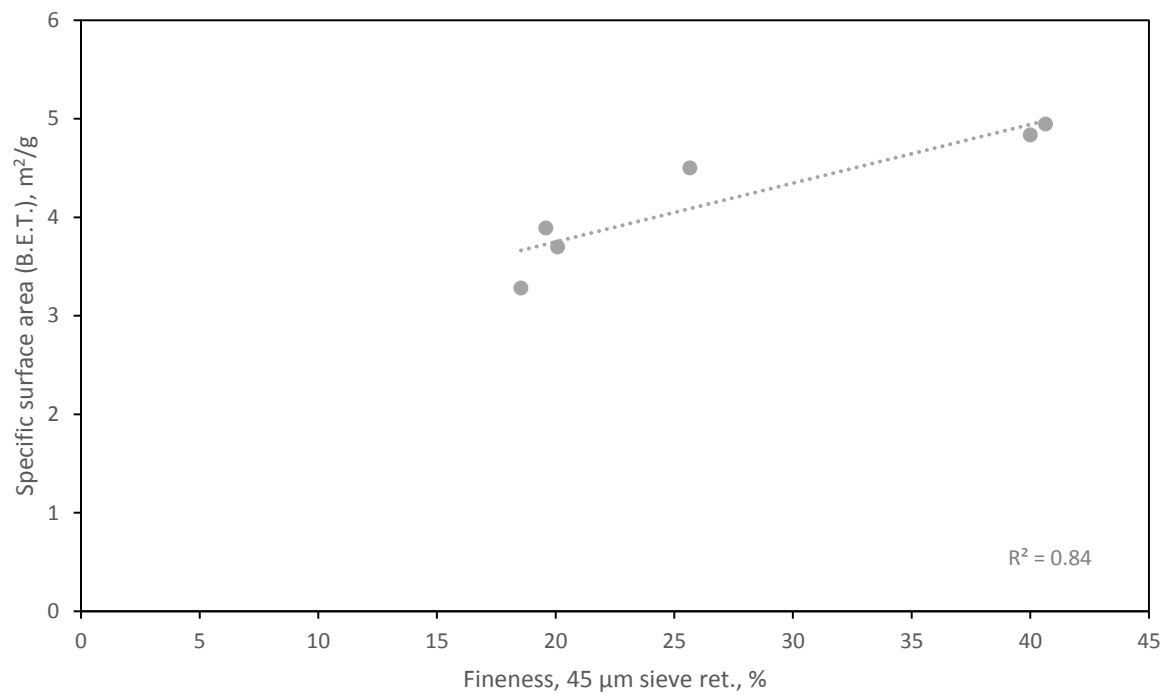
Figure 68 - Relationship between specific surface area (B.E.T.) and fineness for DFA 5 laboratory wet-stored at 15% moisture
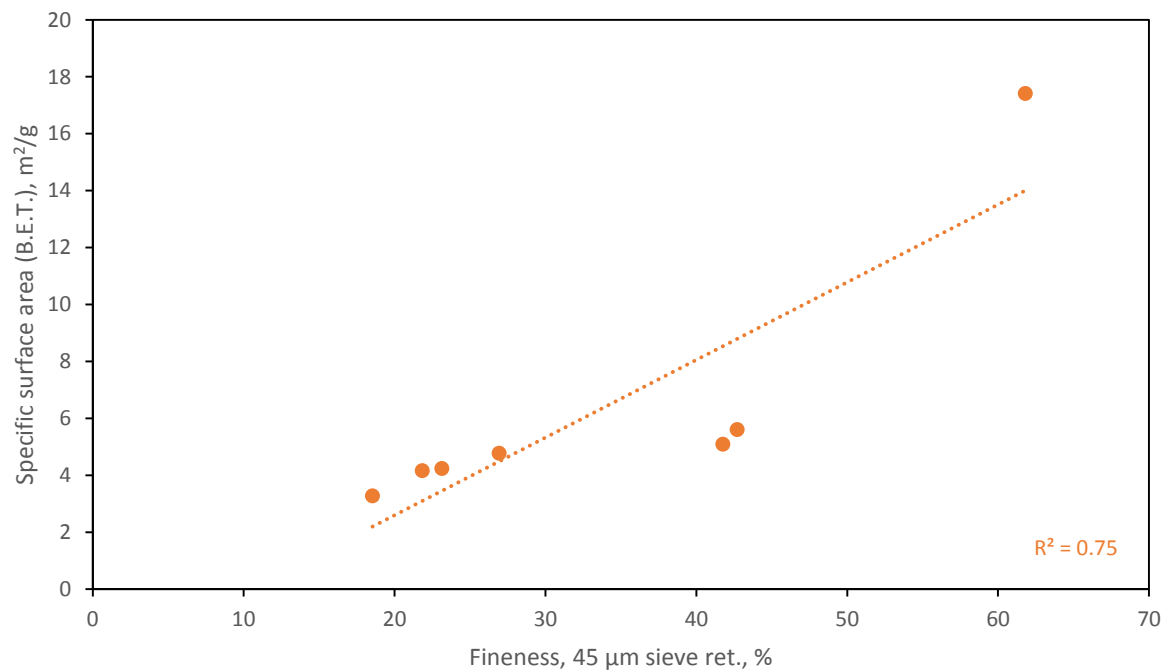
Figure 69 - Relationship between specific surface area (B.E.T.) and fineness for DFA 5 laboratory wet-stored at 20% moisture
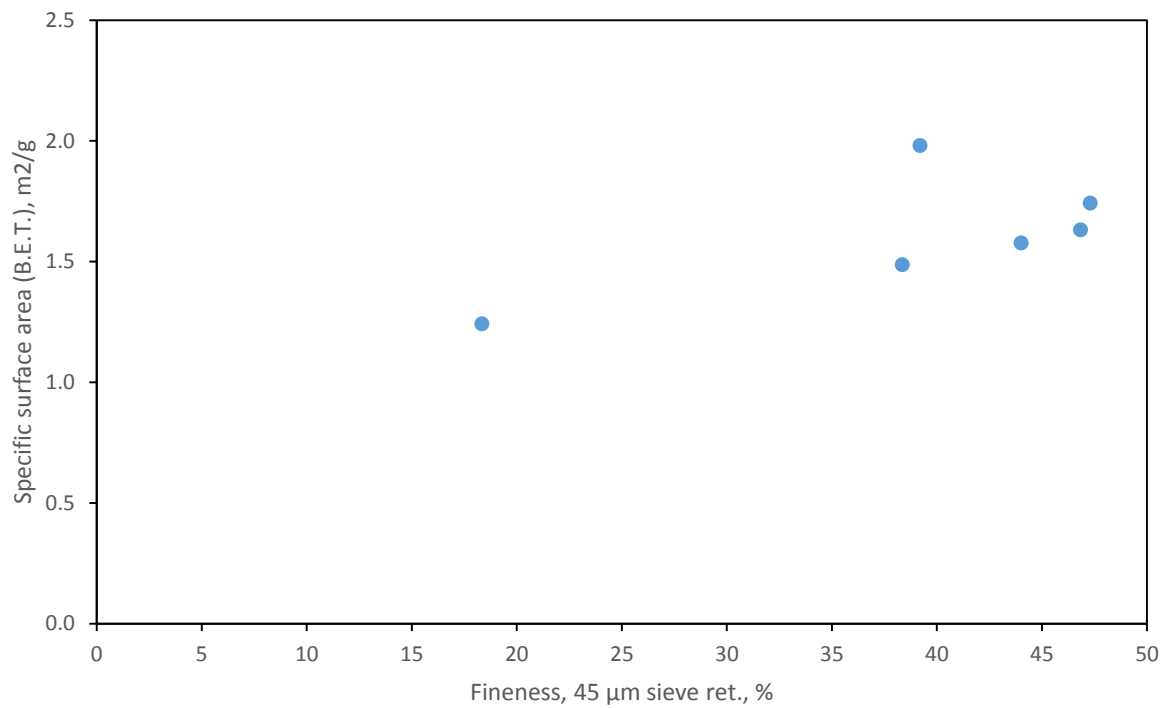
Figure 70 - Relationship between specific surface area (B.E.T.) and fineness for DFA 6 laboratory wet-stored at 10% moisture
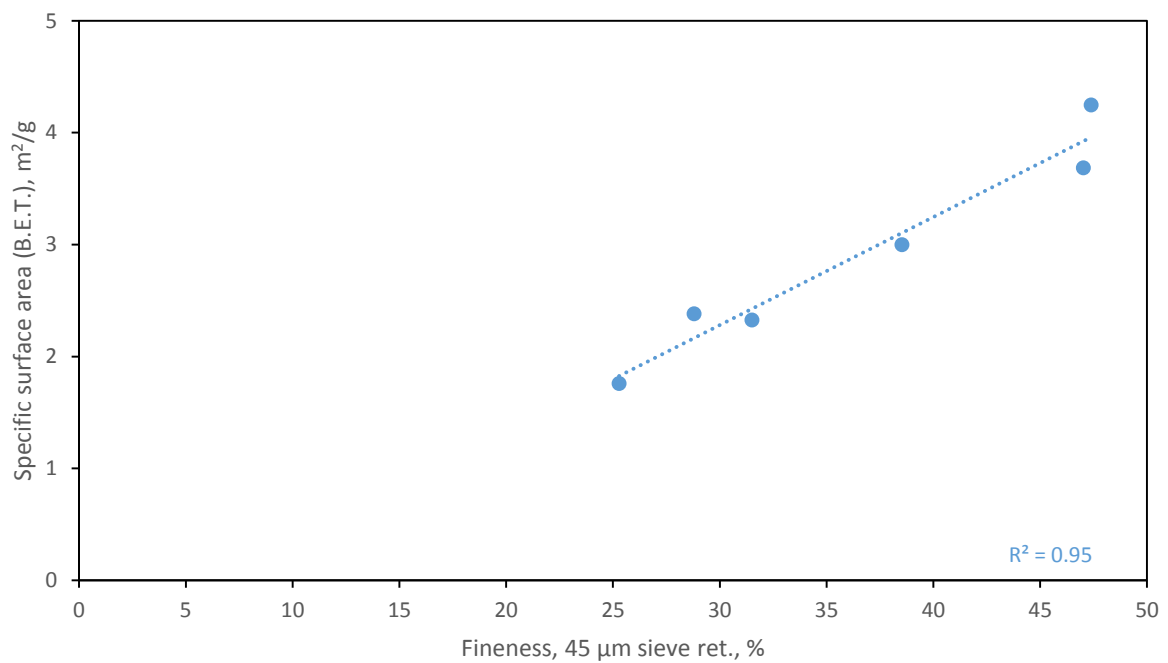
Figure 71 - Relationship between specific surface area (B.E.T.) and fineness for DFA 8 laboratory wet-stored at 10% moisture
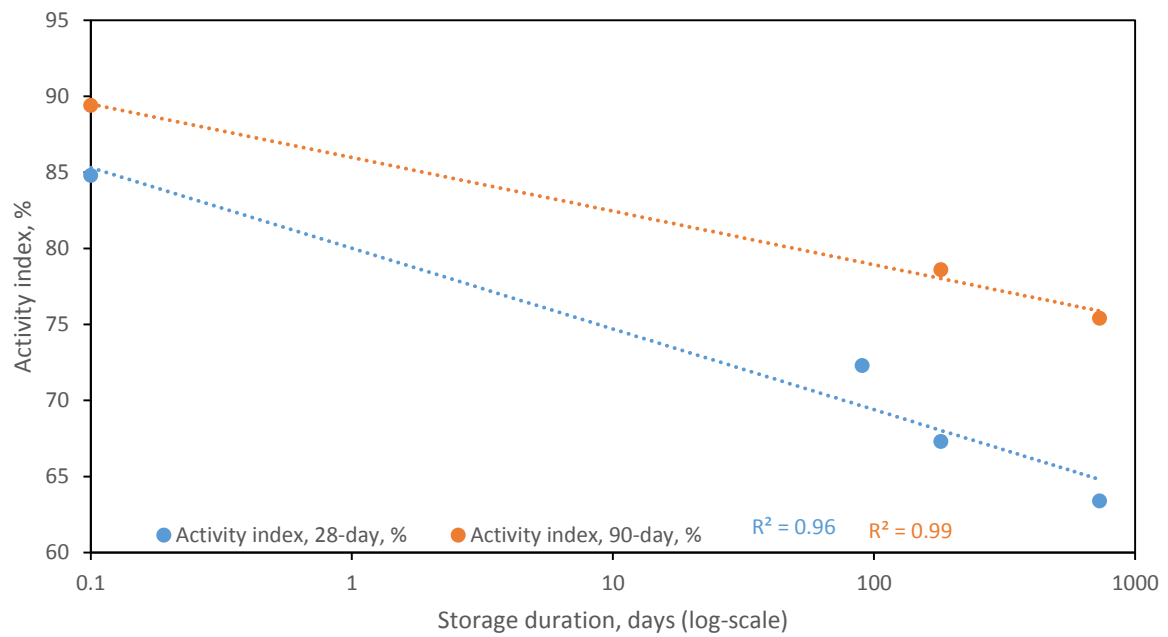
Figure 72 - Relationship between activity index, at 28 and 90-days, and storage duration for DFA 1 laboratory wet-stored at 10% moisture
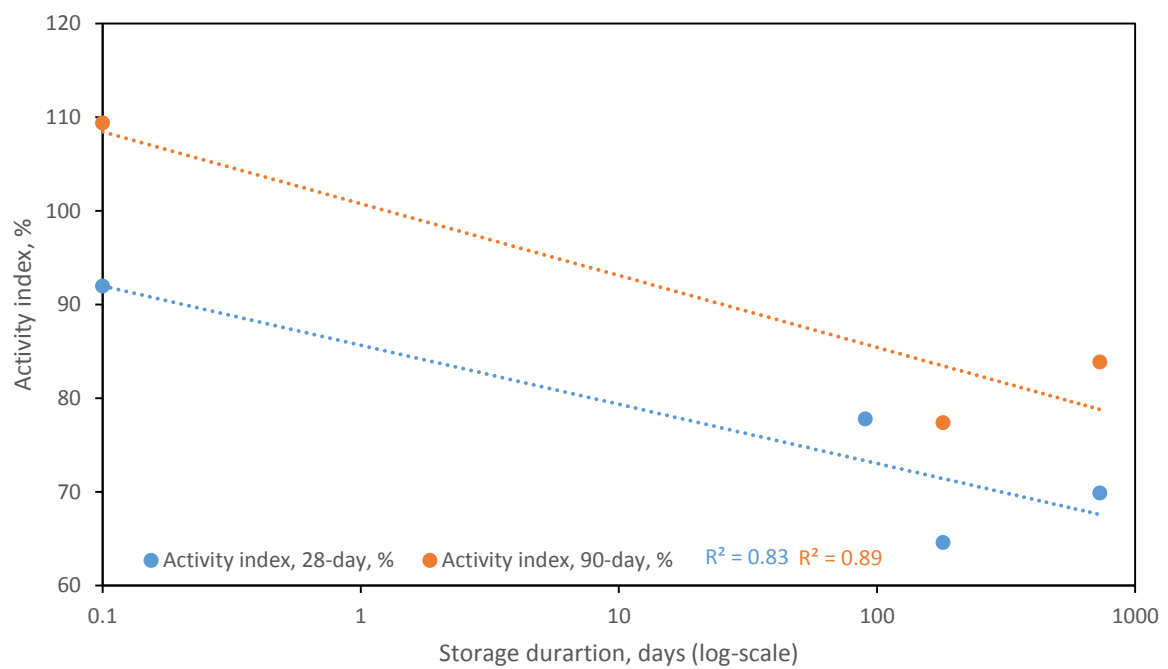
Figure 73 - Relationship between activity index, at 28 and 90-days, and storage duration for DFA 3 laboratory wet-stored at 10% moisture
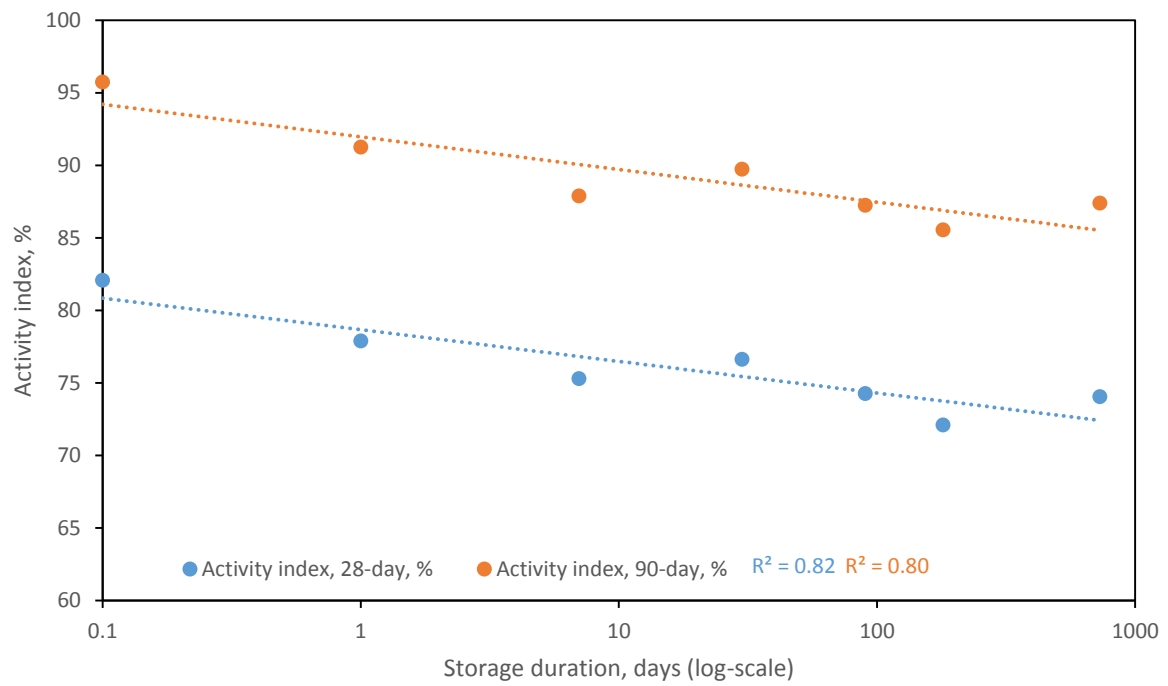
Figure 74 - Relationship between activity index, at 28 and 90-days, and storage duration for DFA 4 laboratory wet-stored at 10% moisture
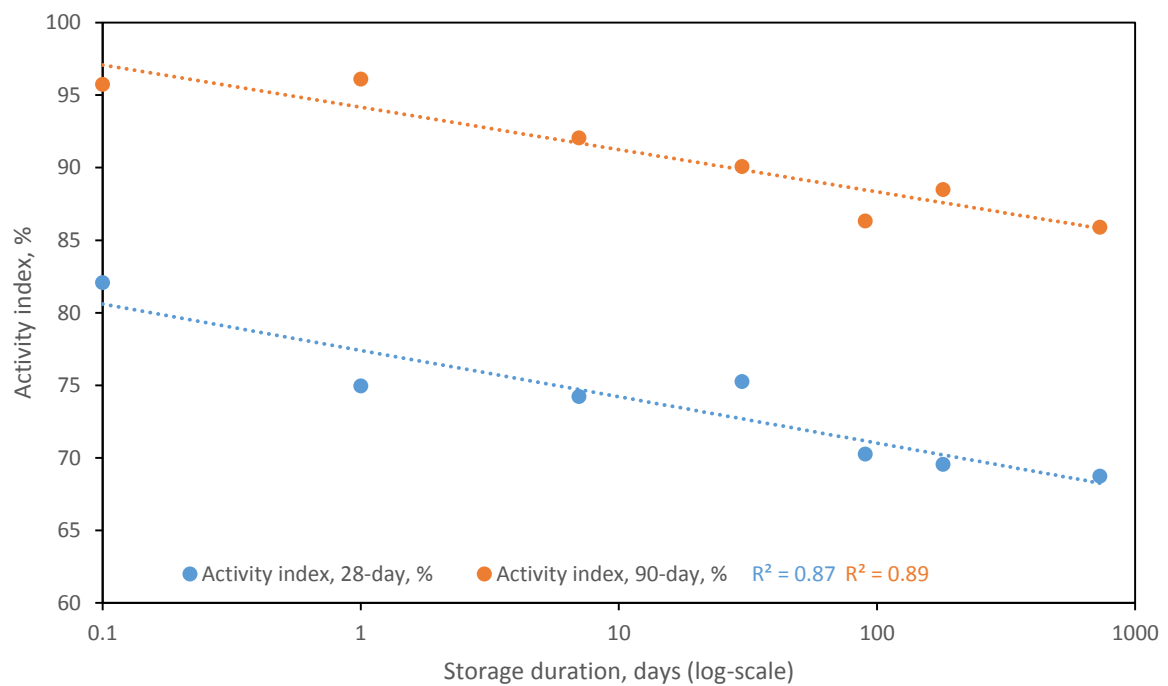
Figure 75 - Relationship between activity index, at 28 and 90-days, and storage duration for DFA 4 laboratory wet-stored at 20% moisture
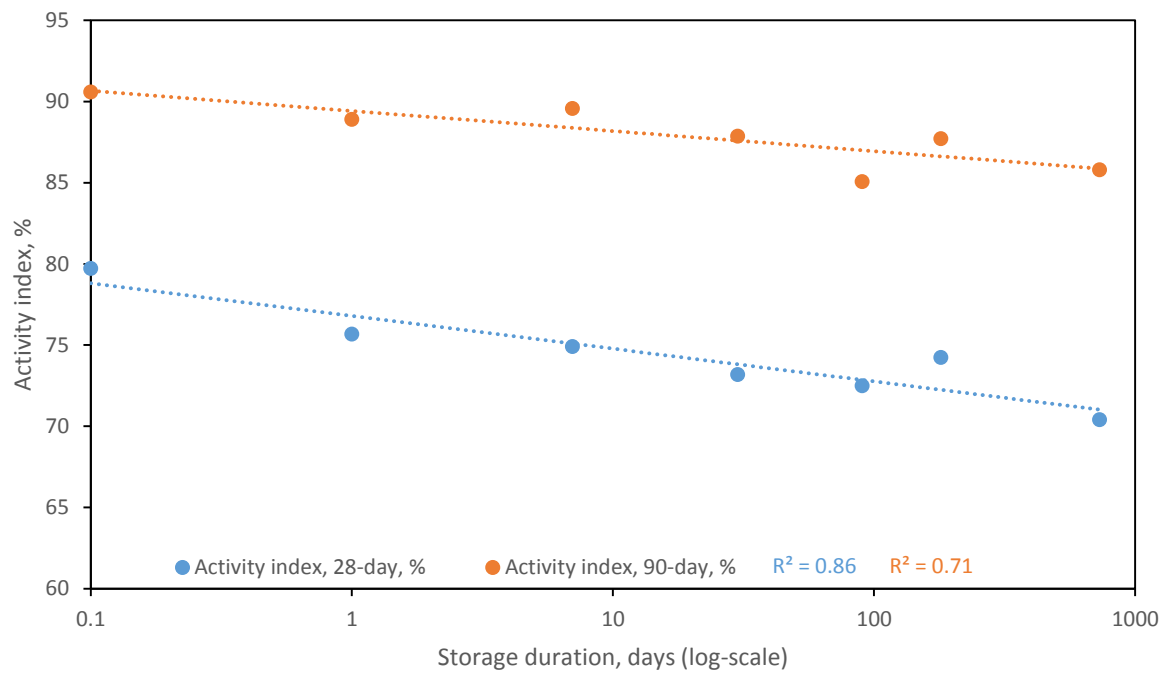
Figure 76 - Relationship between activity index, at 28 and 90-days, and storage duration for DFA 5 laboratory wet-stored at 10% moisture
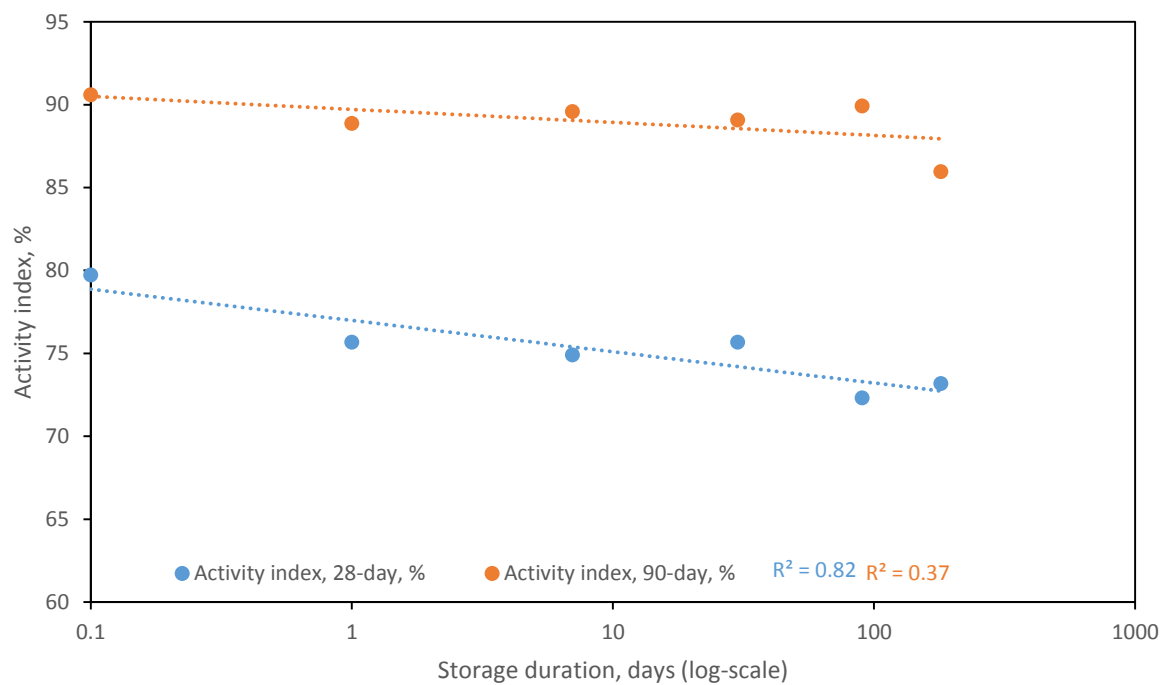
Figure 77 - Relationship between activity index, at 28 and 90-days, and storage duration for DFA 5 laboratory wet-stored at 15% moisture
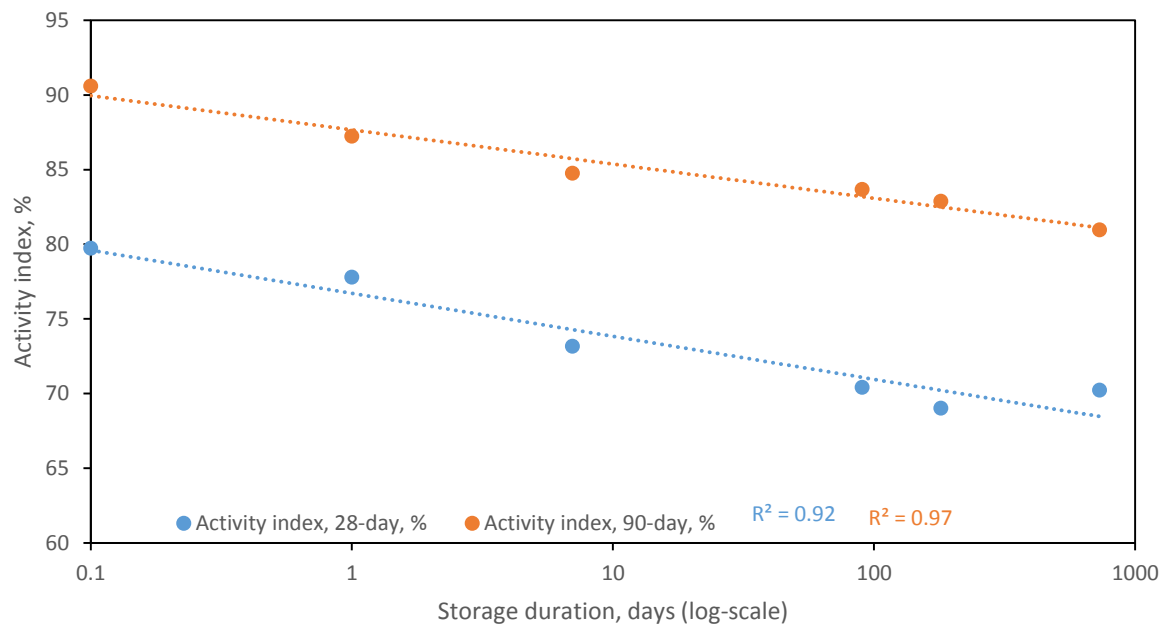
Figure 78 - Relationship between activity index, at 28 and 90-days, and storage duration for DFA 5 laboratory wet-stored at 20% moisture
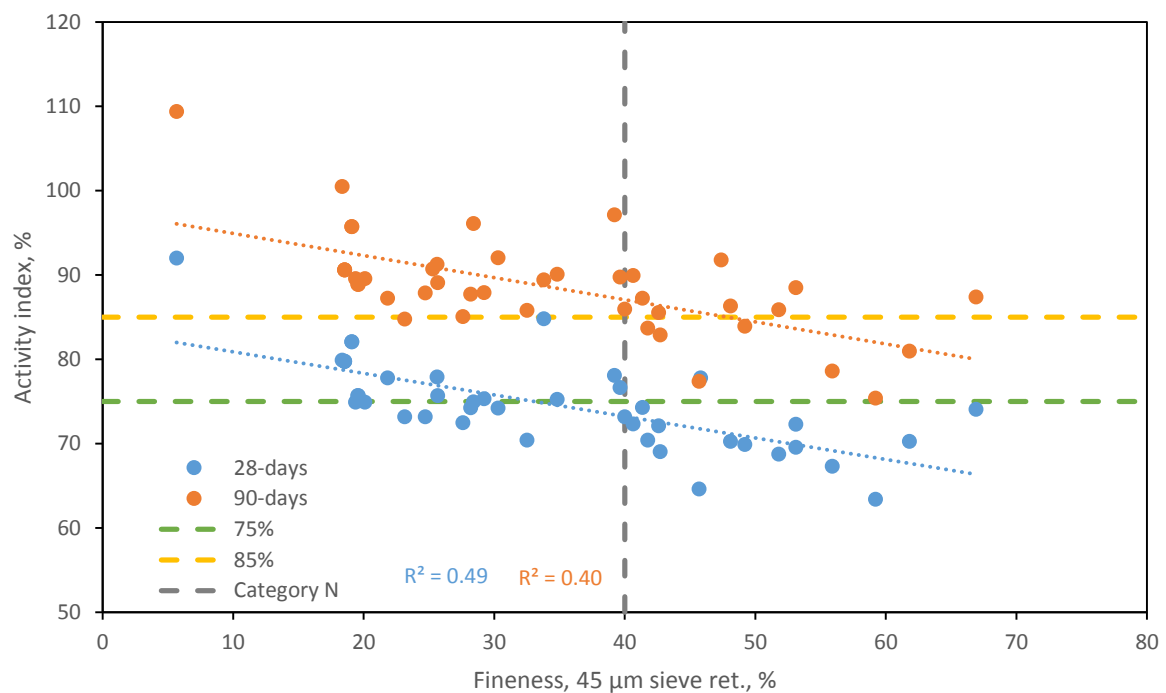
Figure 79 - Relationship between activity index and fineness for all laboratory wet-stored materials evaluated, with EN 450-1 limits for 28 and 90-day activity index and Category N sieve retention given.
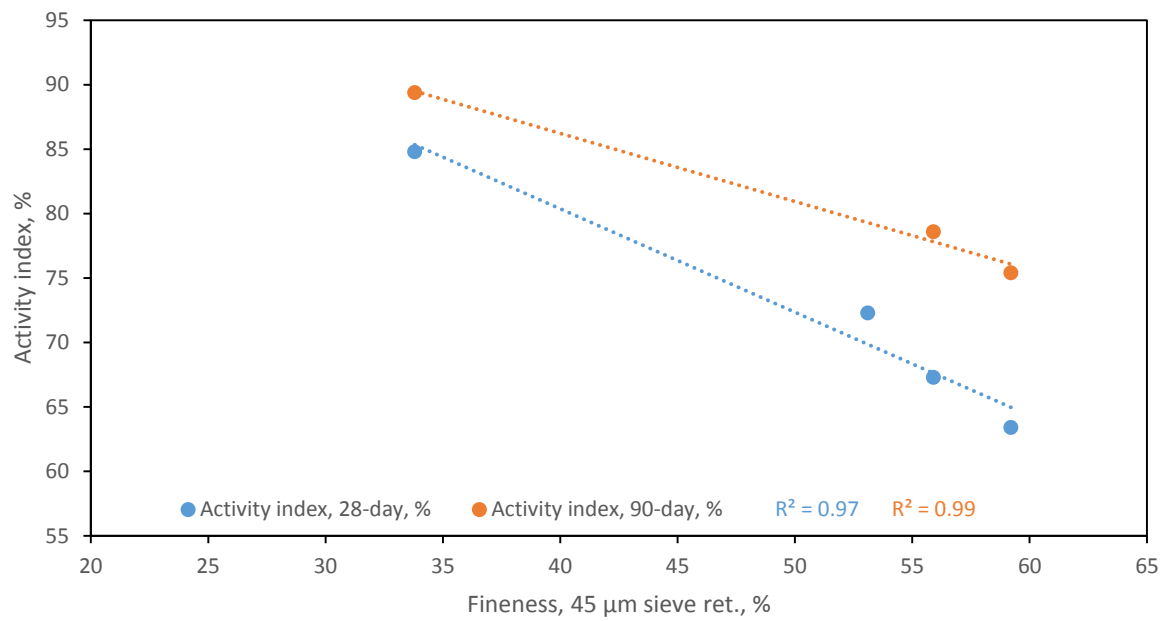
Figure 80 - Relationship between activity index, at 28 and 90-days, and fineness for DFA 1 laboratory wet-stored at 10% moisture
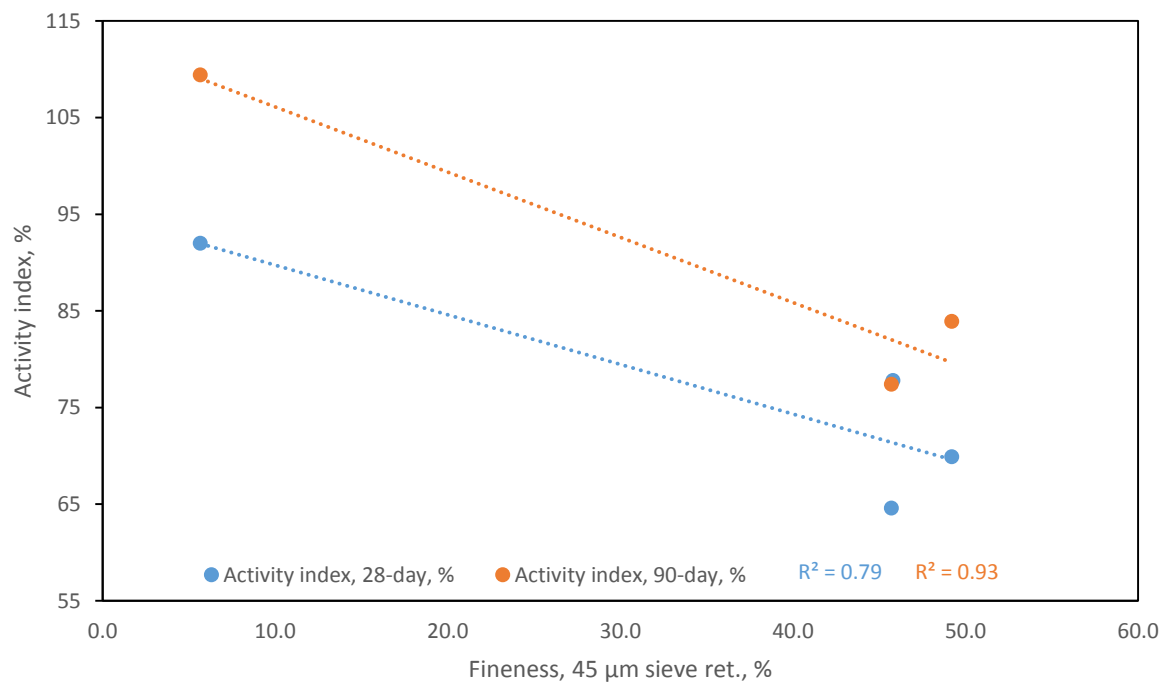
Figure 81 - Relationship between activity index, at 28 and 90-days, and fineness for DFA 3 laboratory wet-stored at 10% moisture
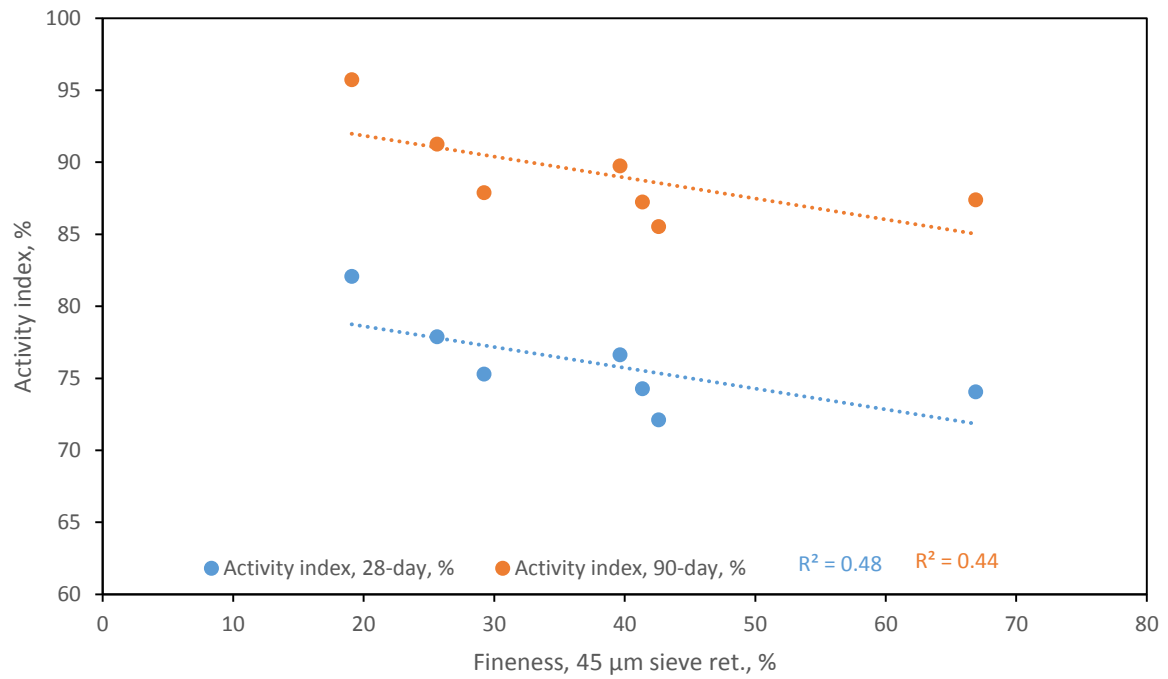
Figure 82 - Relationship between activity index, at 28 and 90-days, and fineness for DFA 4 laboratory wet-stored at 10% moisture
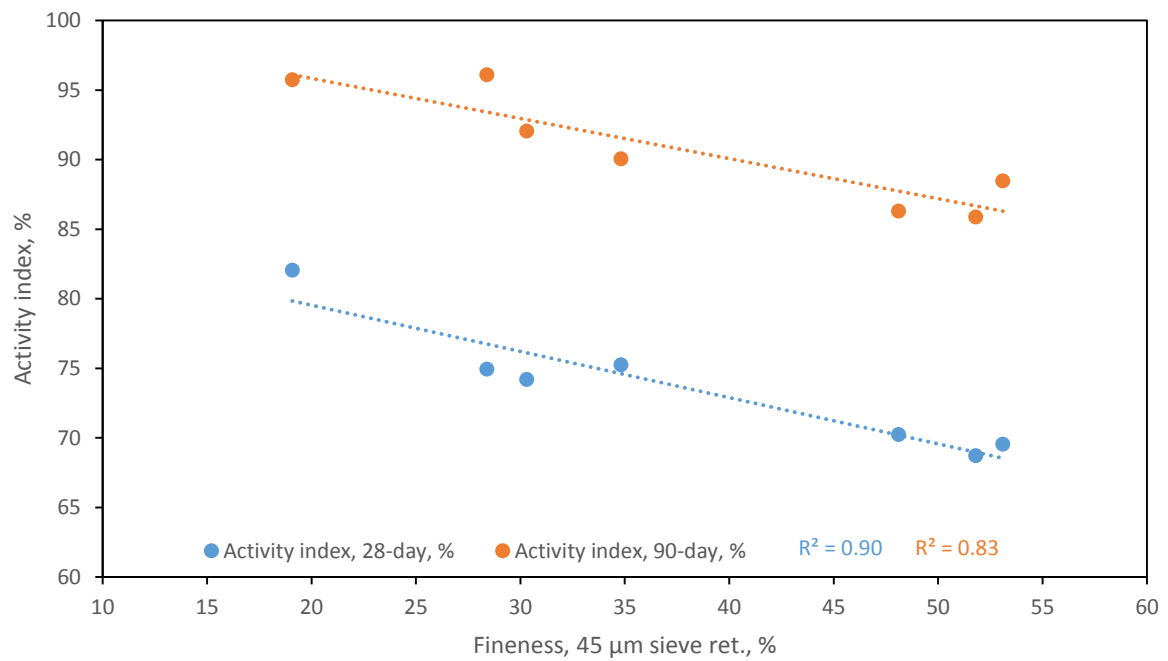
Figure 83 - Relationship between activity index, at 28 and 90-days, and fineness for DFA 4 laboratory wet-stored at 20% moisture
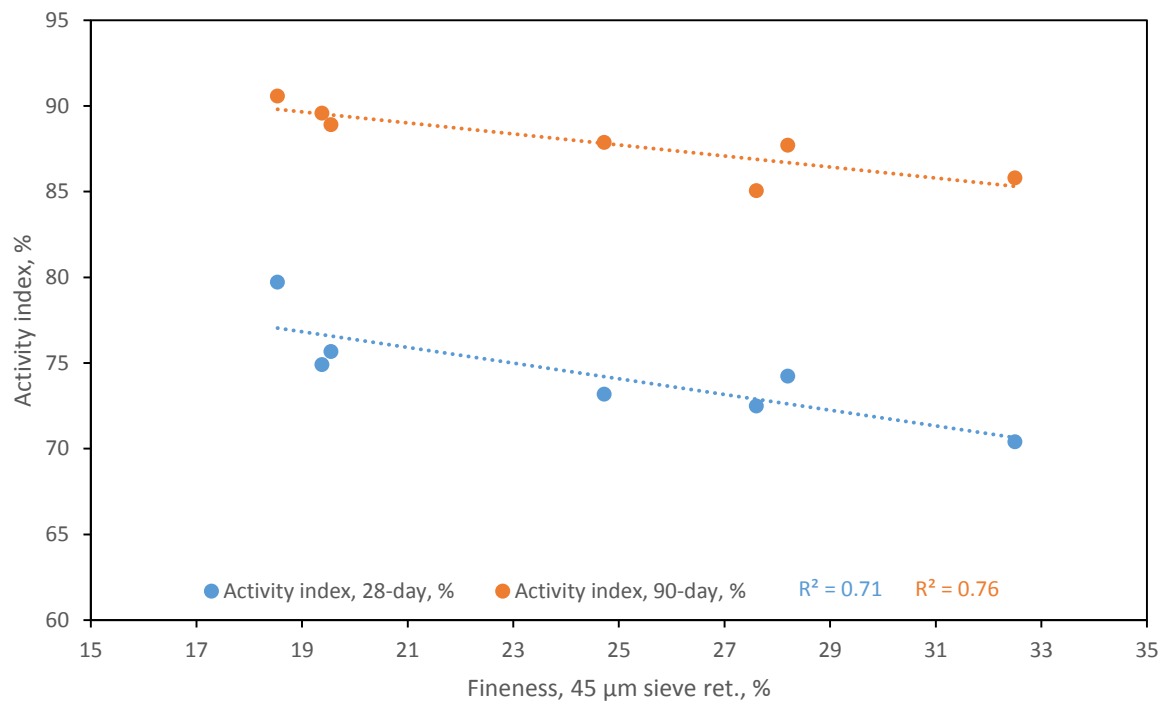
Figure 84 - Relationship between activity index, at 28 and 90-days, and fineness for DFA 5 laboratory wet-stored at 10% moisture
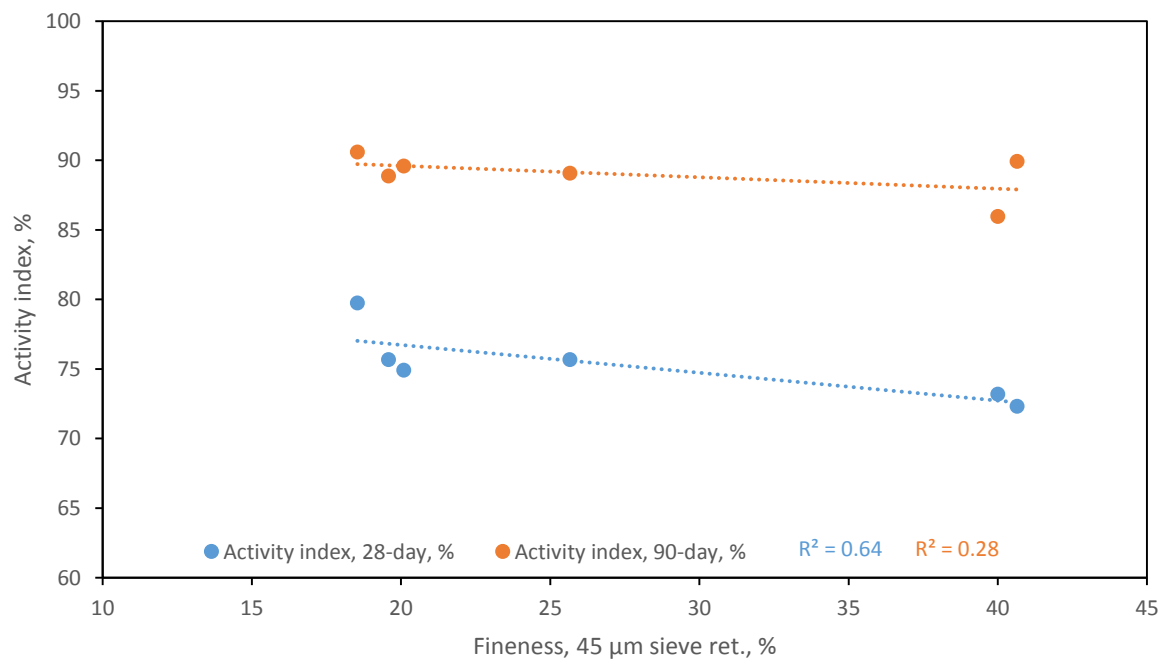
Figure 85 - Relationship between activity index, at 28 and 90-days, and fineness for DFA 5 laboratory wet-stored at 15% moisture
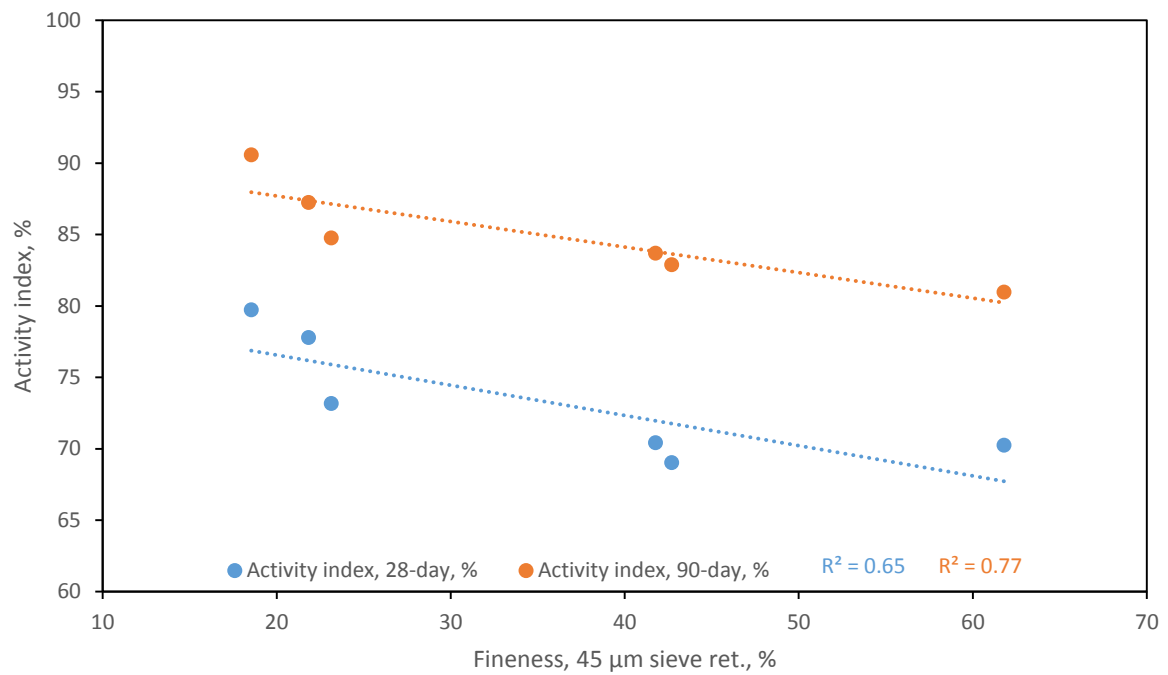
Figure 86 - Relationship between activity index, at 28 and 90-days, and fineness for DFA 5 laboratory wet-stored at 20% moisture
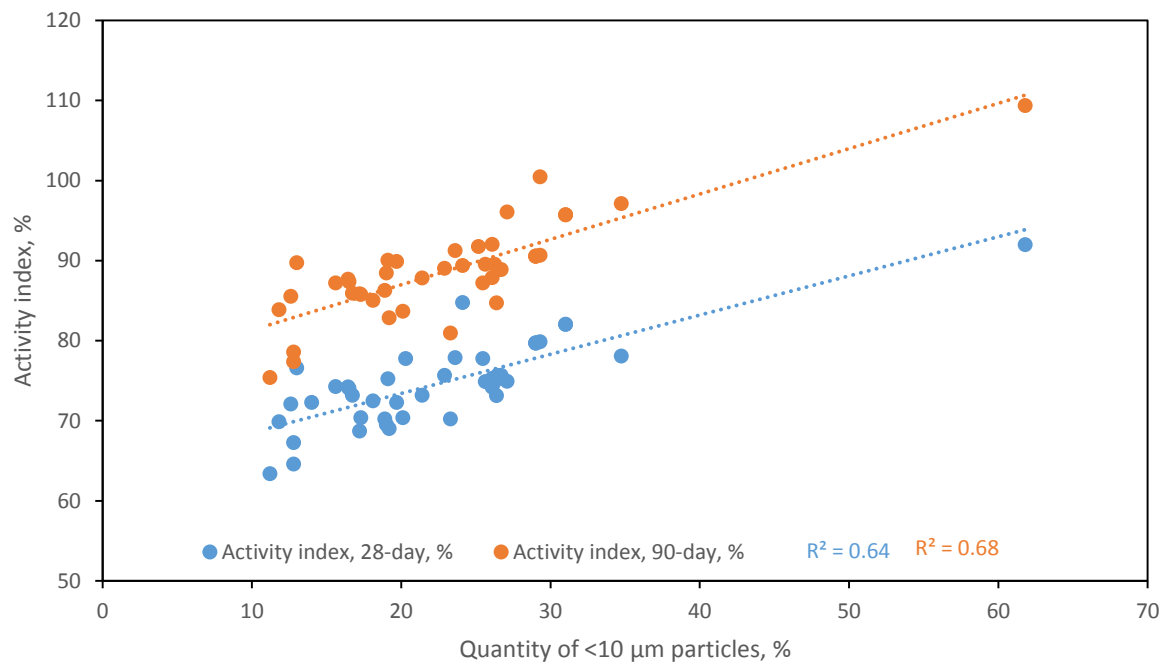
Figure 87 - Relationship between activity index, at 28 and 90-days, and quantity of <10 μm particles of all laboratory wet-stored materials evaluated

161
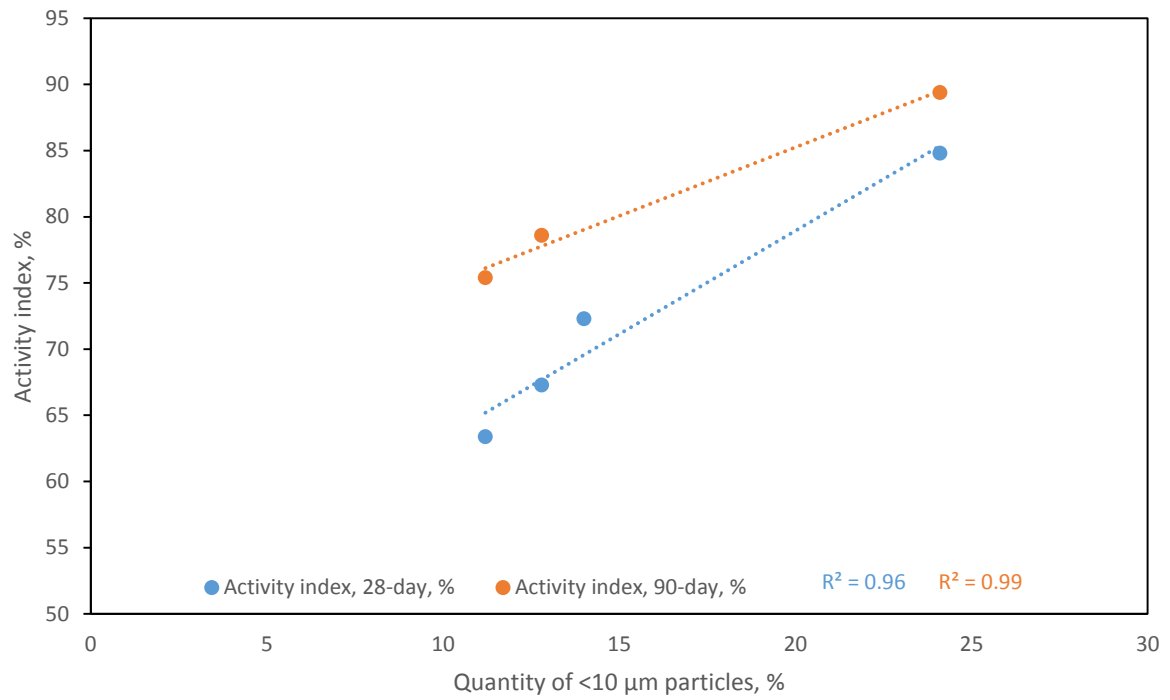
Figure 88 - Relationship between activity index, at 28 and 90-days, and quantity of <10 µm particles of DFA 1 laboratory wet-stored at 10% moisture
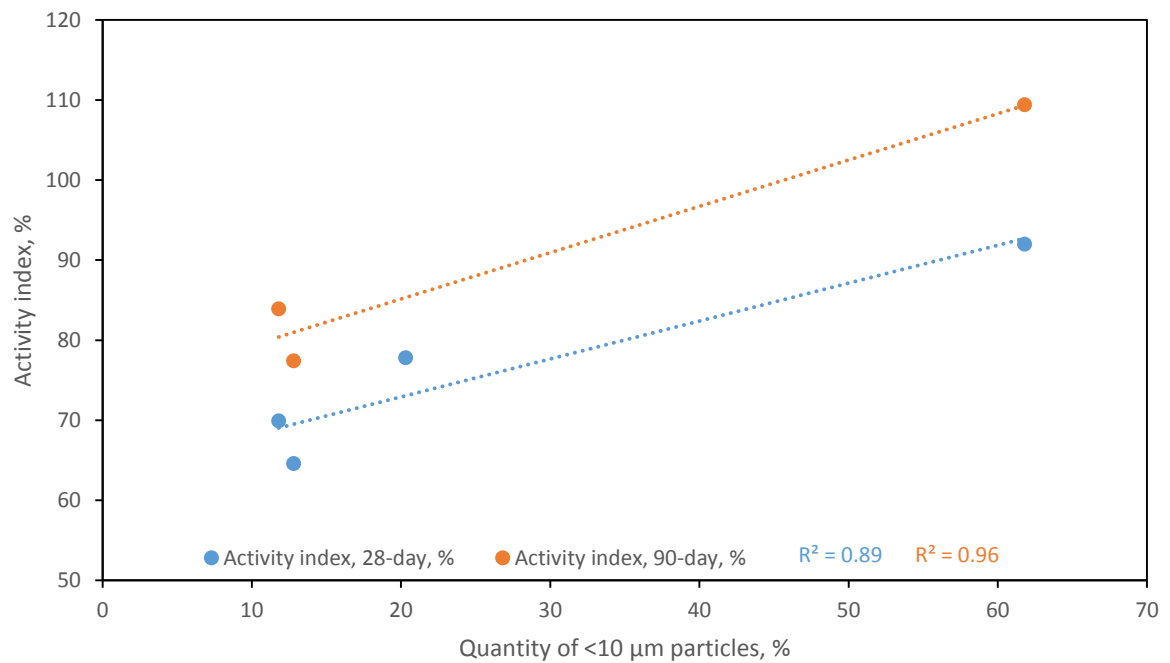
Figure 89 - Relationship between activity index, at 28 and 90-days, and quantity of <10 µm particles of DFA 3 laboratory wet-stored at 10% moisture

162
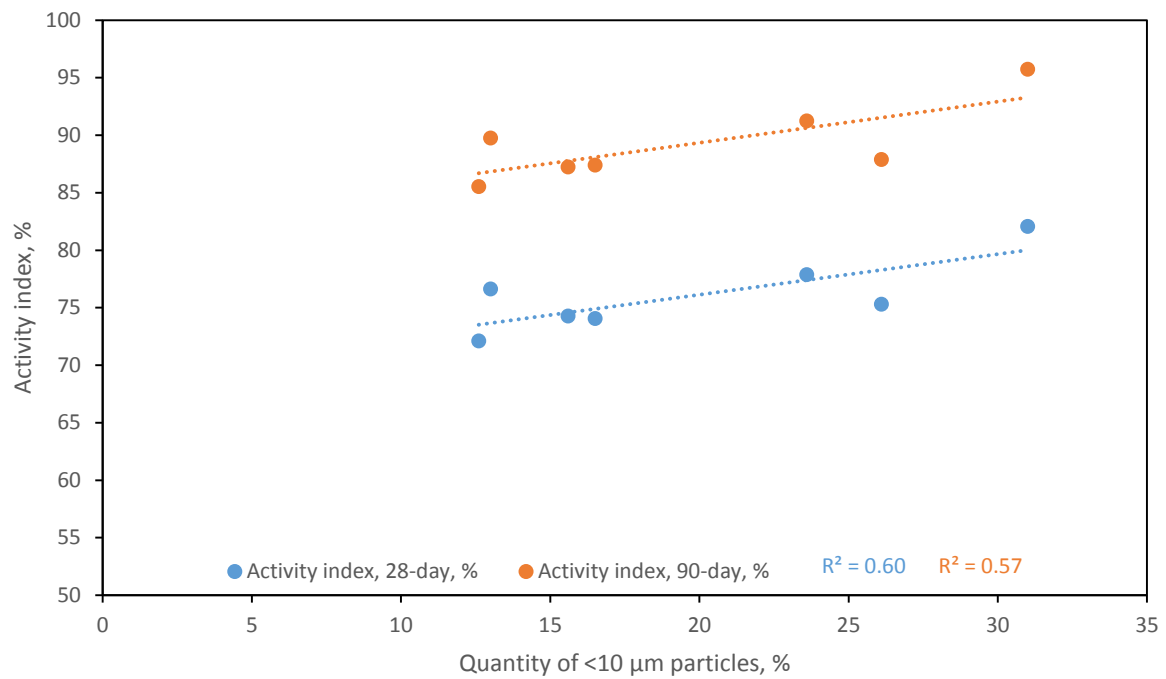
Figure 90 - Relationship between activity index, at 28 and 90-days, and quantity of <10 μm particles of DFA 4 laboratory wet-stored at 10% moisture
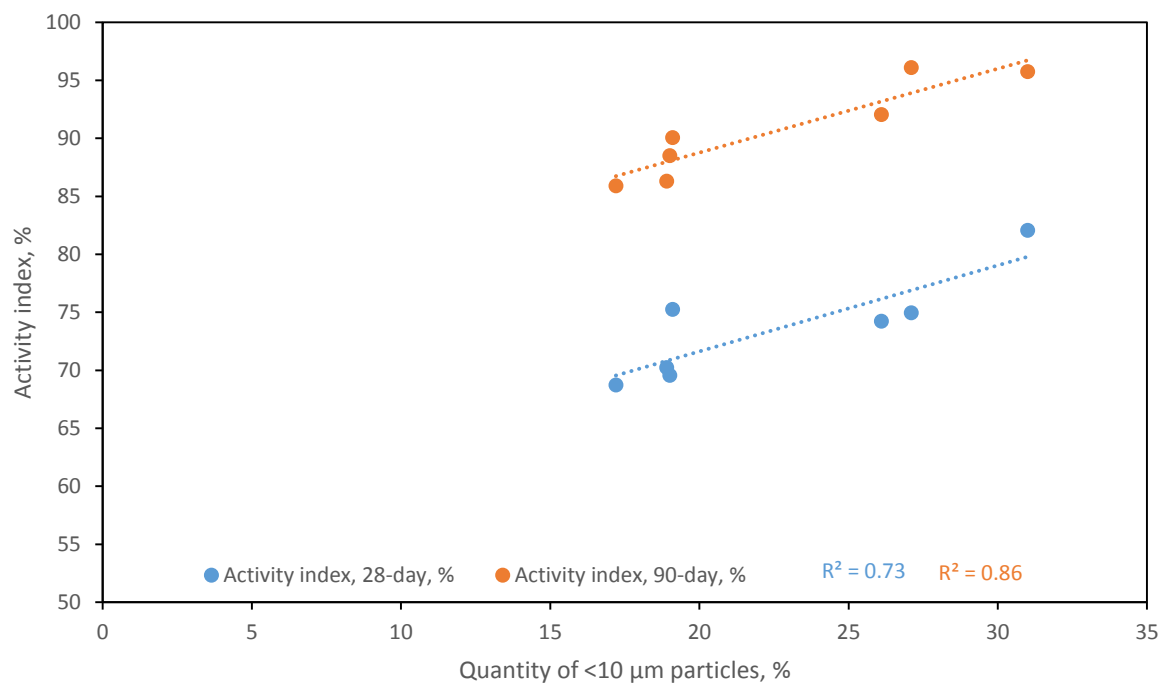
Figure 91 - Relationship between activity index, at 28 and 90-days, and quantity of <10 μm particles of DFA 4 laboratory wet-stored at 20% moisture
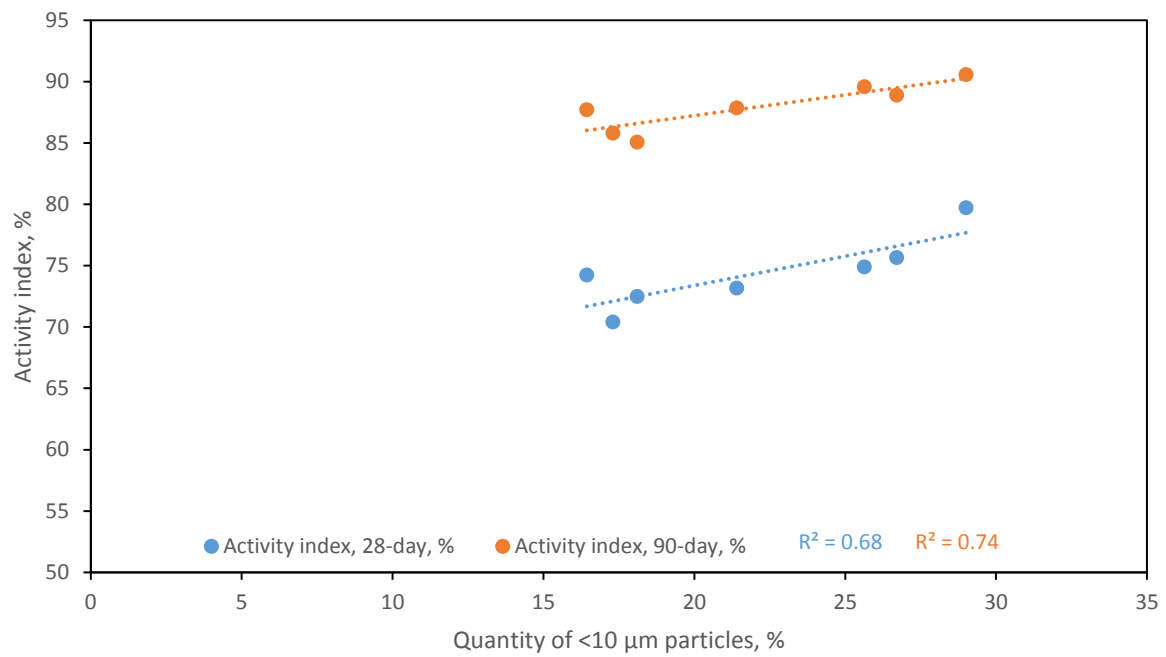
Figure 92 - Relationship between activity index, at 28 and 90-days, and quantity of <10 μm particles of DFA 5 laboratory wet-stored at 10% moisture
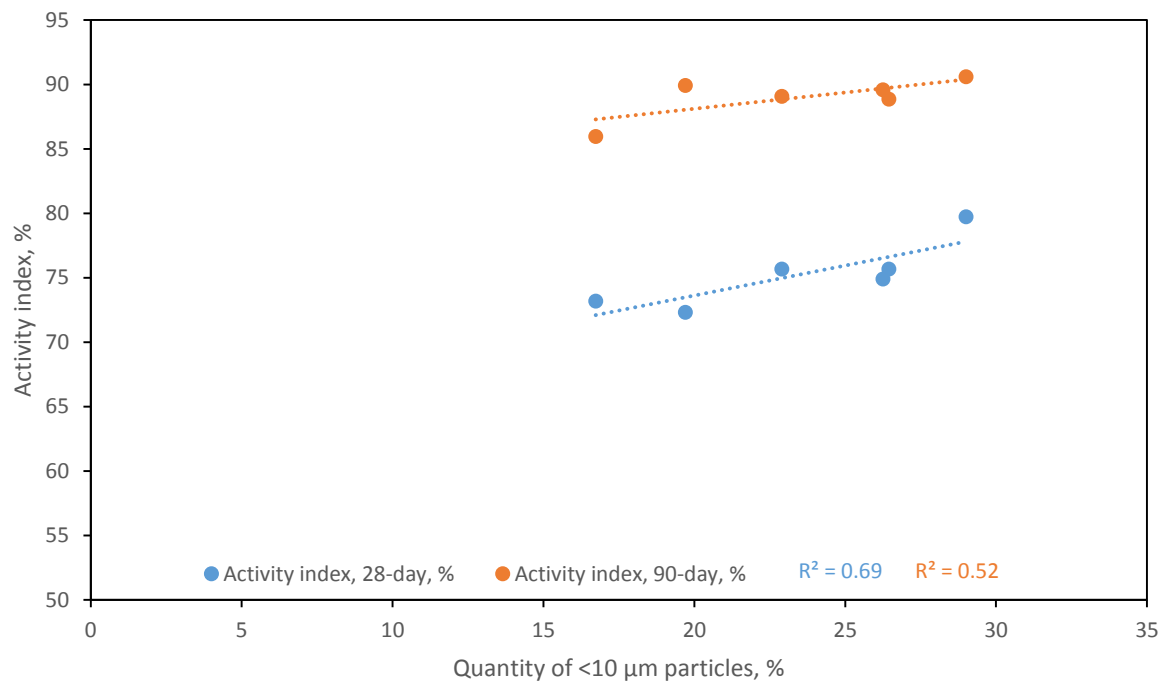
Figure 93 - Relationship between activity index, at 28 and 90-days, and quantity of <10 μm particles of DFA 5 laboratory wet-stored at 15% moisture
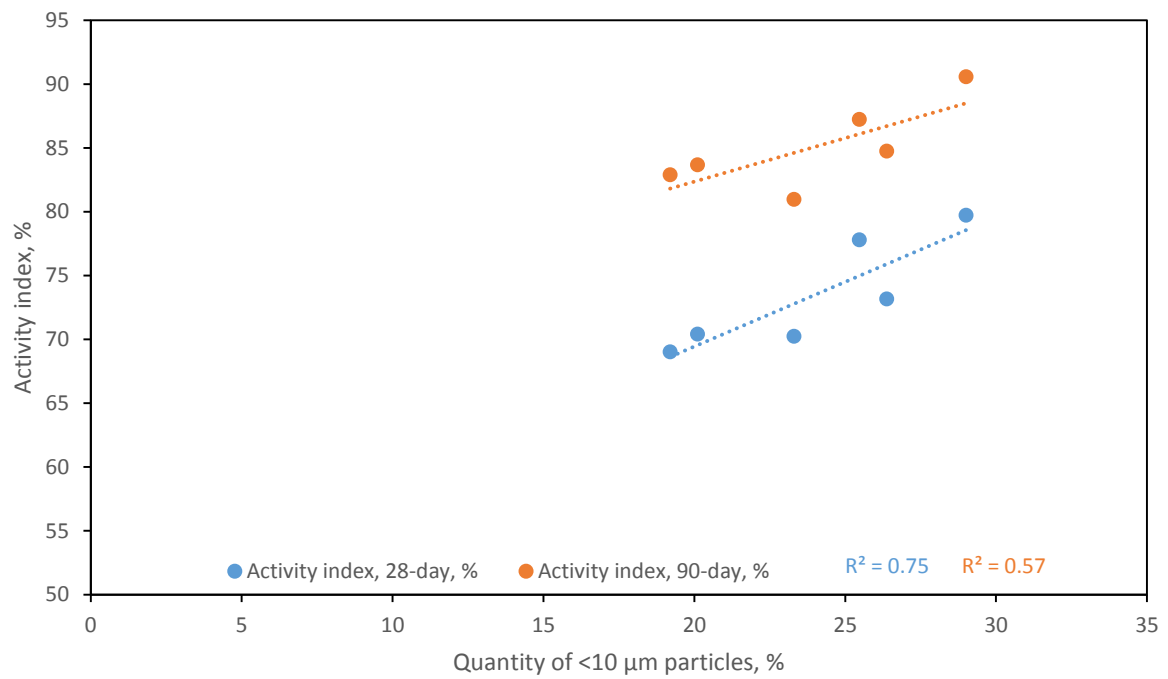
Figure 94 - Relationship between activity index, at 28 and 90-days, and quantity of <10 μm particles of DFA 5 laboratory wet-stored at 20% moisture
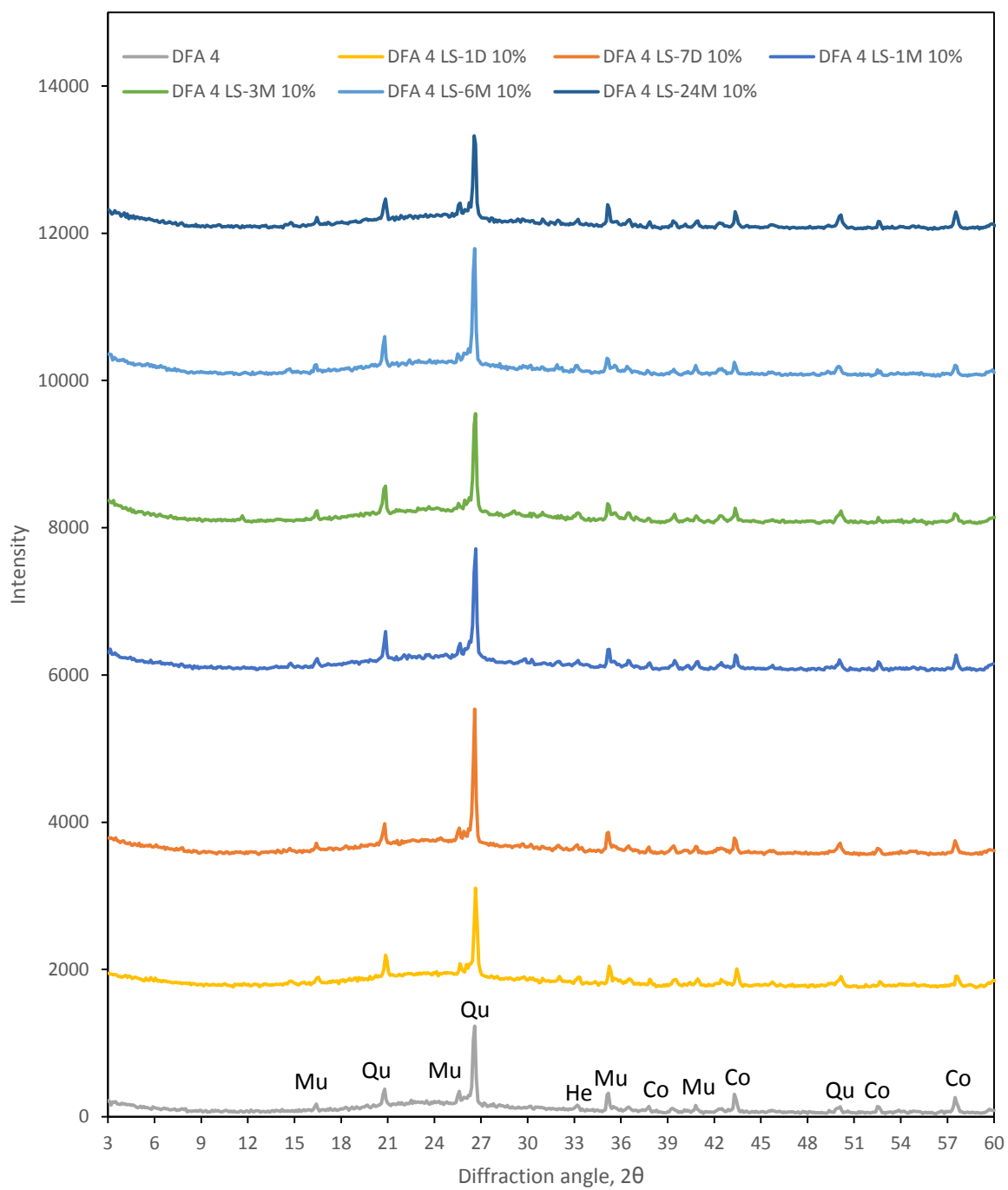
Figure 95 – X-ray diffractogram of DFA 4 laboratory wet-stored at 10% moisture
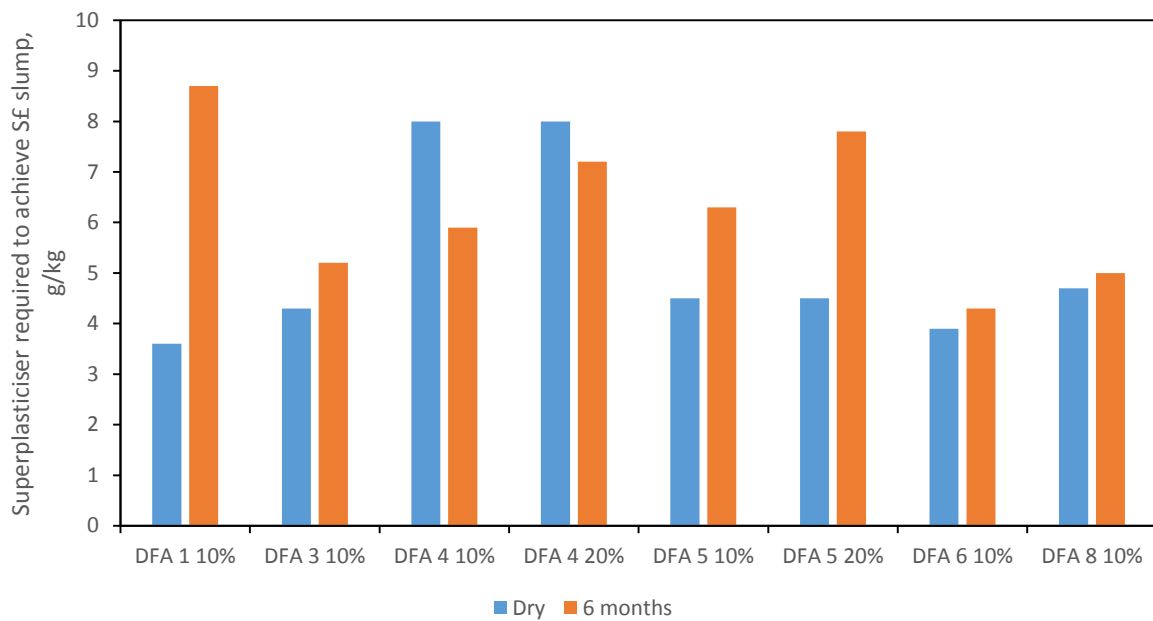
Figure 96 – Superplasticizer admixture required to achieve S3 slump for laboratory wet-stored materials before and after wet-storage in a 0.5 w/c ratio, 30 % fly ash replacement concrete mix
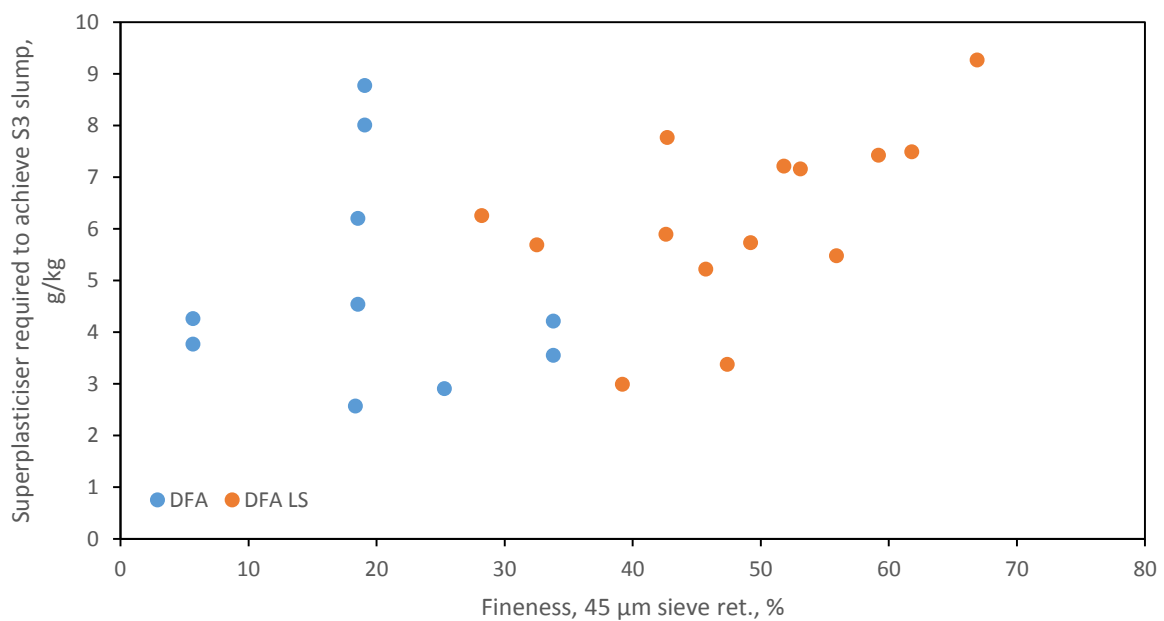
Figure 97 – Superplasticizer admixture require to achieve S3 slump for dry and laboratory wet-stored materials compared to fineness in a 0.5 w/c ratio, 30 % fly ash replacement concrete mix
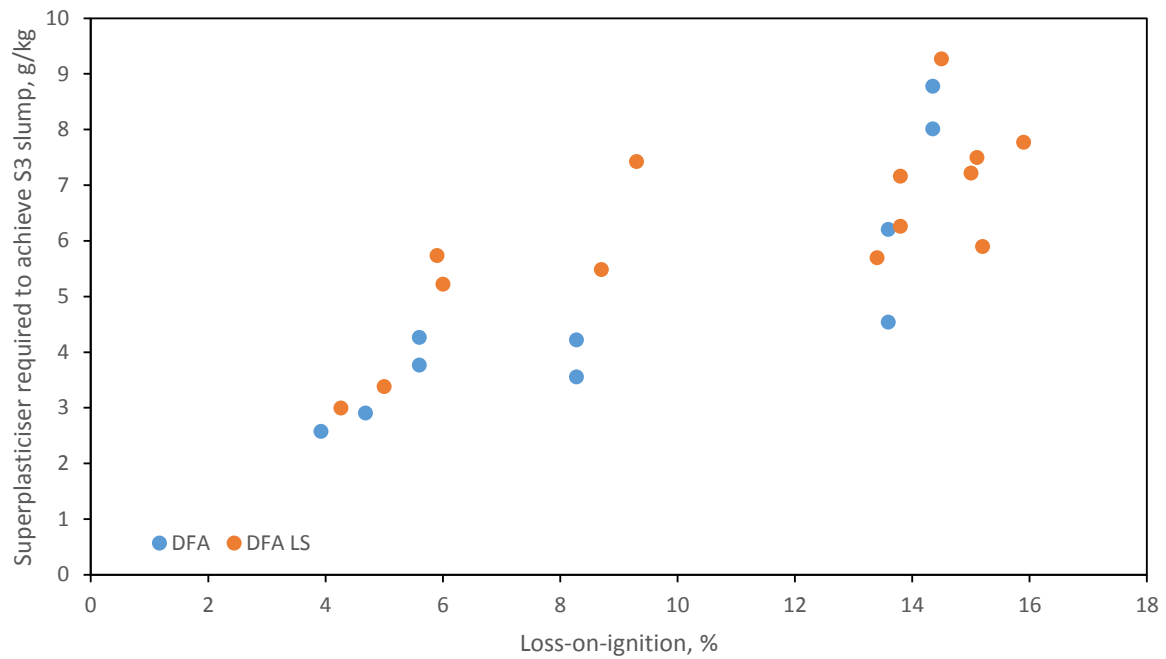
Figure 98 – Superplasticizer admixture require to achieve S3 slump for dry and laboratory wet-stored materials compared to loss-on-ignition in a 0.5 w/c ratio, 30 % fly ash replacement concrete mix
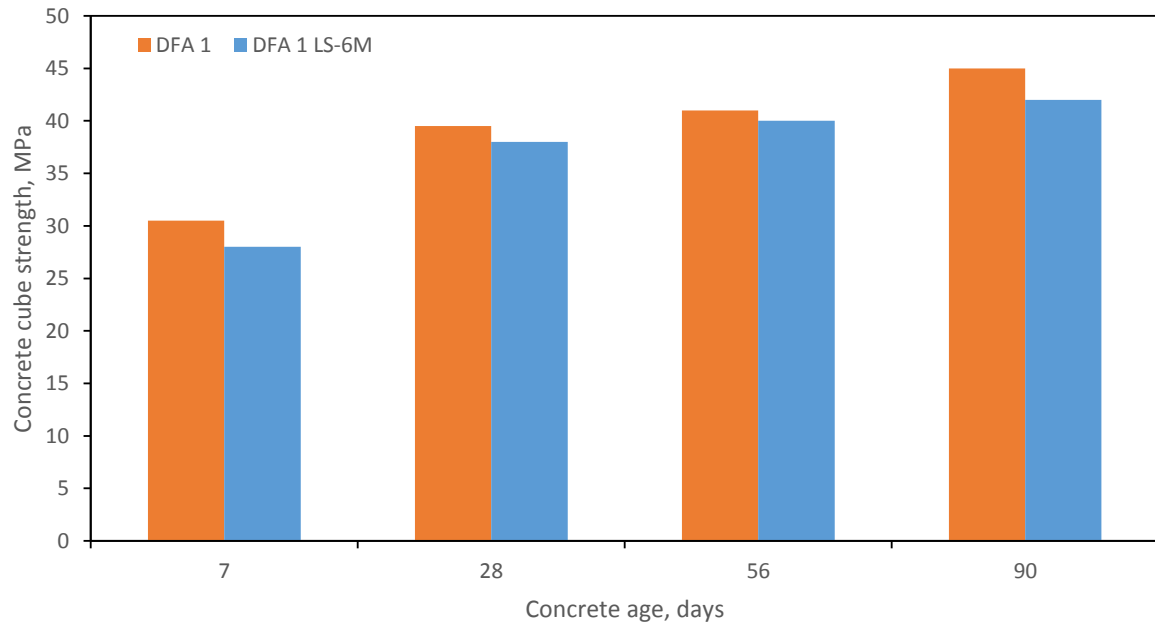
Figure 99 – Concrete cube strength of DFA 1 before and after laboratory wet-storage for 6 months at 10 % initial moisture content in a 0.5 w/c, 30 % fly ash concrete mix
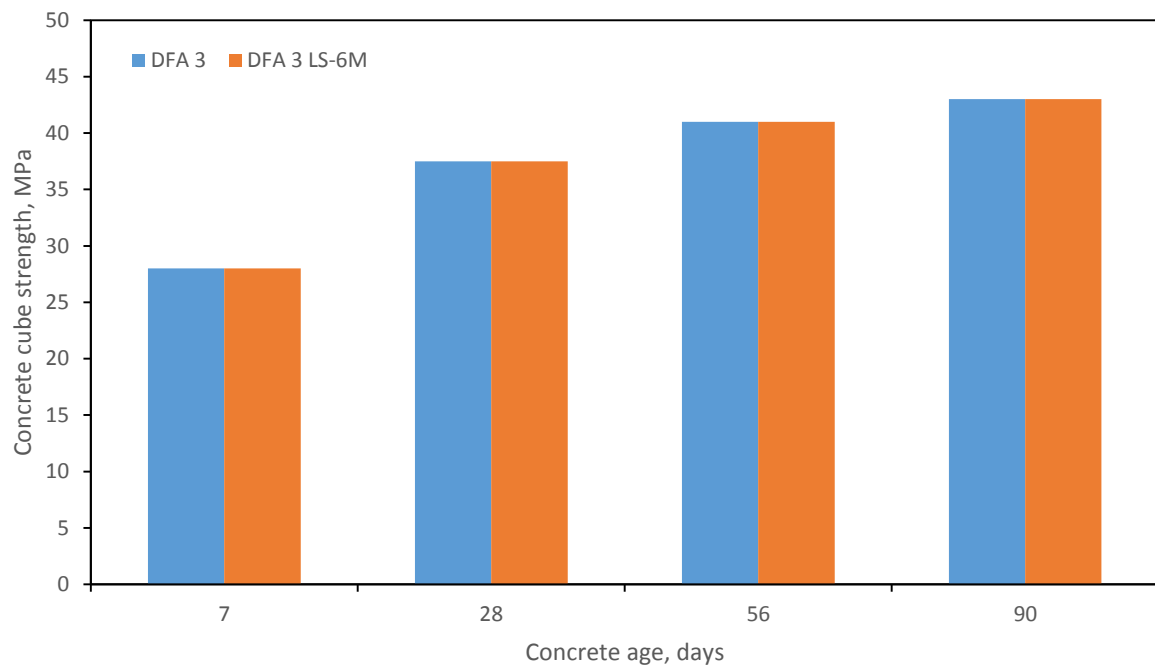
Figure 100 - Concrete cube strength of DFA 3 before and after laboratory wet-storage for 6 months at 10 % initial moisture content in a 0.5 w/c, 30 % fly ash concrete mix
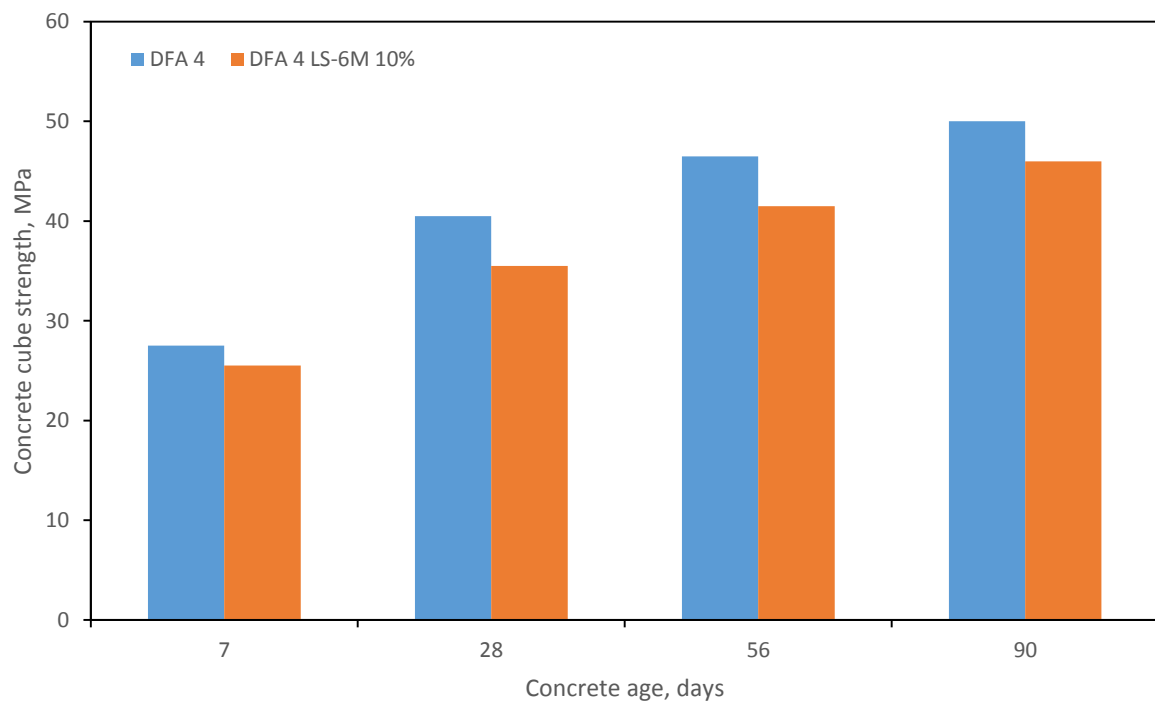
Figure 101 - Concrete cube strength of DFA 4 before and after laboratory wet-storage for 6 months at 10 % initial moisture content in a 0.5 w/c, 30 % fly ash concrete mix

169
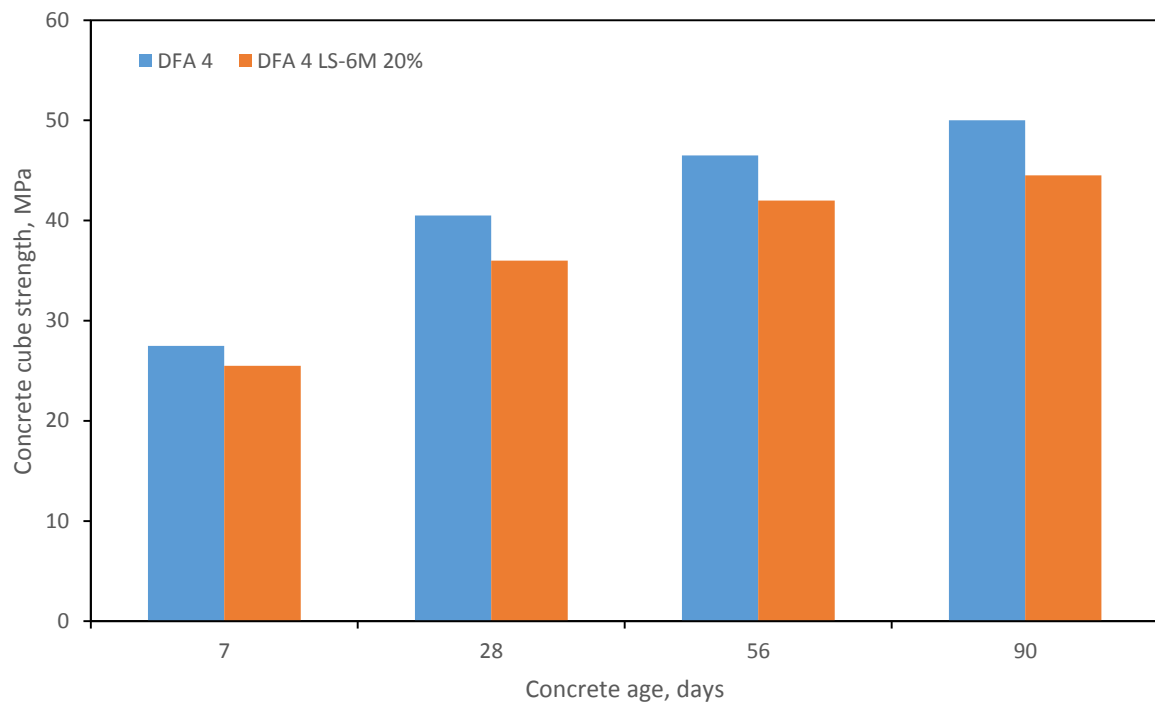
Figure 102 - Concrete cube strength of DFA 4 before and after laboratory wet-storage for 6 months at 20 % initial moisture content in a 0.5 w/c, 30 % fly ash concrete mix
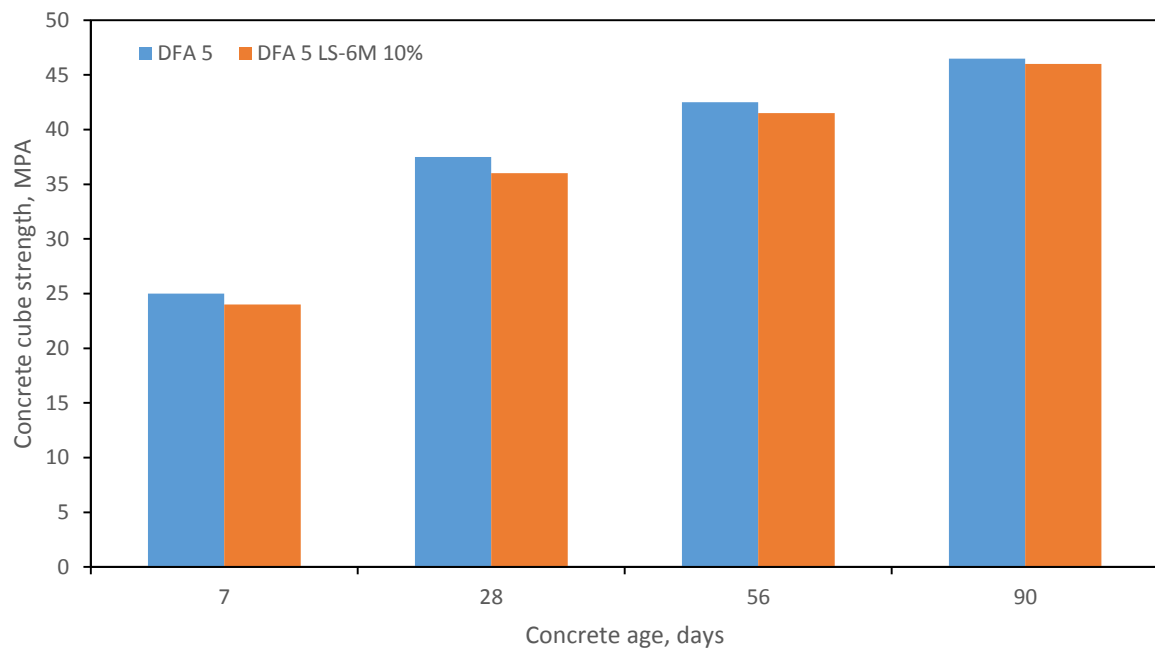
Figure 103 - Concrete cube strength of DFA 5 before and after laboratory wet-storage for 6 months at 10 % initial moisture content in a 0.5 w/c, 30 % fly ash concrete mix
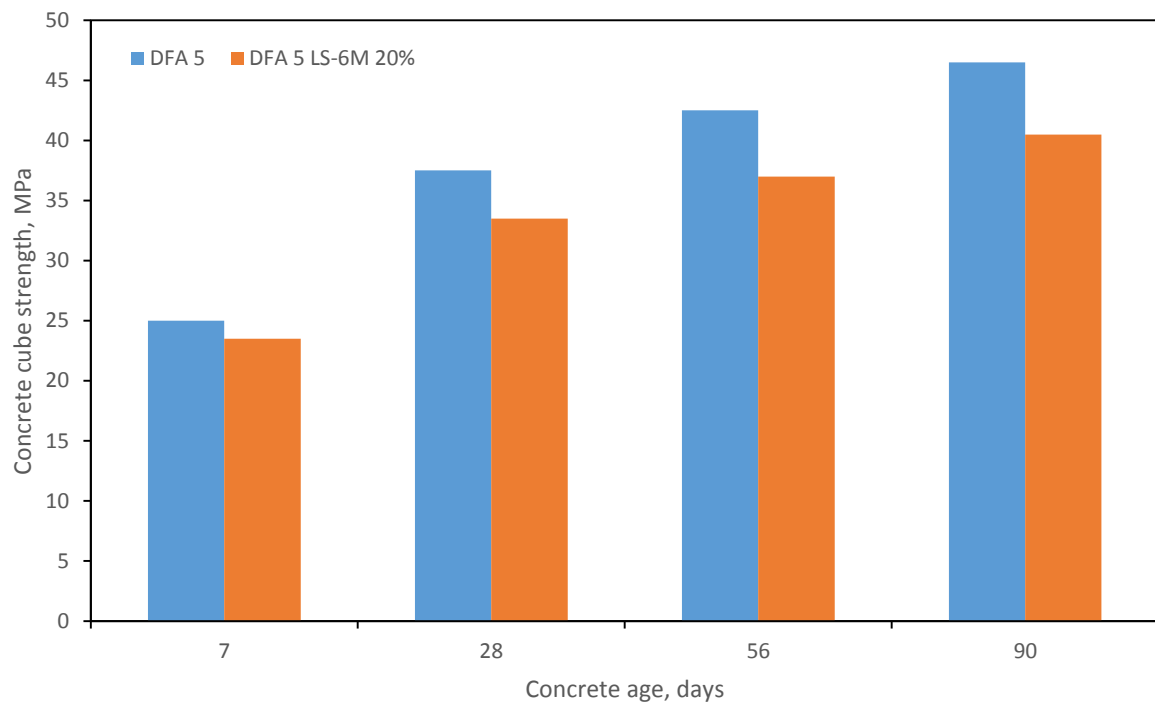
Figure 104 - Concrete cube strength of DFA 5 before and after laboratory wet-storage for 6 months at 20 % initial moisture content in a 0.5 w/c, 30 % fly ash concrete mix
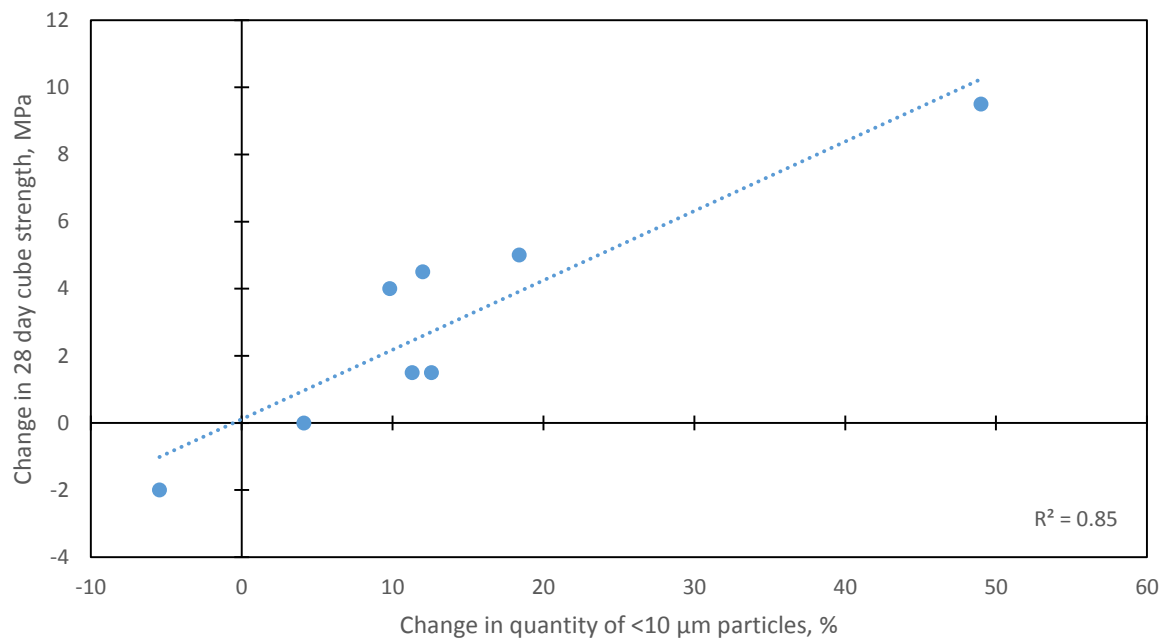
Figure 105 – Relationship between the reduction in 28-day strength, as a percentage, of laboratory wet-stored materials and reduction in quantity of <10 μm particles in a0.5 w/c, 30 fly ash concrete mixes

18.3. On-site wet-storage
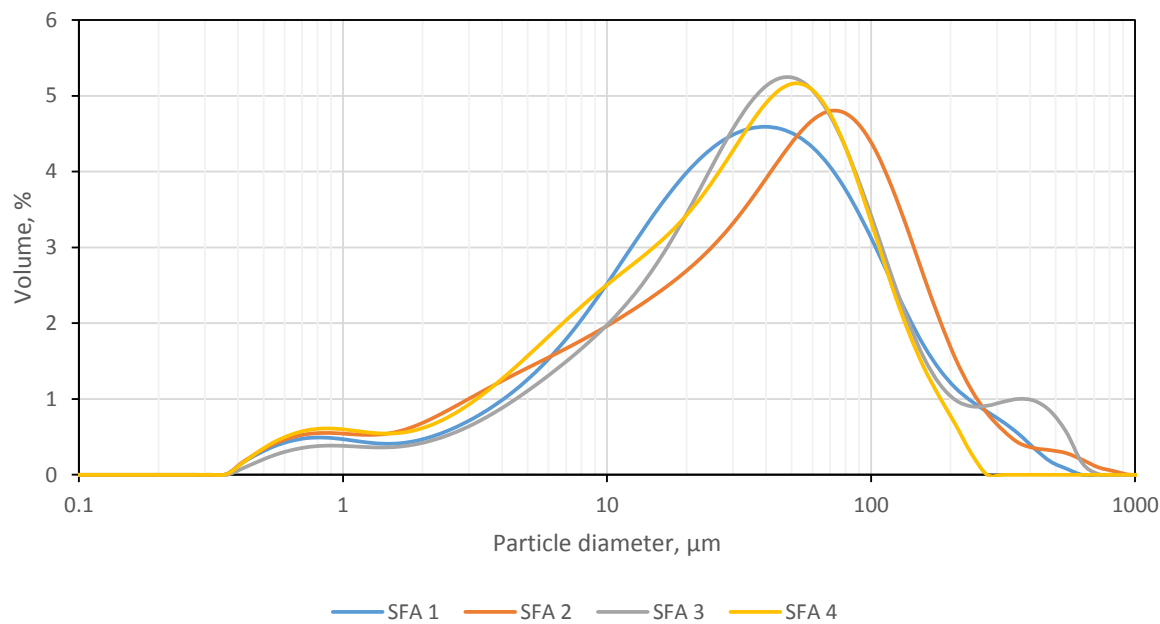
Figure 106 - Particle size distributions of on-site wet-stored materials SFA 1, SFA 2, SFA 3 and SFA 4
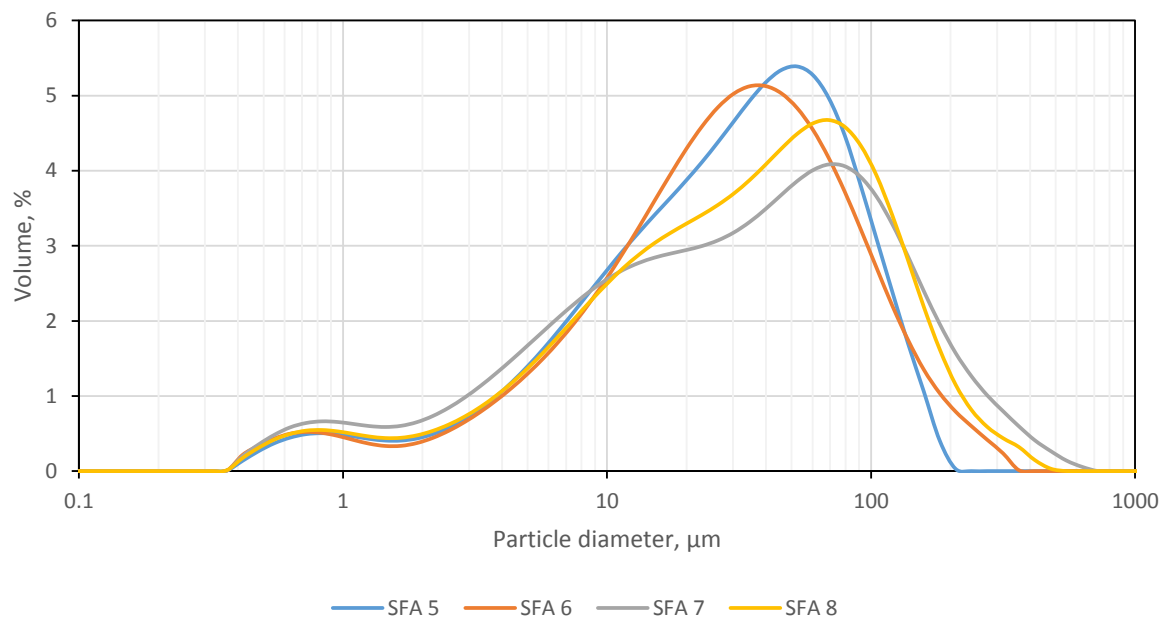
Figure 107 - Particle size distributions of on-site wet-stored materials SFA 5, SFA 6, SFA 7 and SFA 8
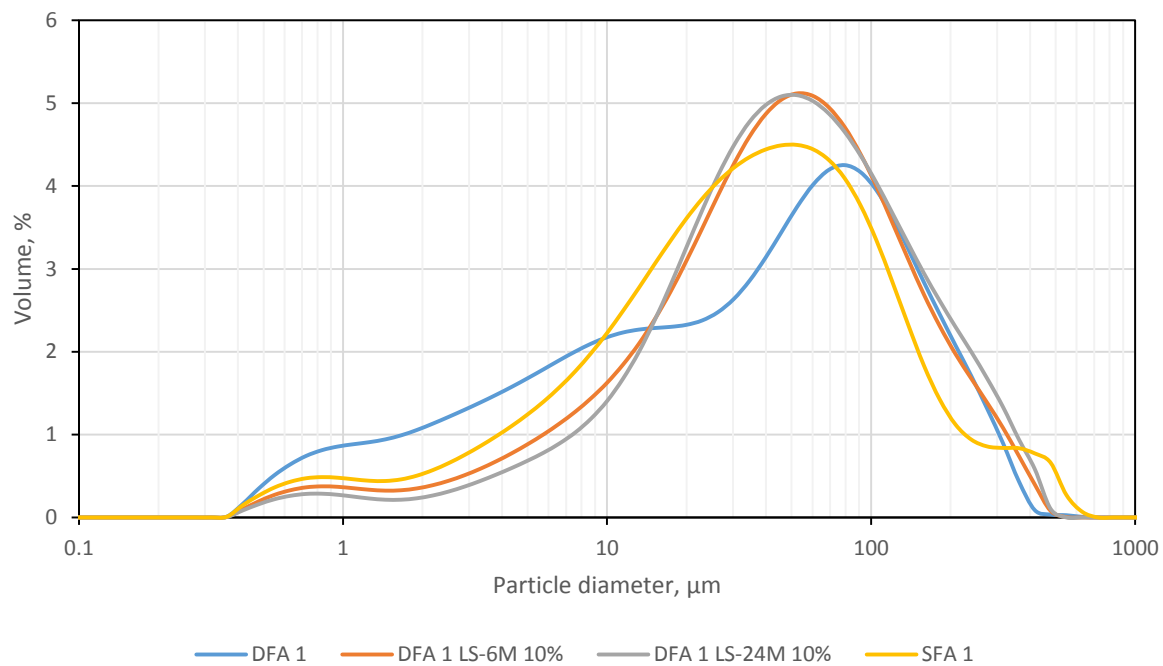
Figure 108 - Comparison between particle size distribution curves of DFA 1, DFA 1 after laboratory wet-storage and SFA 1
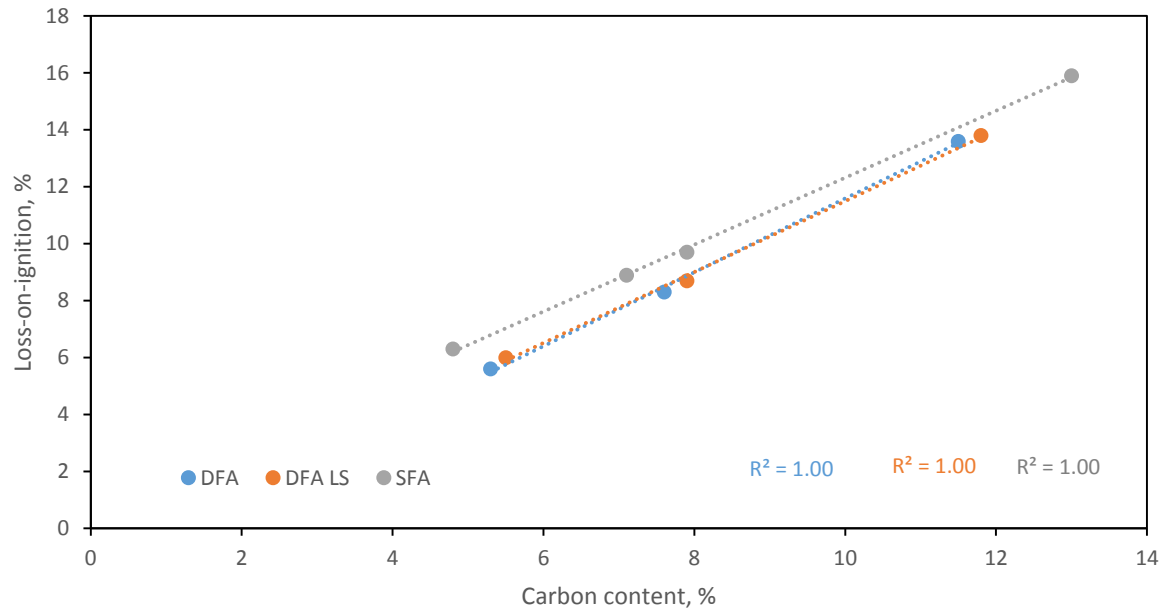
Figure 109 - Relationship between carbon content and loss-on-ignition of dry, on-site and laboratory wet-stored materials
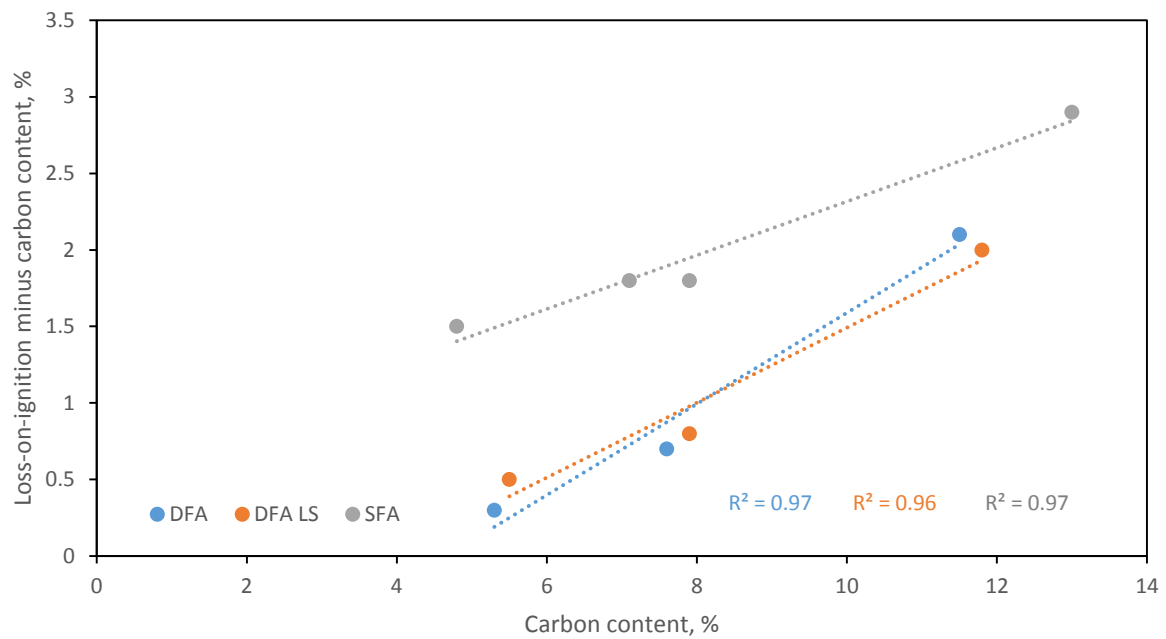
Figure 110 - Relationship between carbon content and the non-carbon content also recorded in the loss-on-ignition test for dry, on-site and laboratory wet-stored materials
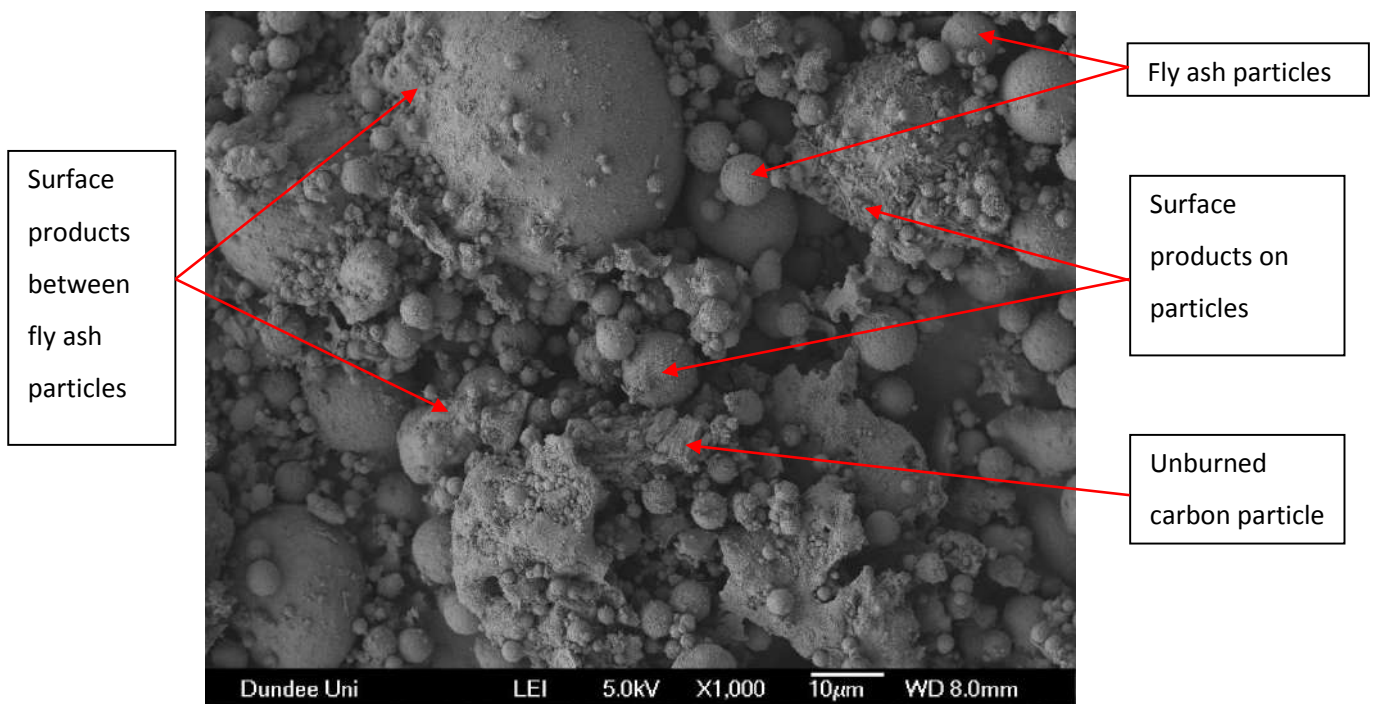
Figure 111 - Scanning Electron Microscopy image of SFA 1 (x1000)
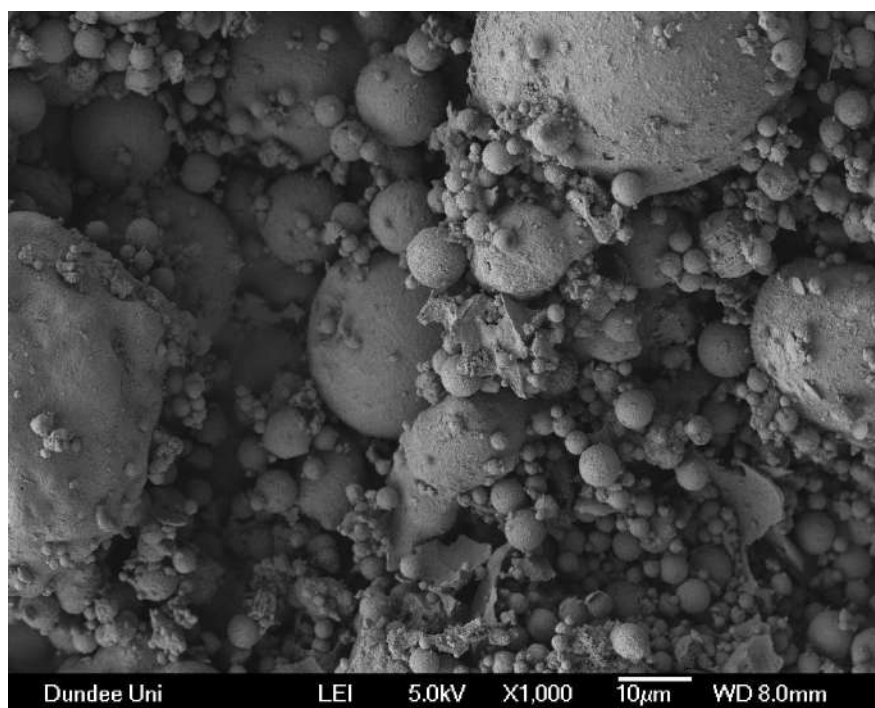
Figure 112 - Scanning Electron Microscopy image of SFA 2 (x1000)
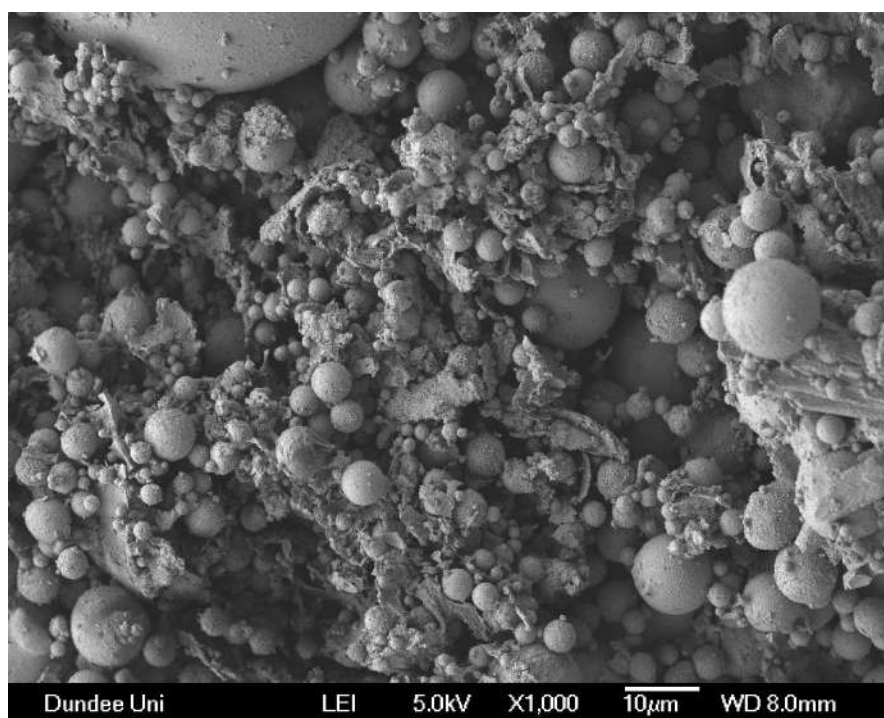
Figure 113 - Scanning Electron Microscopy image of SFA 4 (x1000)
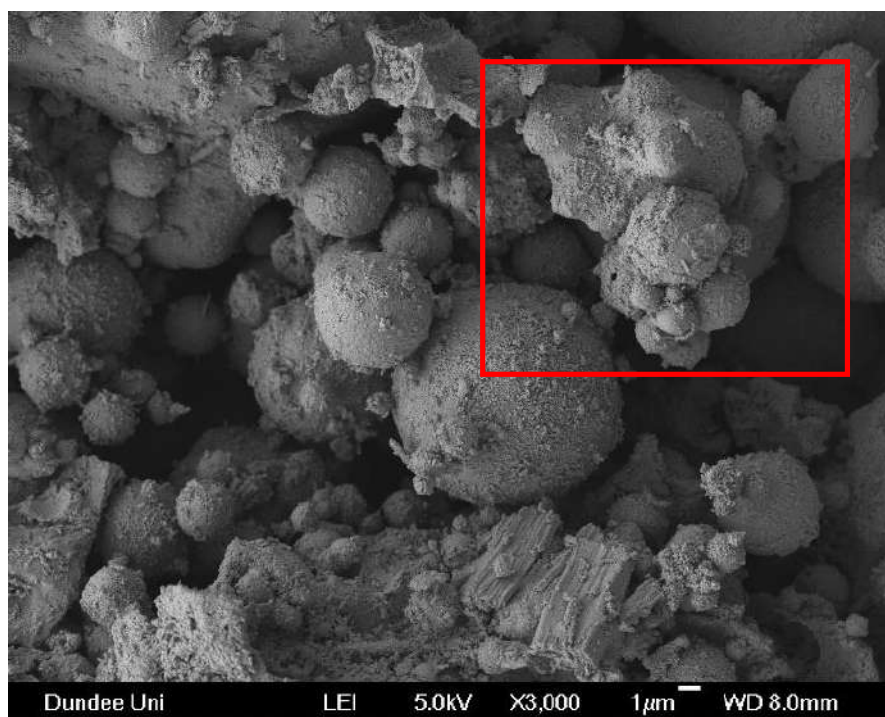
Figure 114 - Scanning Electron Microscopy image of SFA 1 (x3000)
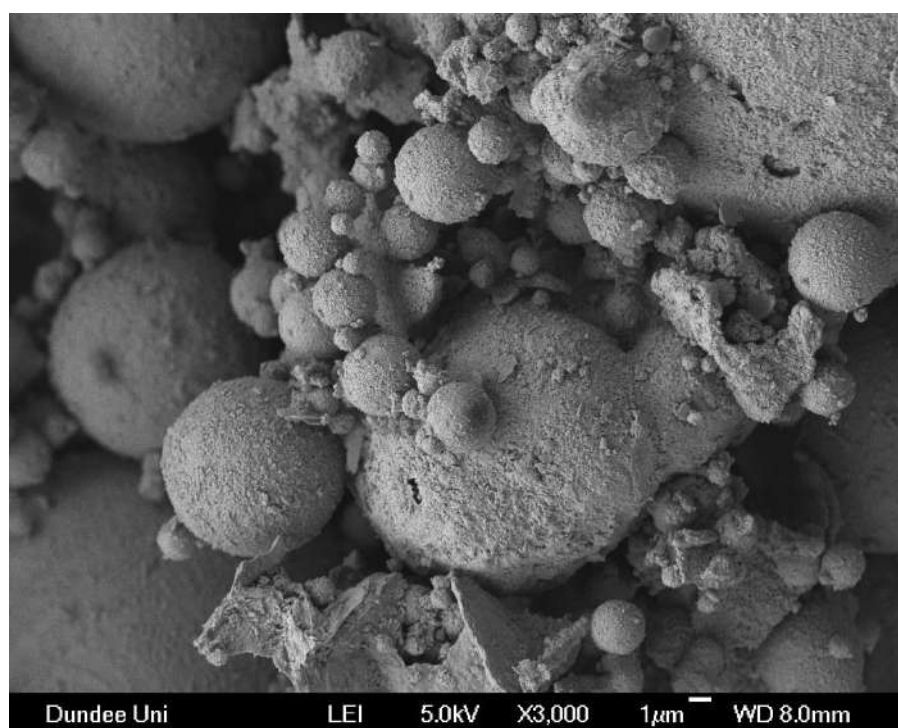
Figure 115 - Scanning Electron Microscopy image of SFA 2 (x3000)

Figure 116 - Scanning Electron Microscopy image of SFA 4 (x3000)
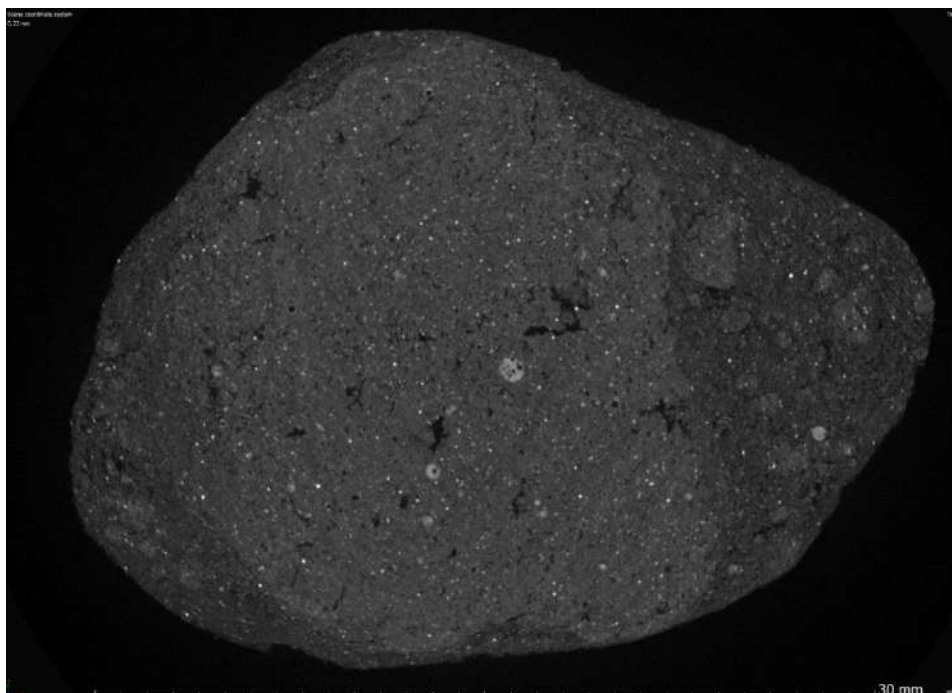
Figure 117 – Cross-section of SFA 5 agglomerate of around Ø30 mm from CT scanner
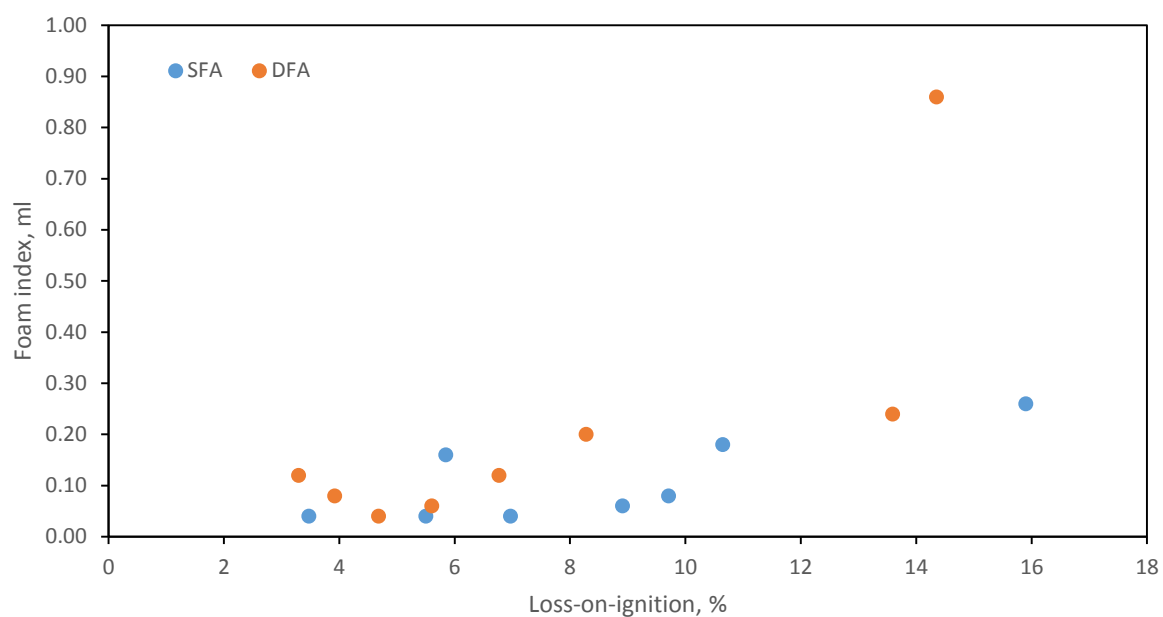
Figure 118 - Comparison between foam index and Loss-on-ignition for both dry and on-site wet-stored materials
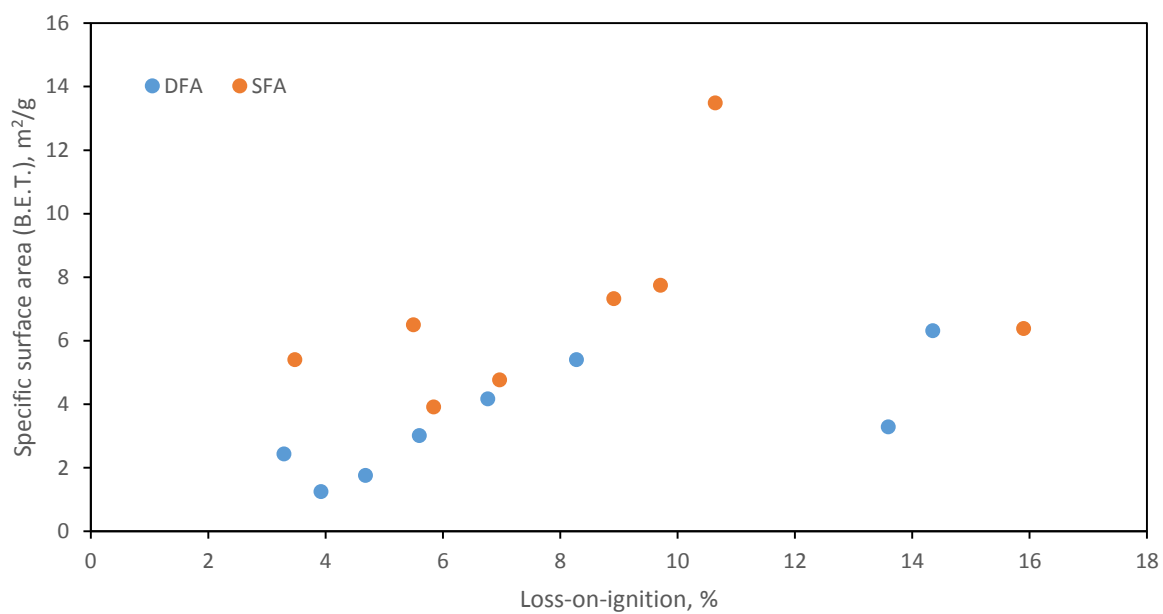
Figure 119 - Comparison between Specific surface area (B.E.T.) and Loss-on-ignition for dry and on-site wet-stored materials
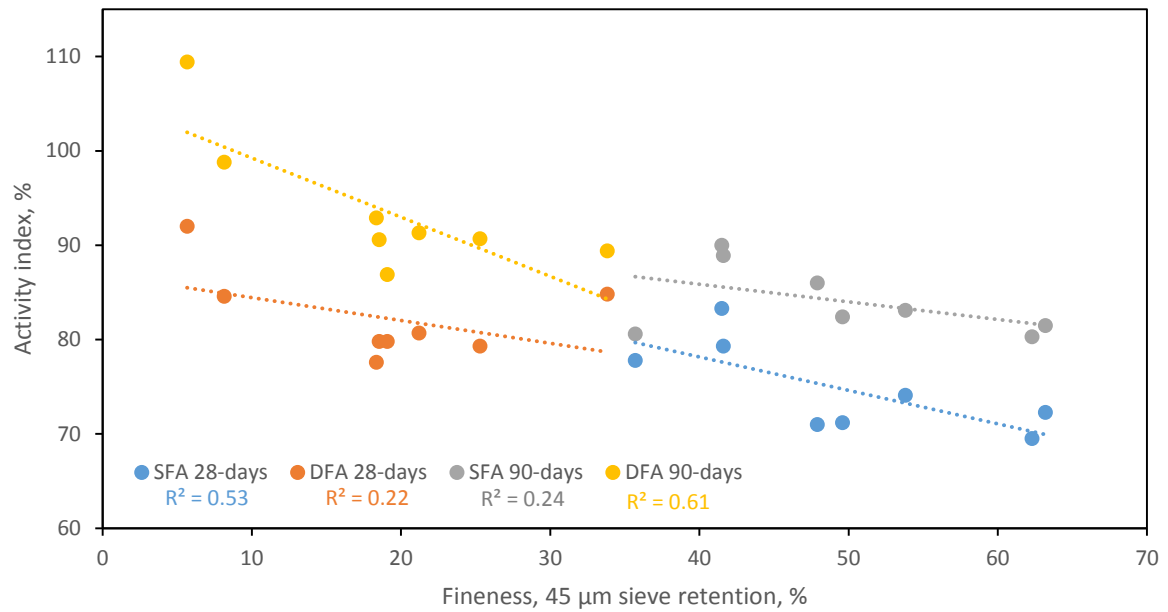
Figure 120 - Relationships between activity index, at 28 and 90-days, and fineness of dry and on-site wet-stored materials
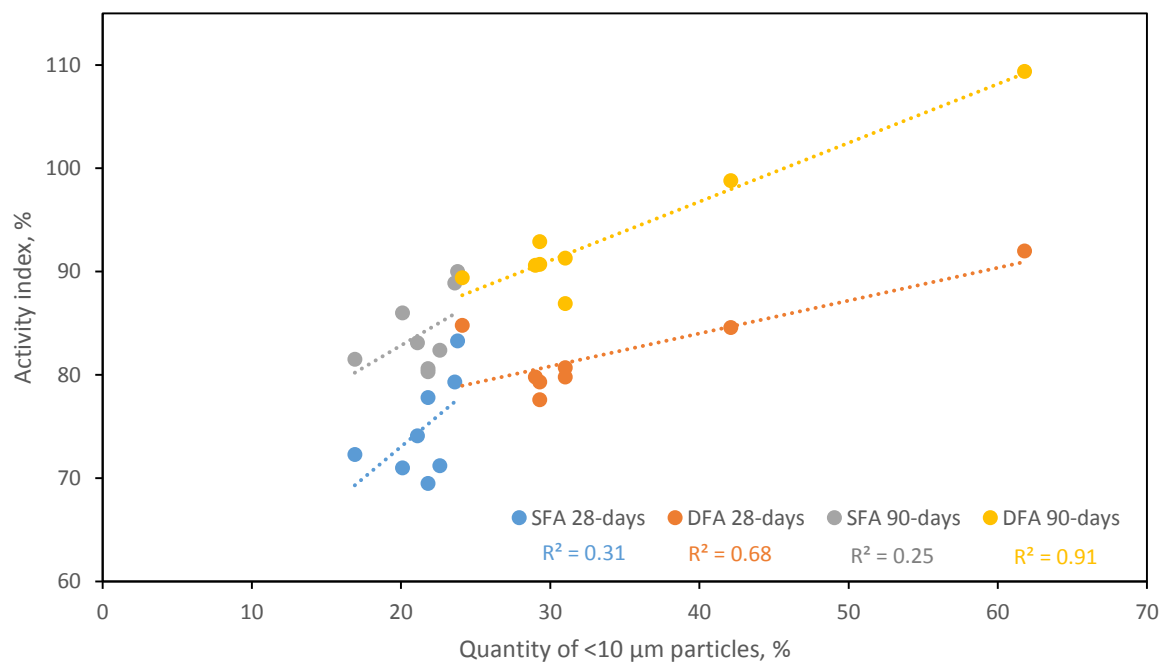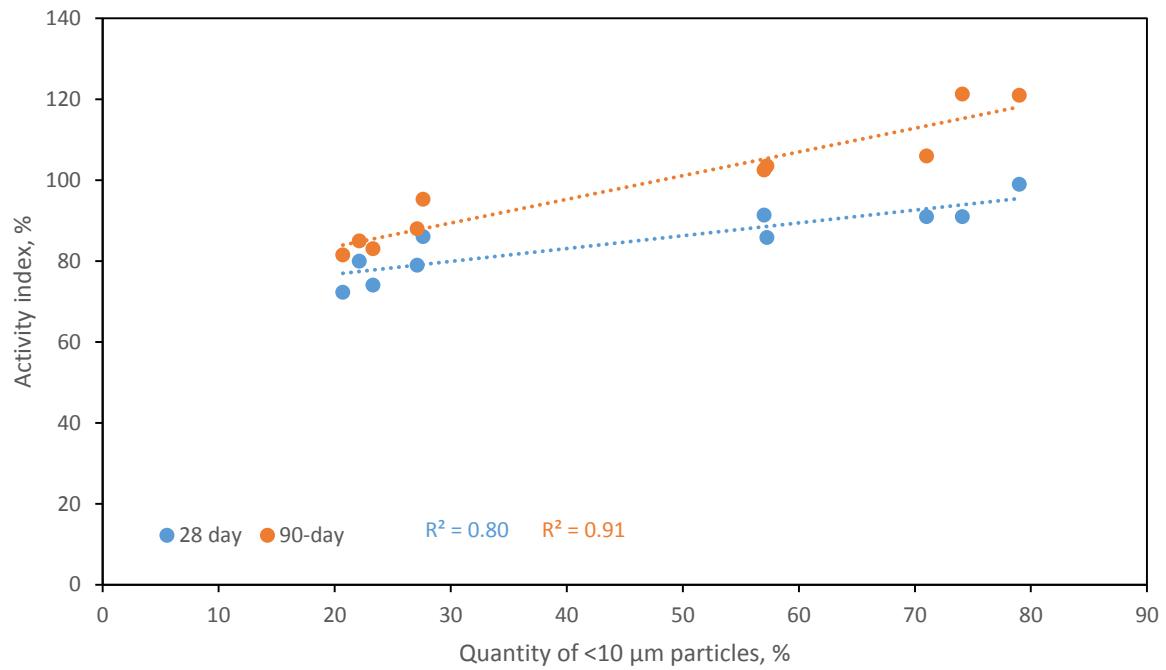

Figure 121 - Relationships between activity index, at 28 and 90-days, and quantity of <10 μm particles of dry and on-site wet-stored materials
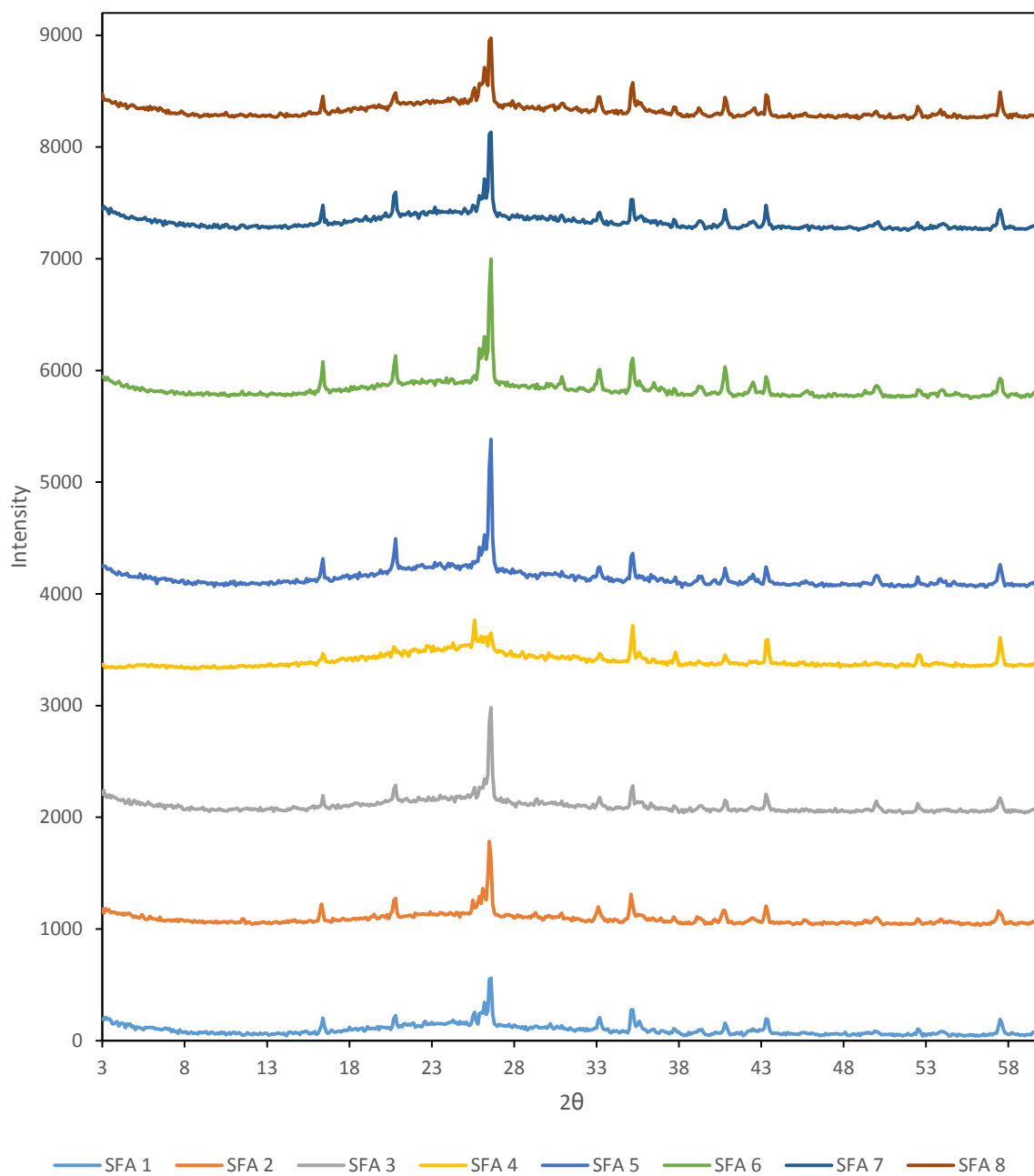
Figure 122 - X-ray diffractogram of on-site wet-stored materials
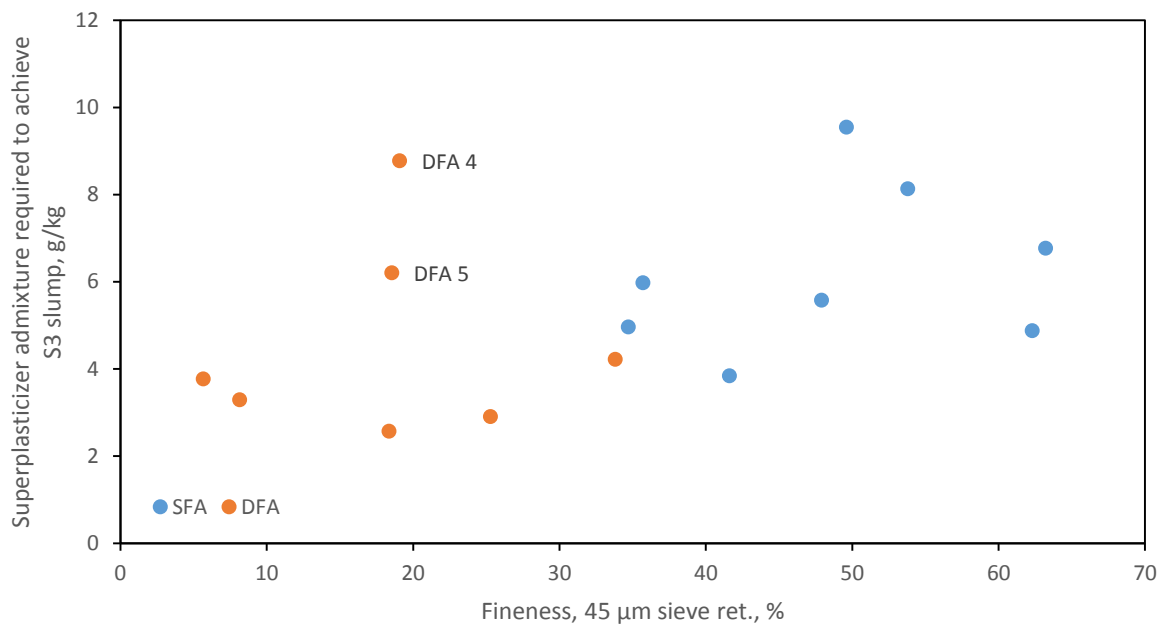
Figure 123 – Superplasticizer admixture required to achieve S3 slump against fineness for dry and on-site wet-stored materials
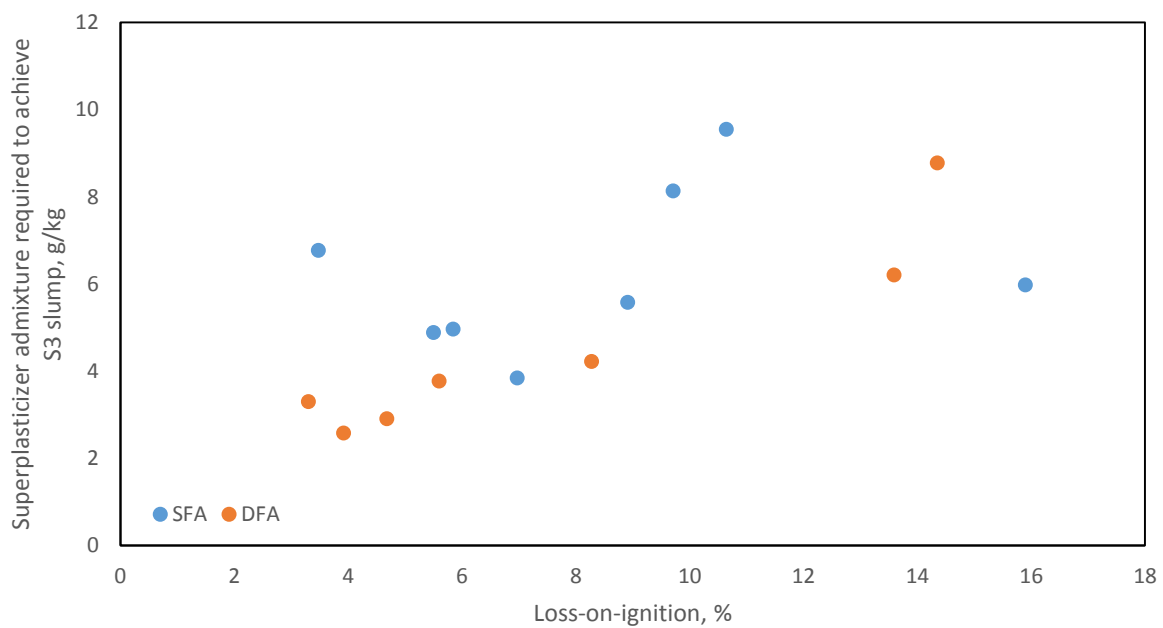
Figure 124 – Superplasticizer admixture required to achieve S3 slump against Loss-on-ignition for dry and on-site wet-stored materials
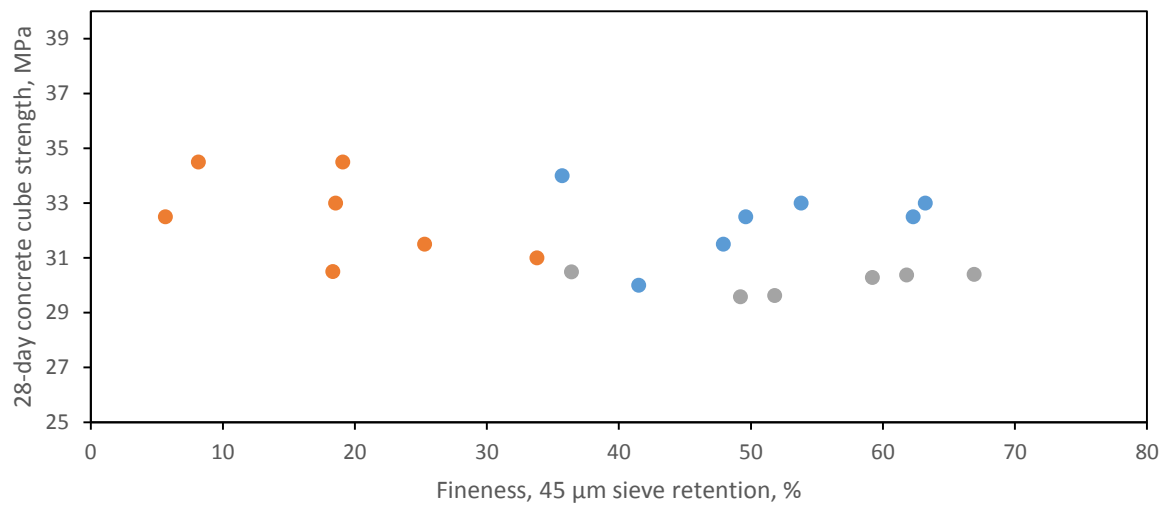
Figure 125 - Comparison between 28-day concrete strength and fineness of dry and on-site wet-stored materials

18.4. Laboratory processing

18.4.1. Pre-screening
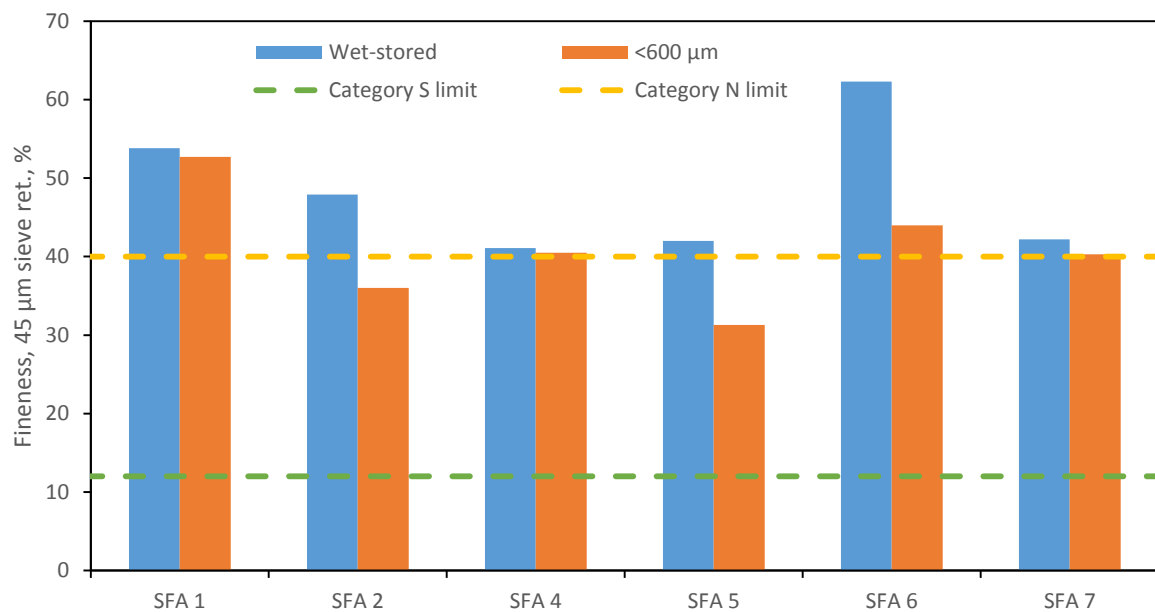
Figure 126 - Change in fineness of on-site wet-stored materials after screening at 600 μm
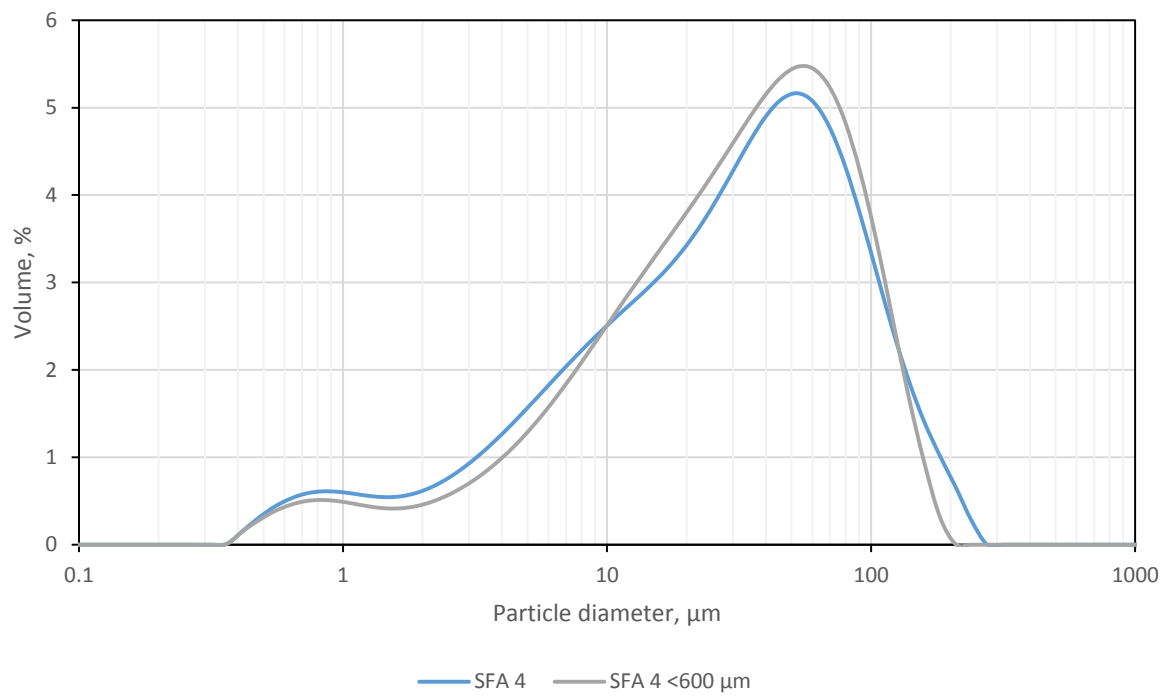
Figure 127 - Particle size distribution of SFA 4 before and after screening at 600 μm
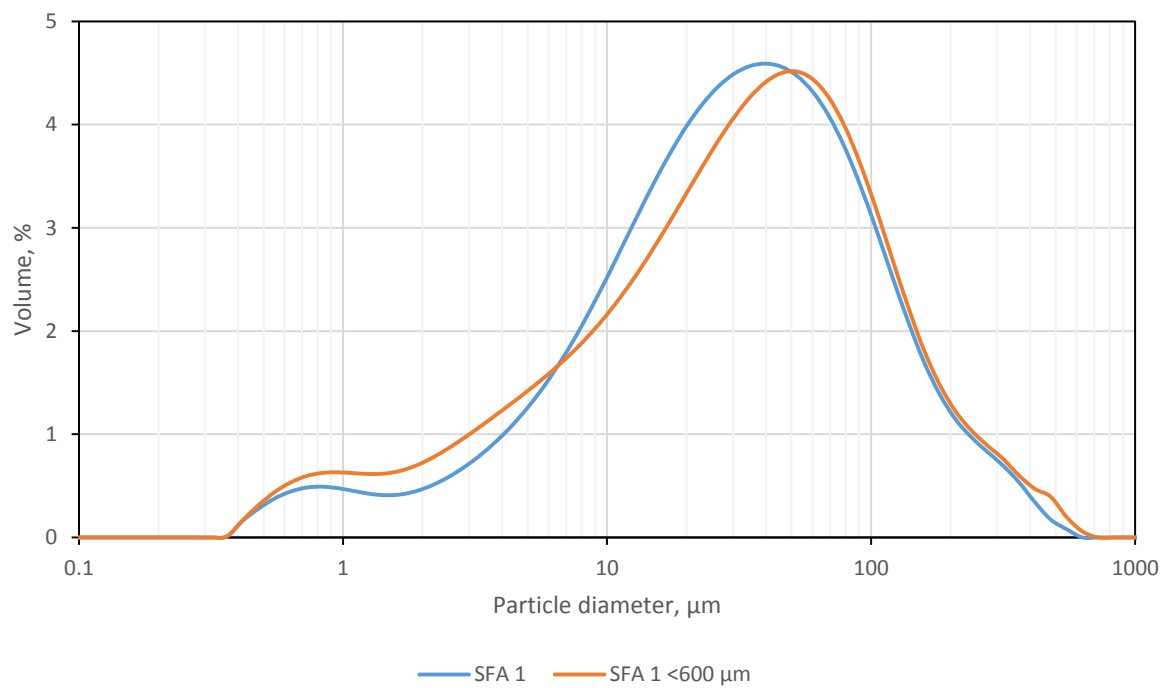
Figure 128 - Particle passing curve of SFA 1 before and after screening at 600 μm

183
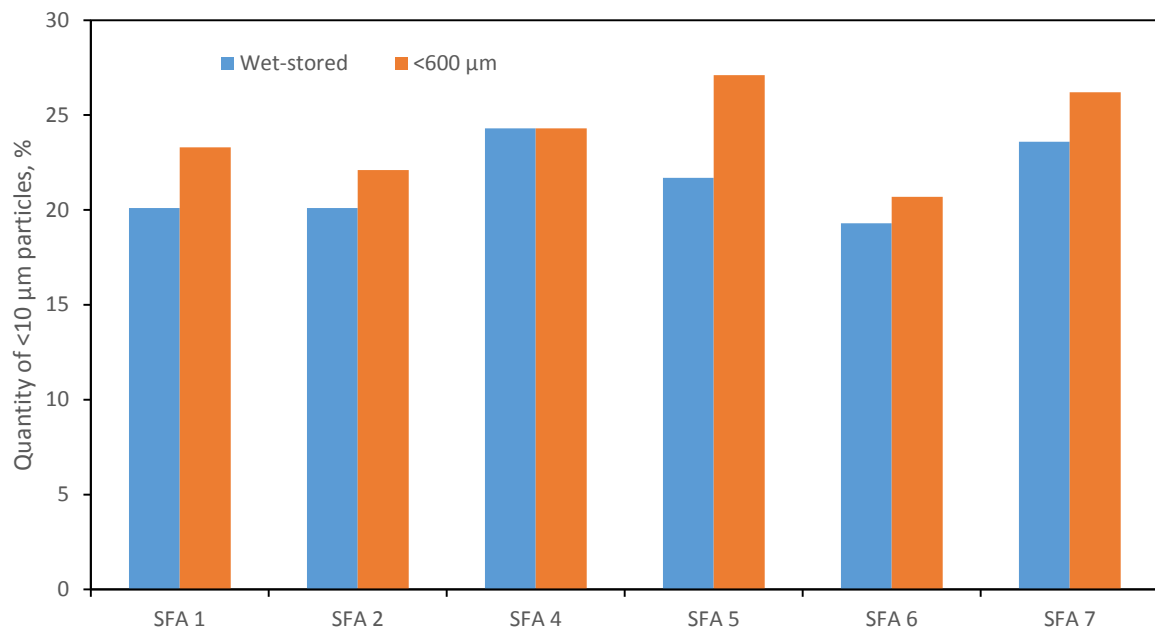
Figure 129 - Change in quantity of <10 µm particles of on-site wet-stored materials after screening at 600 µm
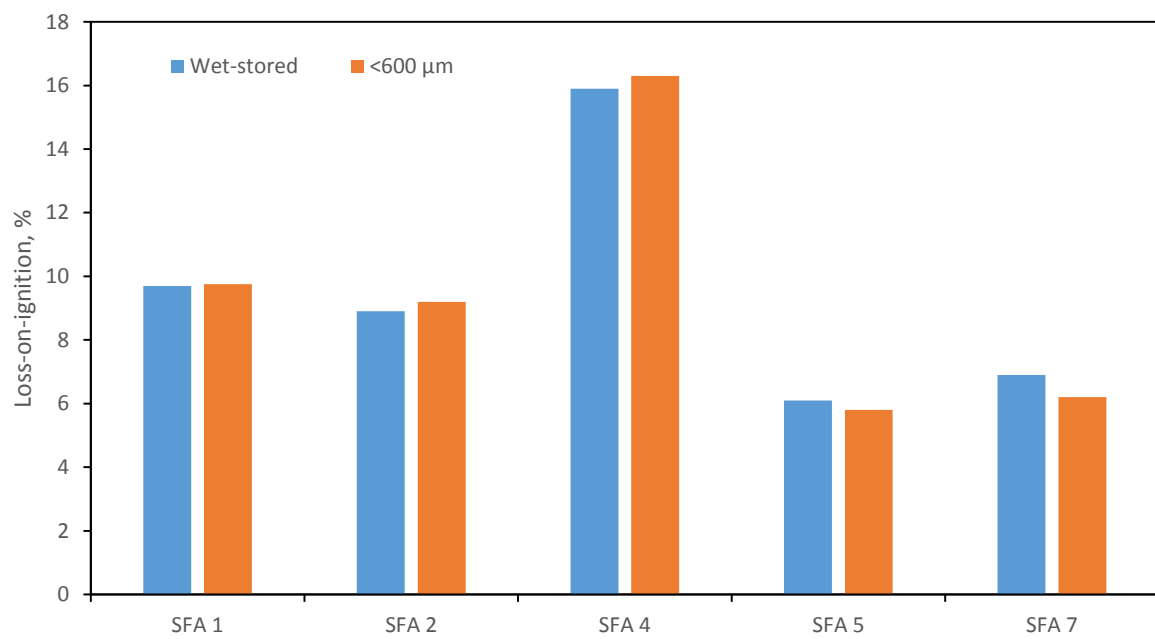
Figure 130 - Change in Loss-on-ignition of select wet-stored materials after screening at 600 µm

184
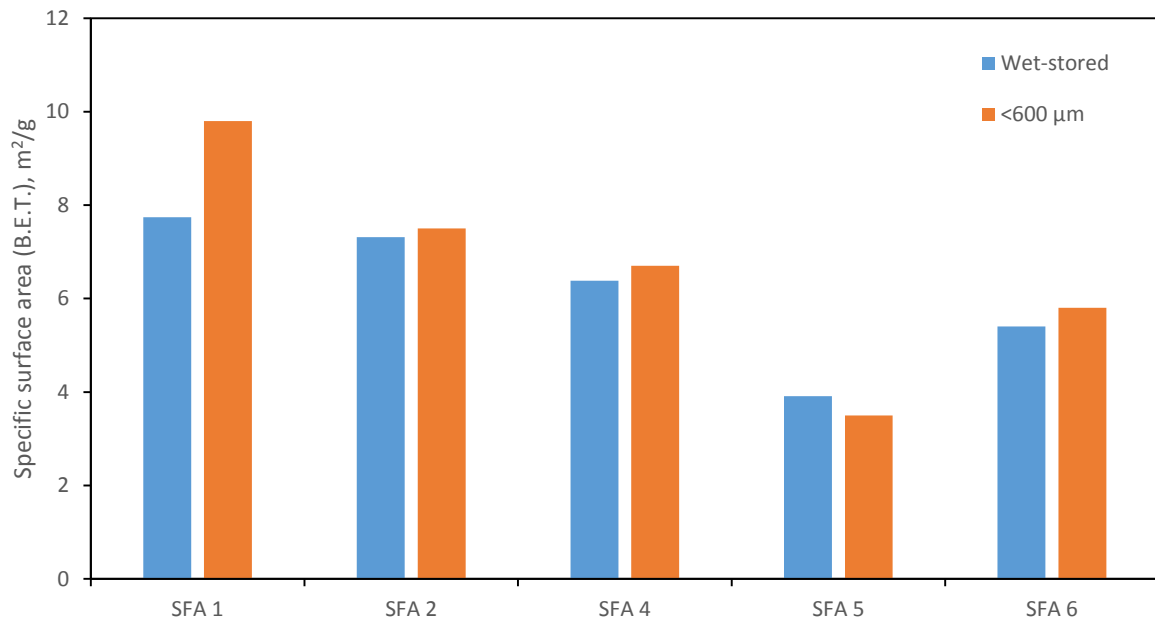
Figure 131 - Change in specific surface area (B.E.T.) in select on-site wet-stored materials after screening at 600 μm
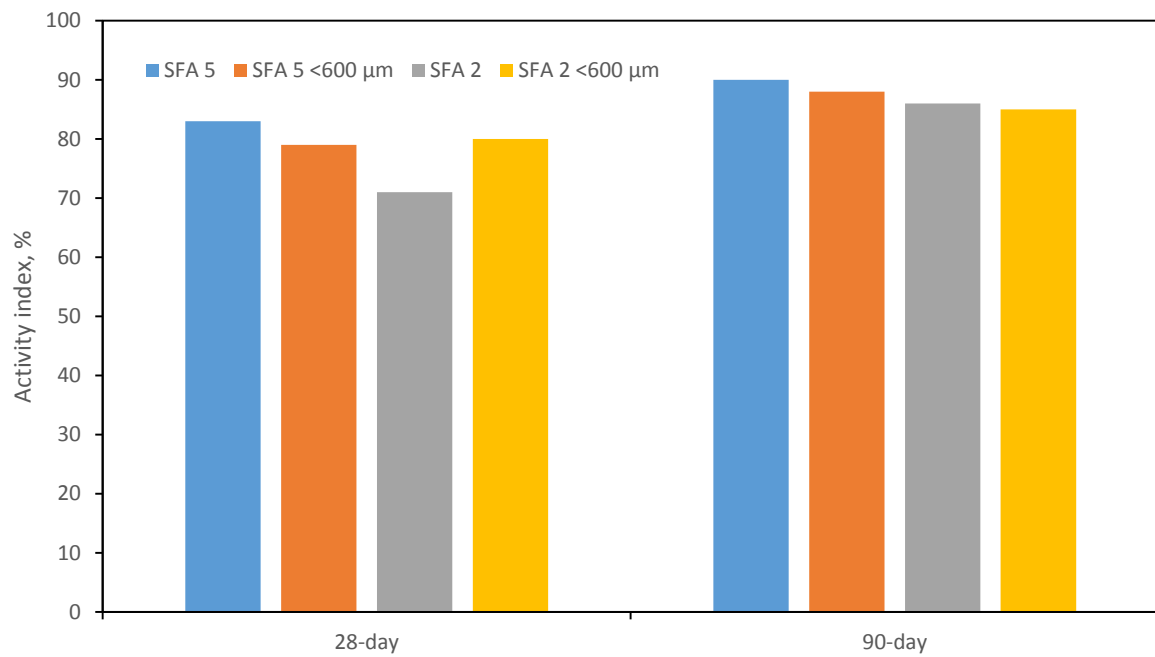
Figure 132 - Change in activity index, at 28 and 90-days, of SFA 2 and SFA 5 after screening at 600 μm
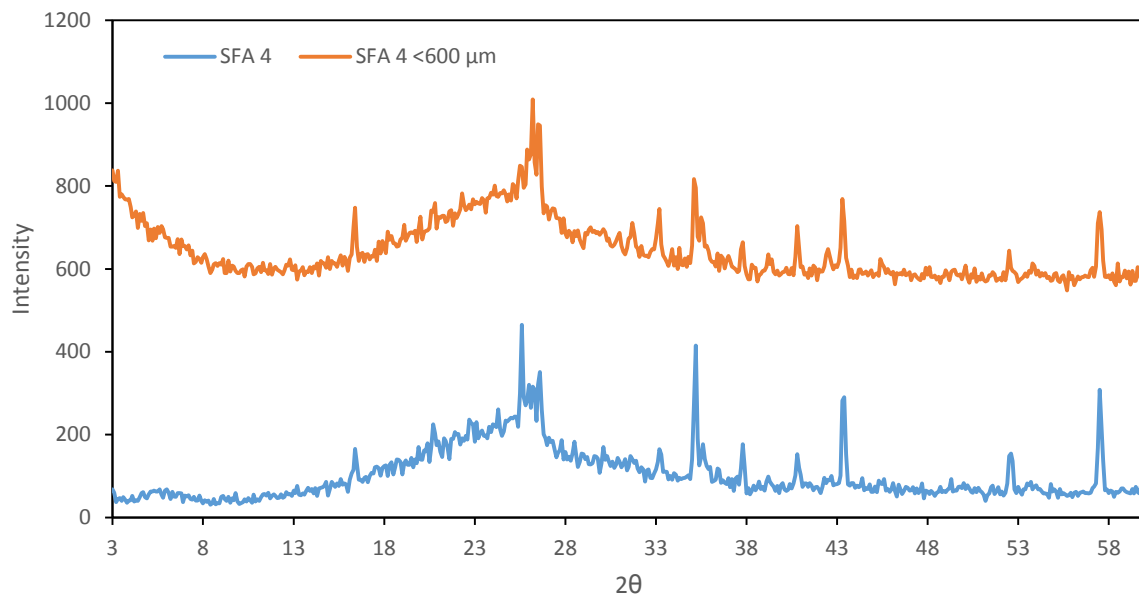
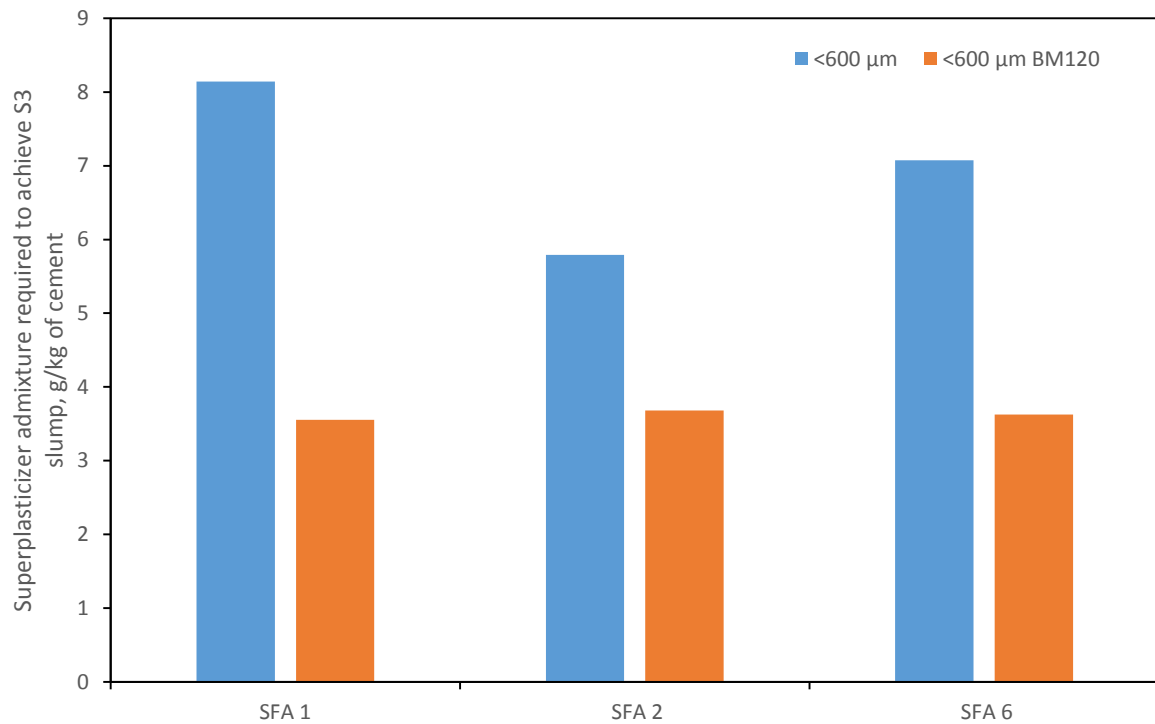*Figure 133 - X-ray diffractogram of on-site wet-stored materials before and after screening at 600 µm*
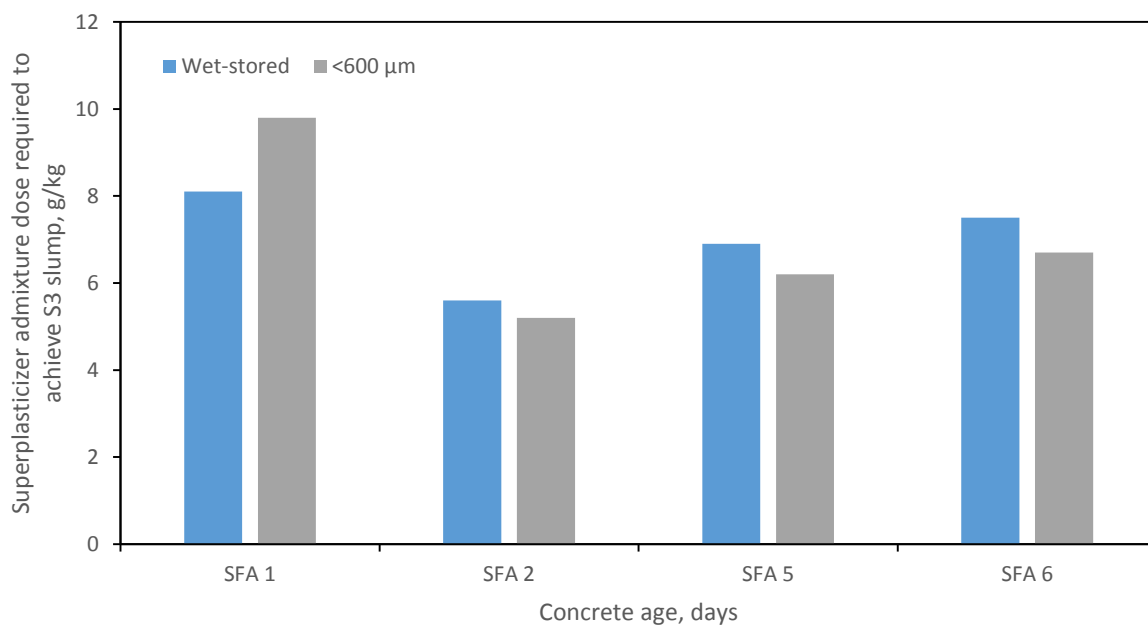
Figure 134 – Superplasticizer admixture dose required to achieve S3 slump in select on-site wet-stored materials before and after screening at 600 µm
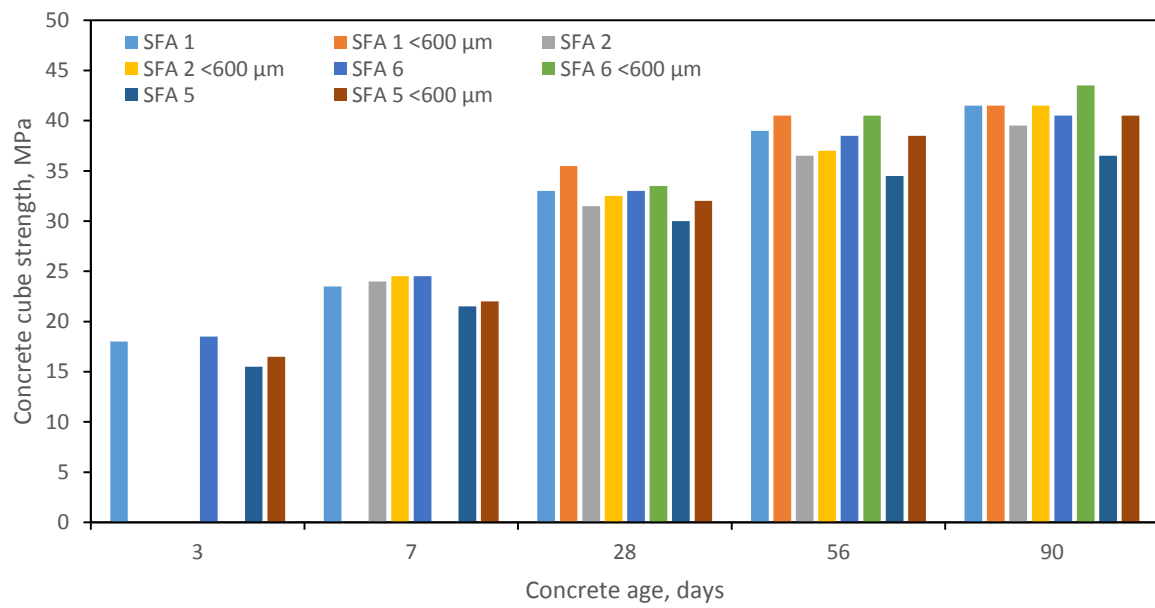
Figure 135 - Change in concrete cube strength of various on-site wet-stored materials after screening at 600 μm

18.4.2. Particle size separation
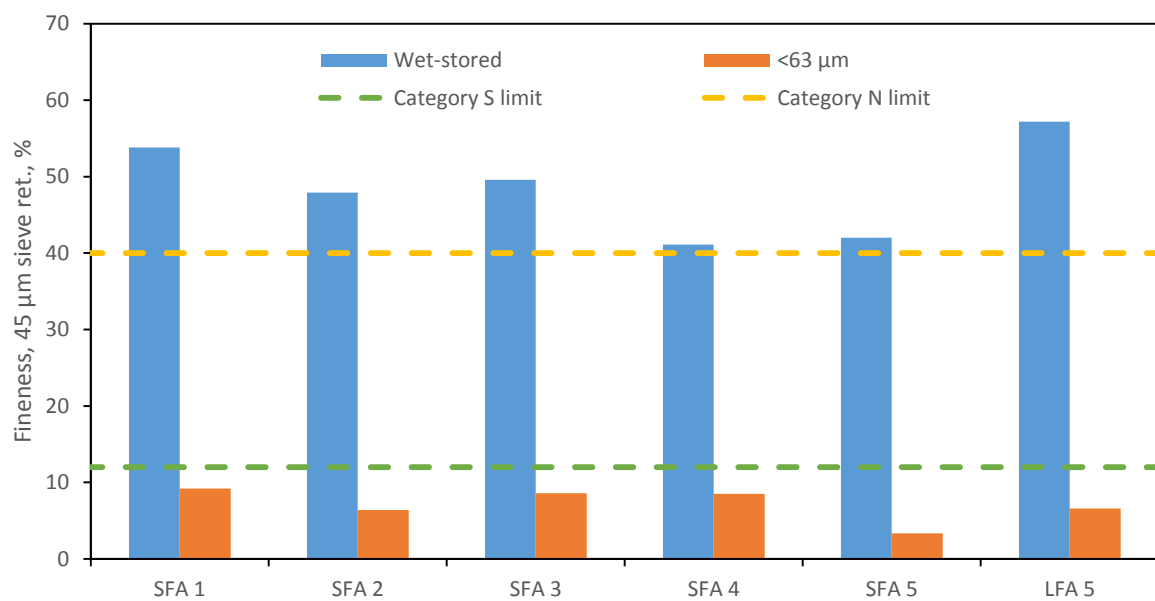
Figure 136 - Fineness values of the on-site wet-stored materials
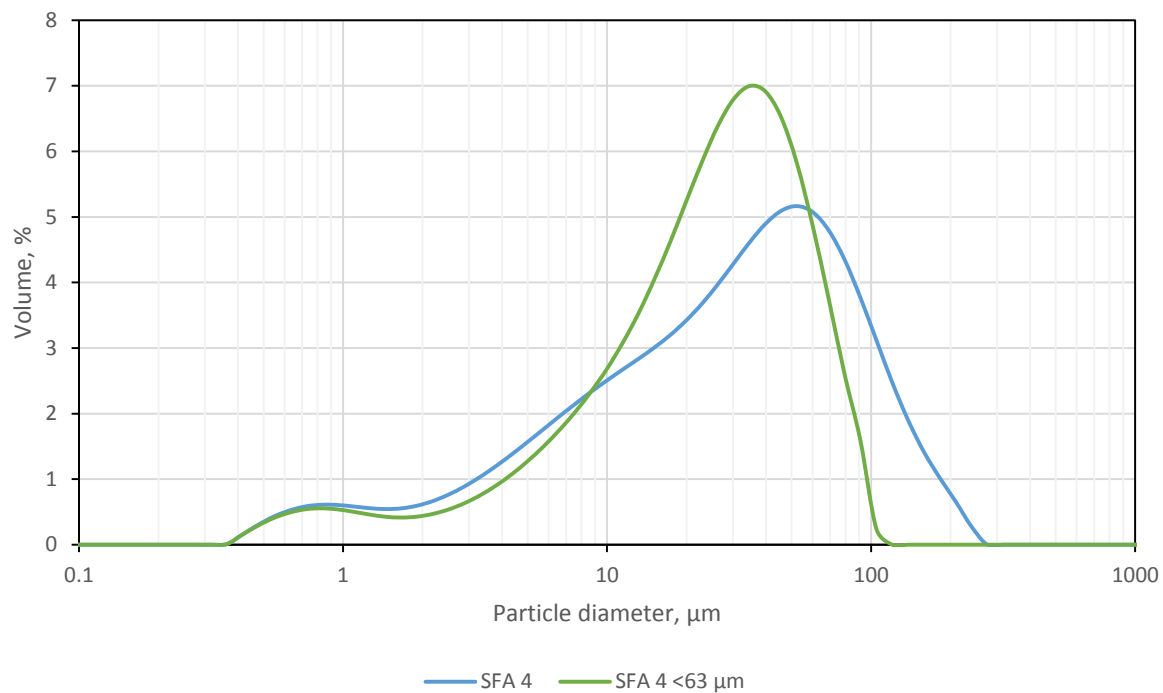
Figure 137 - Particle size distribution of SFA 4 before and after screening at 63 μm
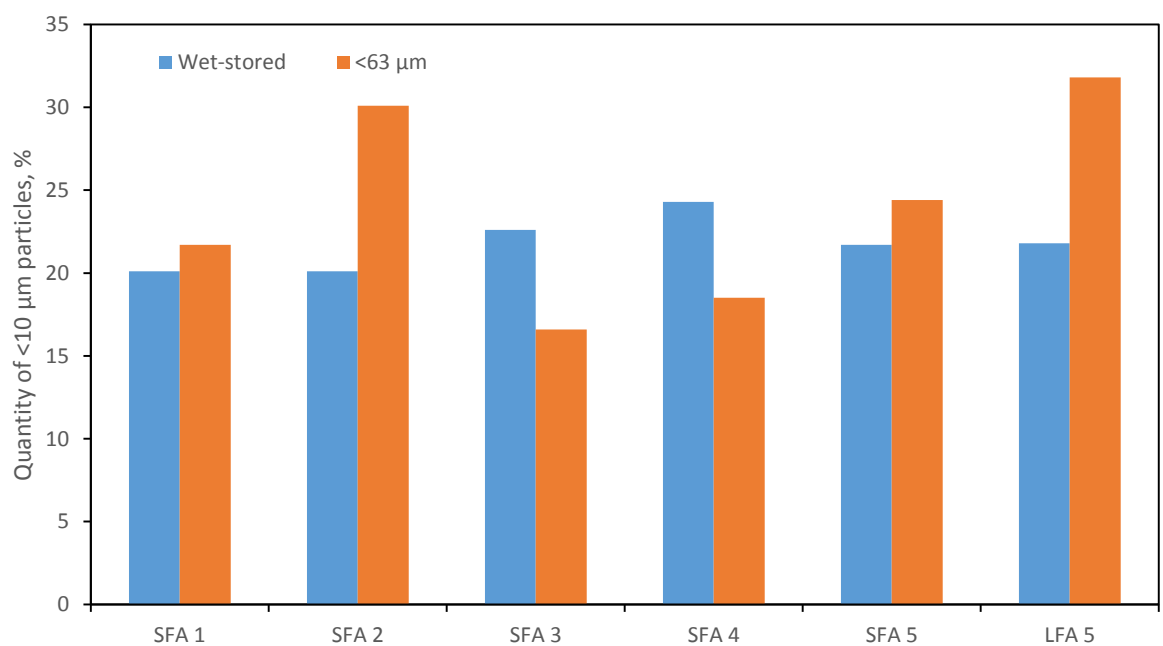
Figure 138 – Change in quantity of <10 μm particles of on-site wet-stored materials after screening at 63 μm
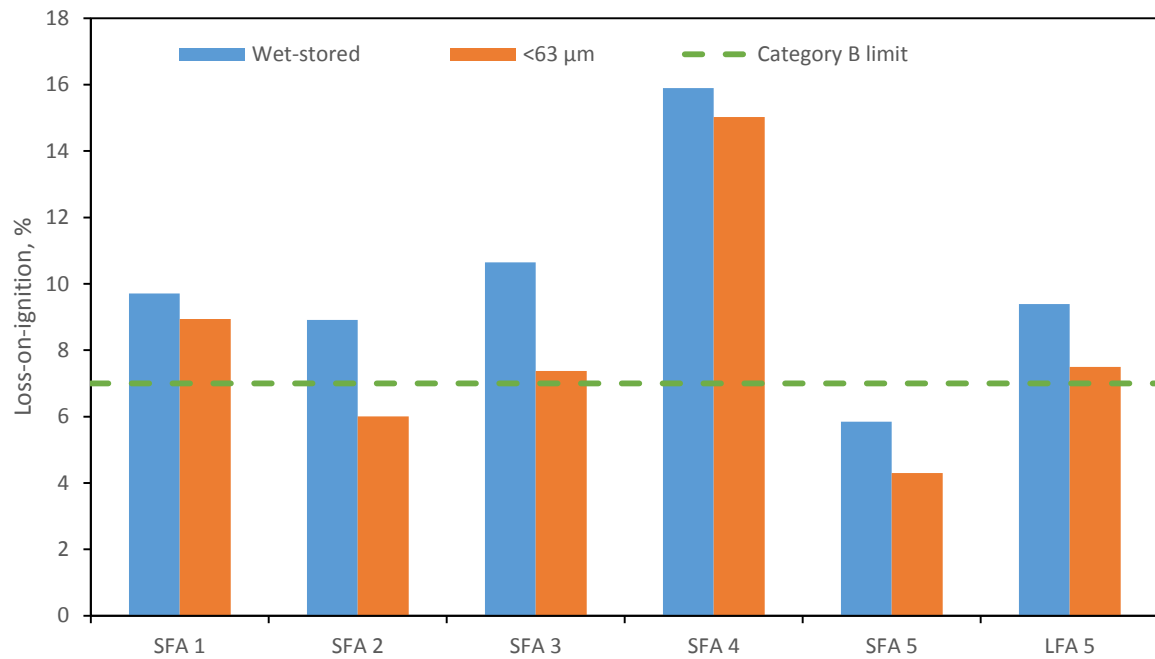
Figure 139 - Change in loss-on-ignition in on-site wet-stored materials after screening at 63 μm
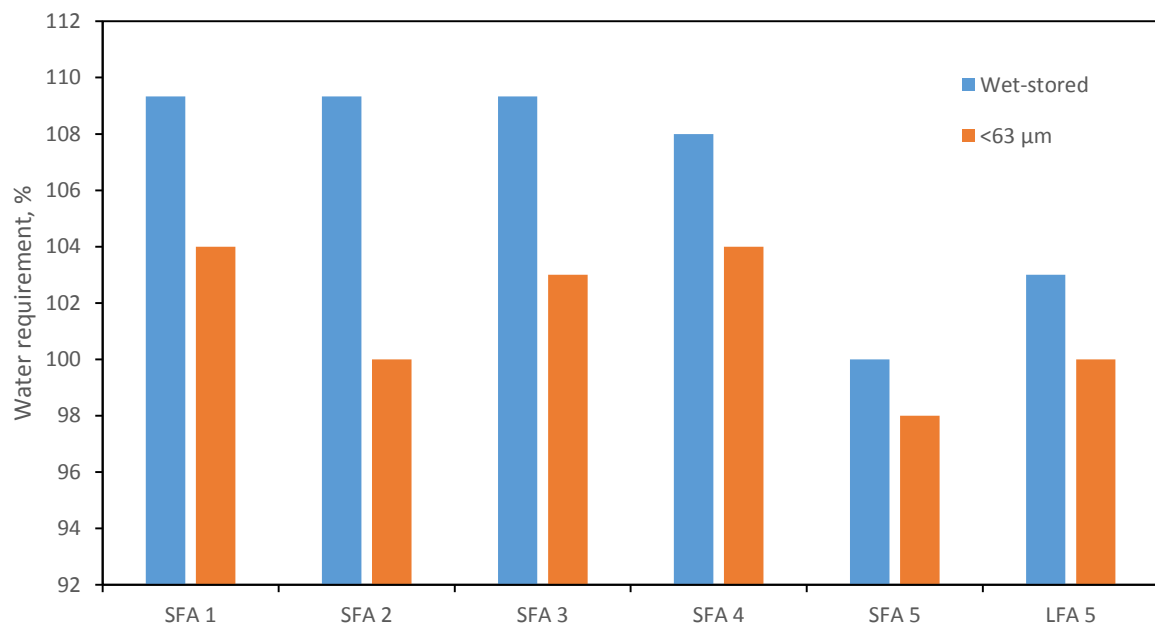
Figure 140 - Change in water requirement in select on-site wet-stored materials after screening at 63 μm
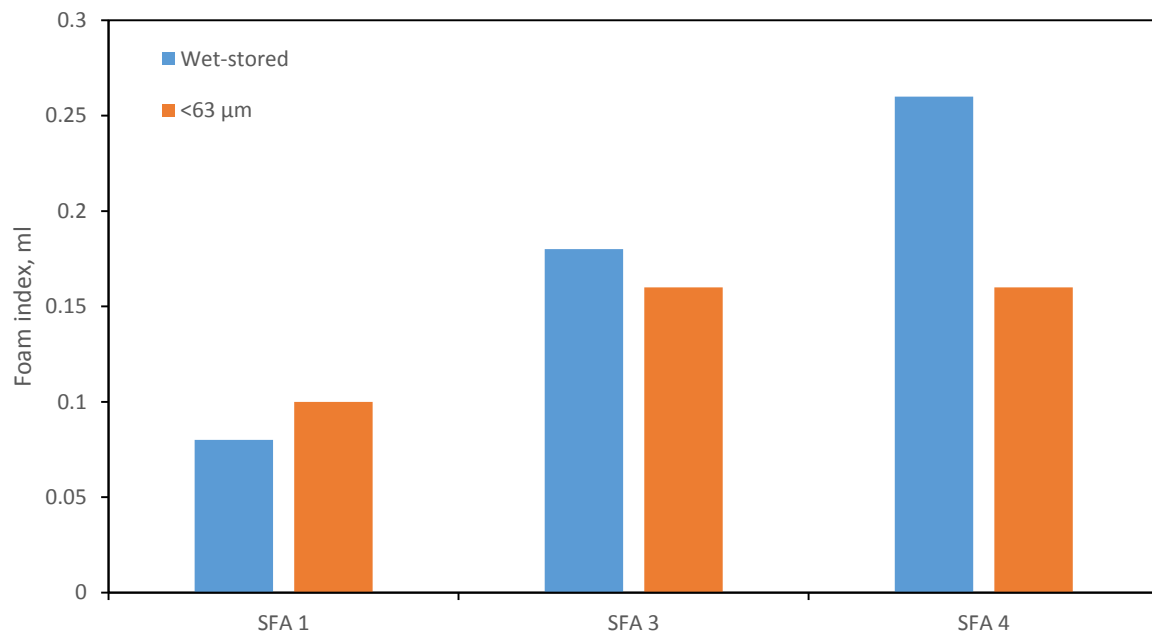
Figure 141 – Change in foam index of selective materials before and after screening at 63 μm
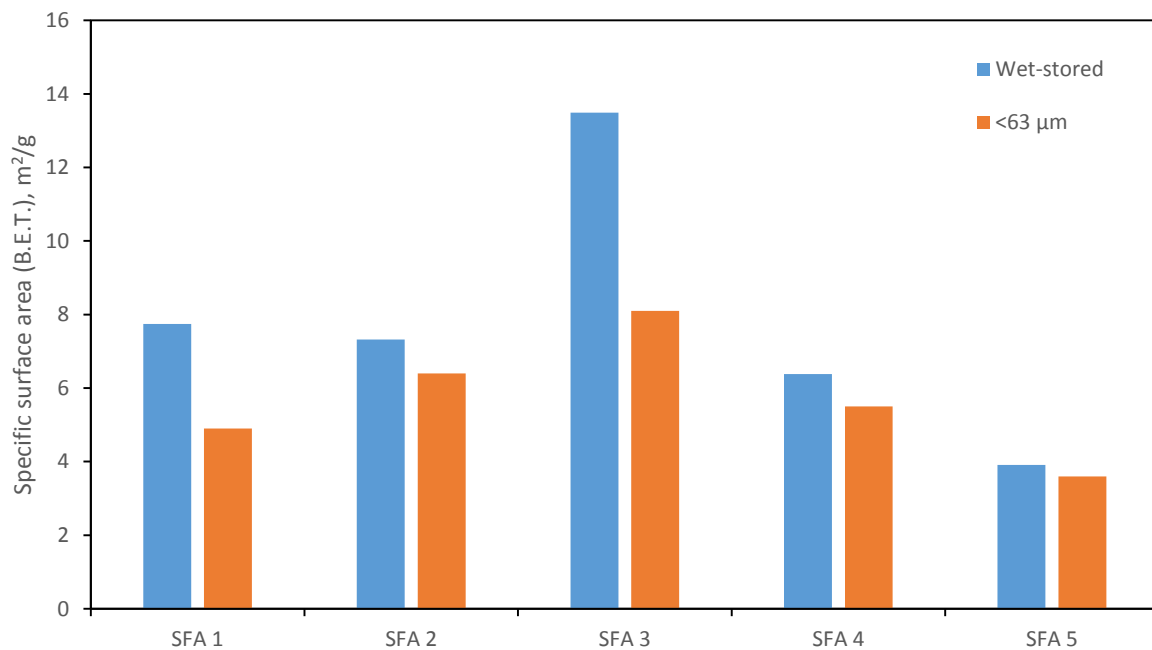
Figure 142 - Change in specific surface area (B.E.T.) in select on-site wet-stored materials after screening at 63 μm
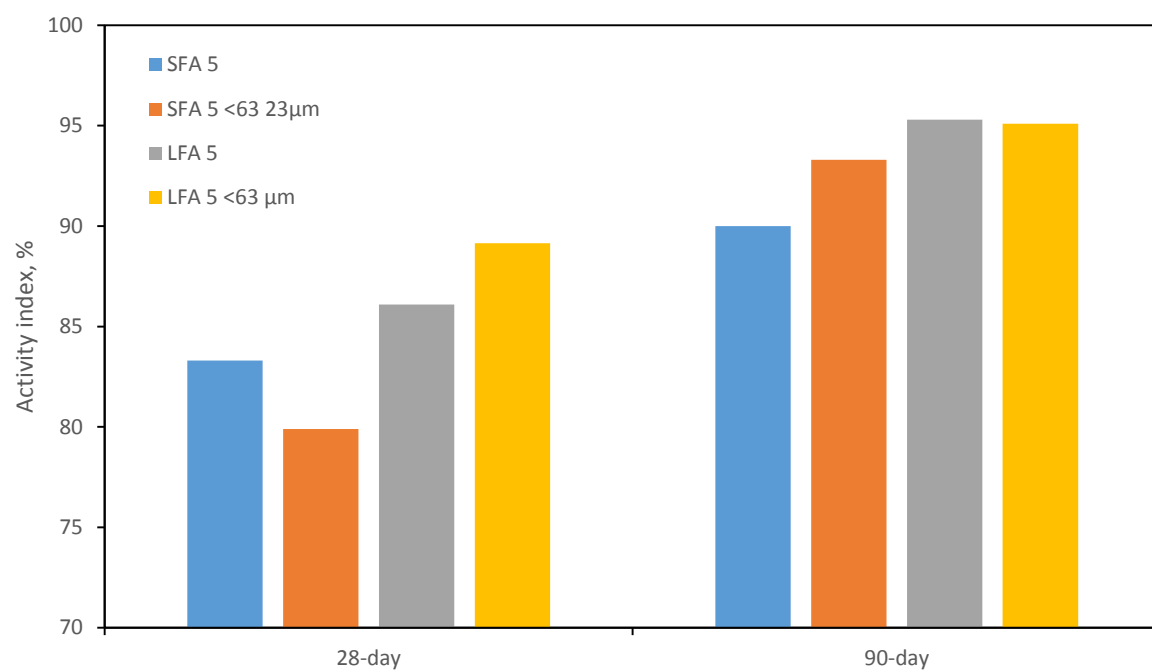
Figure 143 - Change in activity index, at 28 and 90-days, of SFA 5 and LFA 5 after screening at 63 μm
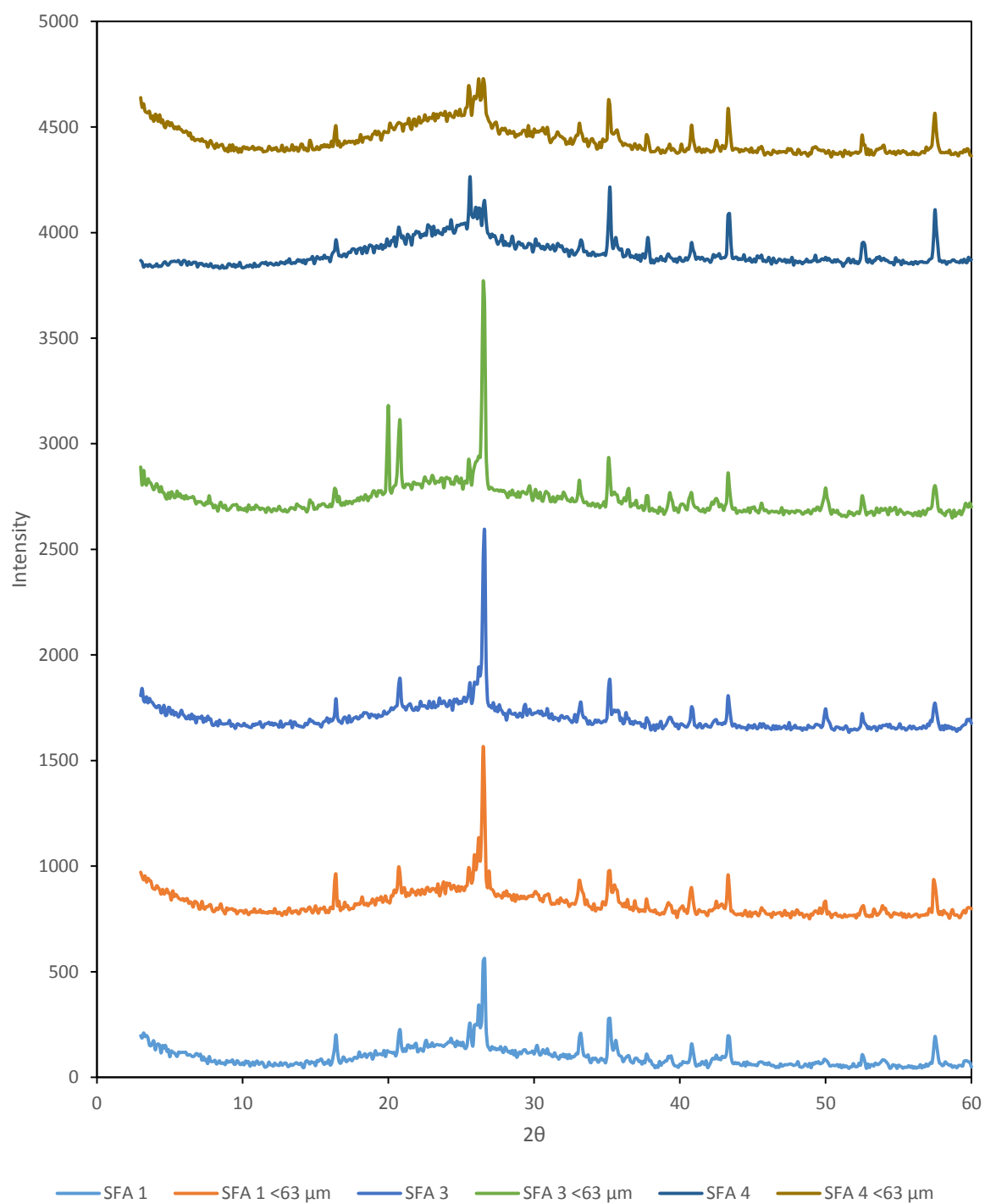
Figure 144 - X-ray diffractogram of on-site wet-stored materials before and after screening at 63 μm
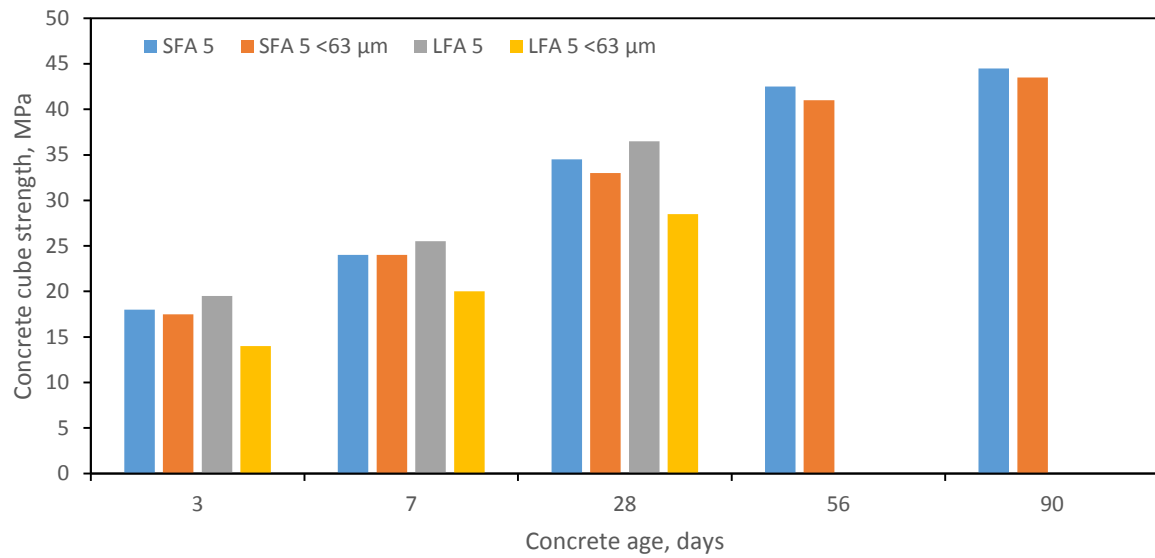
Figure 145 - Change in concrete strength of SFA 5 and LFA 5 after screening at 63 μm

18.4.3. Particle size reduction
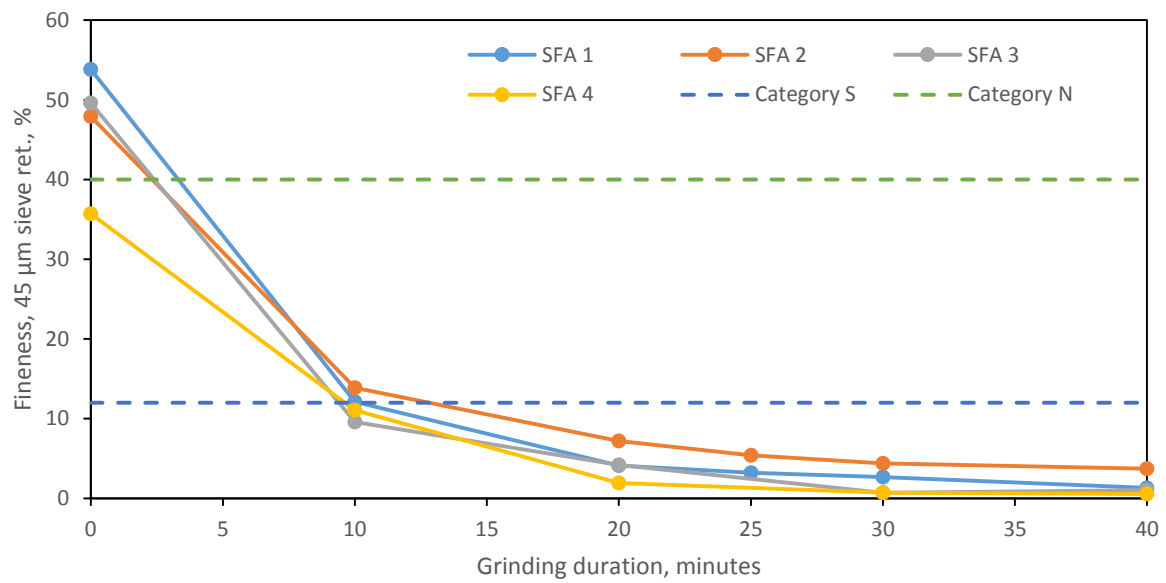
Figure 146 - Change in fineness with ball milling duration for various on-site wet-stored materials in 125 g batches
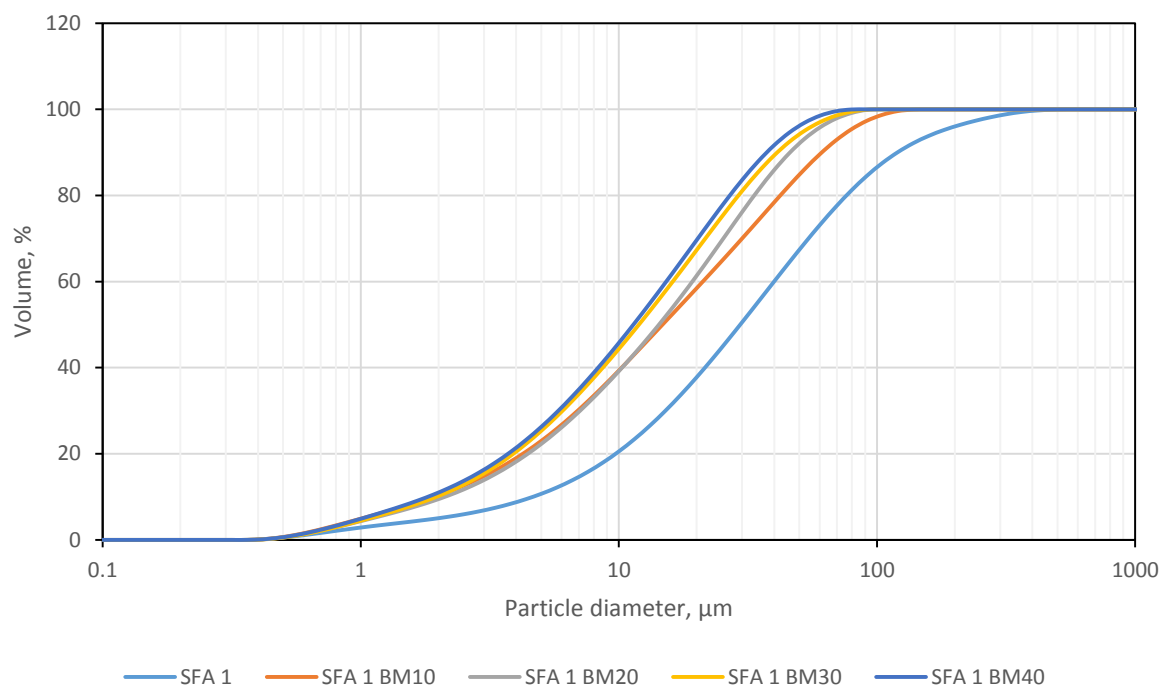
Figure 147 - Comparison of particle passing curves for SFA 1 after ball milling for 10 to 40 minutes
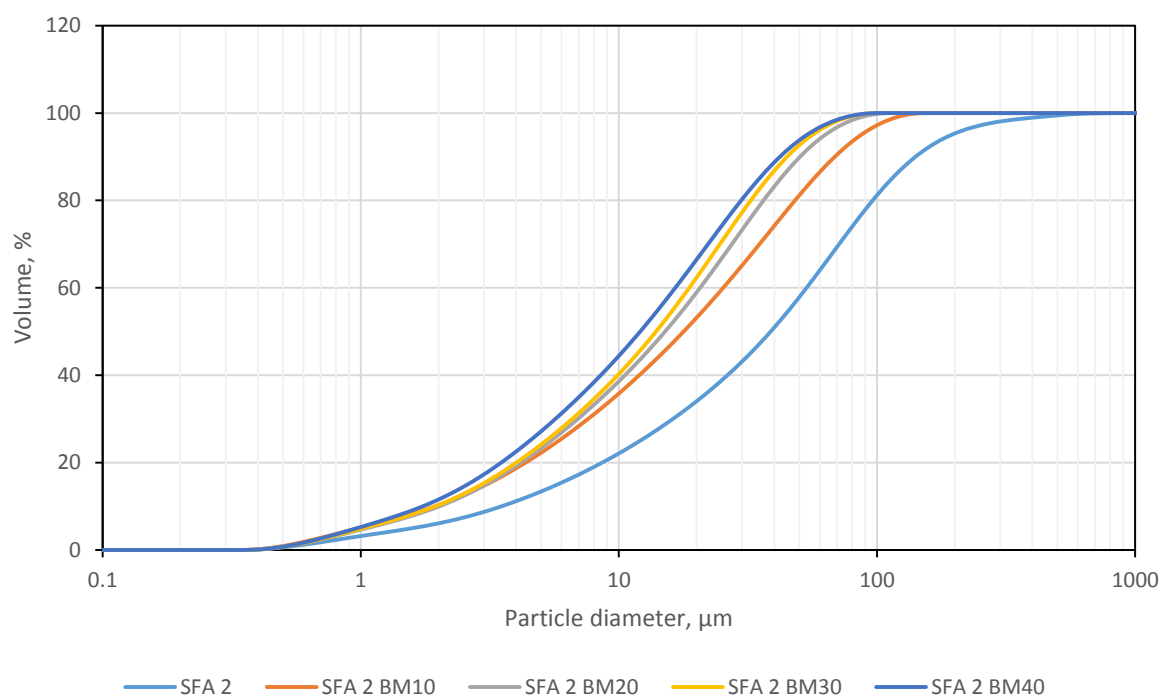
Figure 148 - Comparison of particle passing curves for SFA 2 after ball milling for 10 to 40 minutes
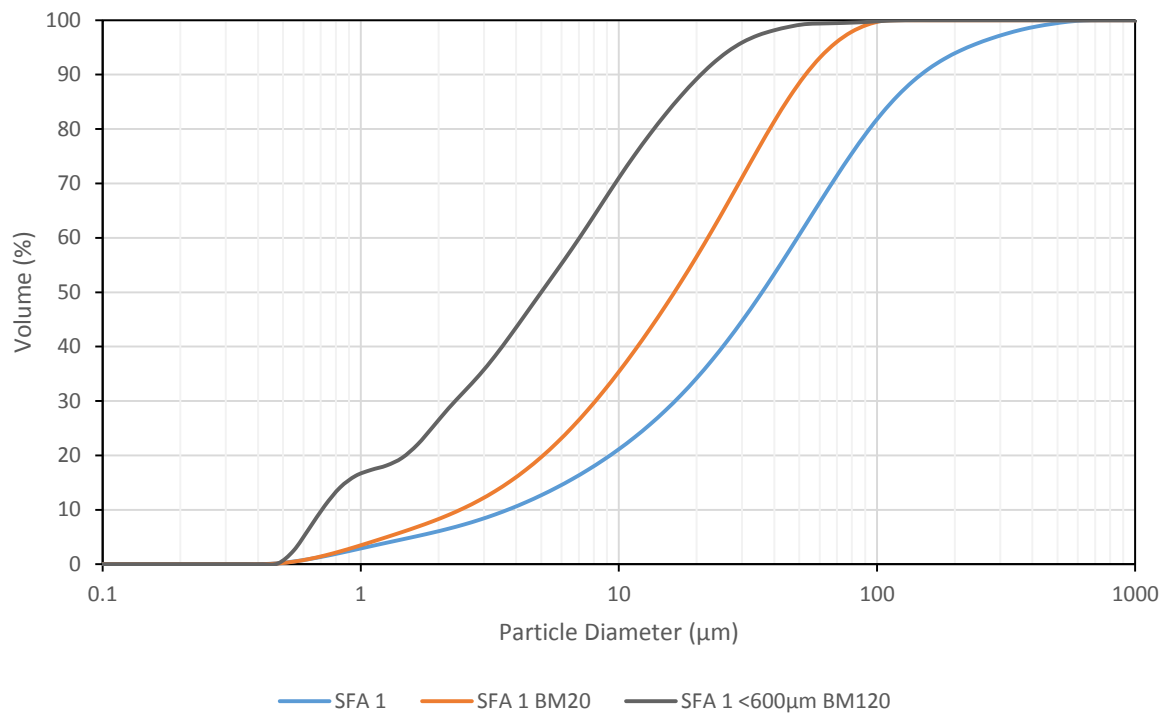
Figure 149 - Comparison of particle passing curves for SFA 1 after ball milling for 20 and 120 minutes
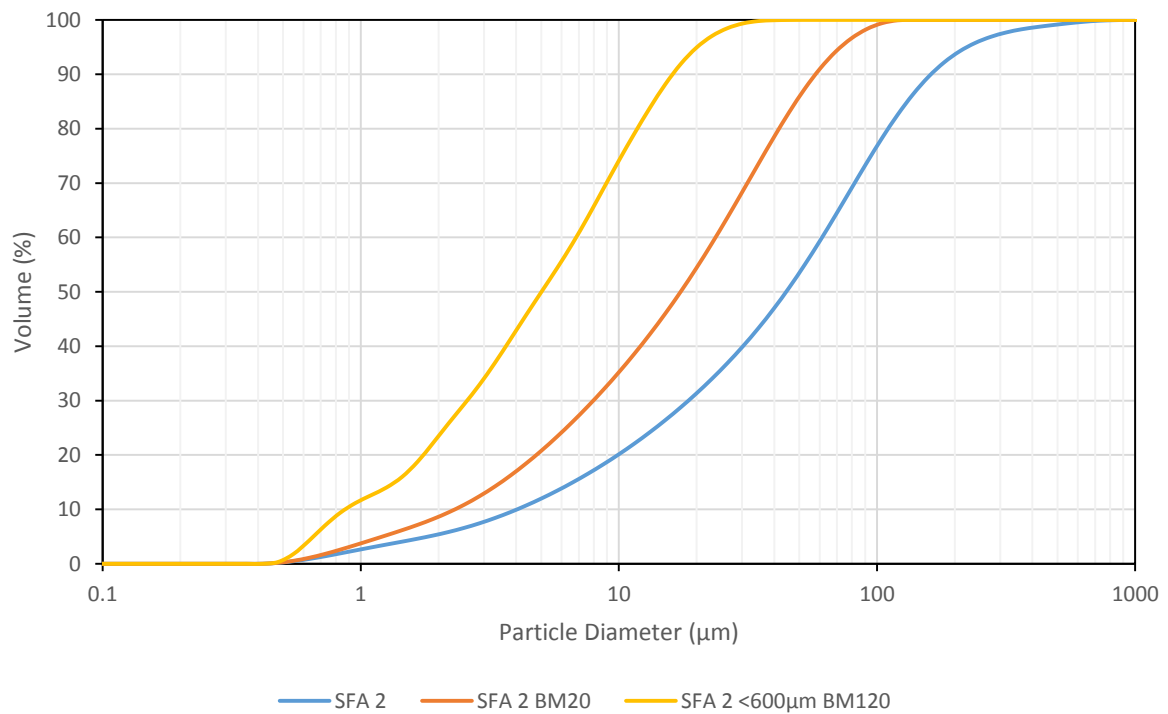
Figure 150 - Comparison of particle passing curves for SFA 2 after ball milling for 20 and 120 minutes
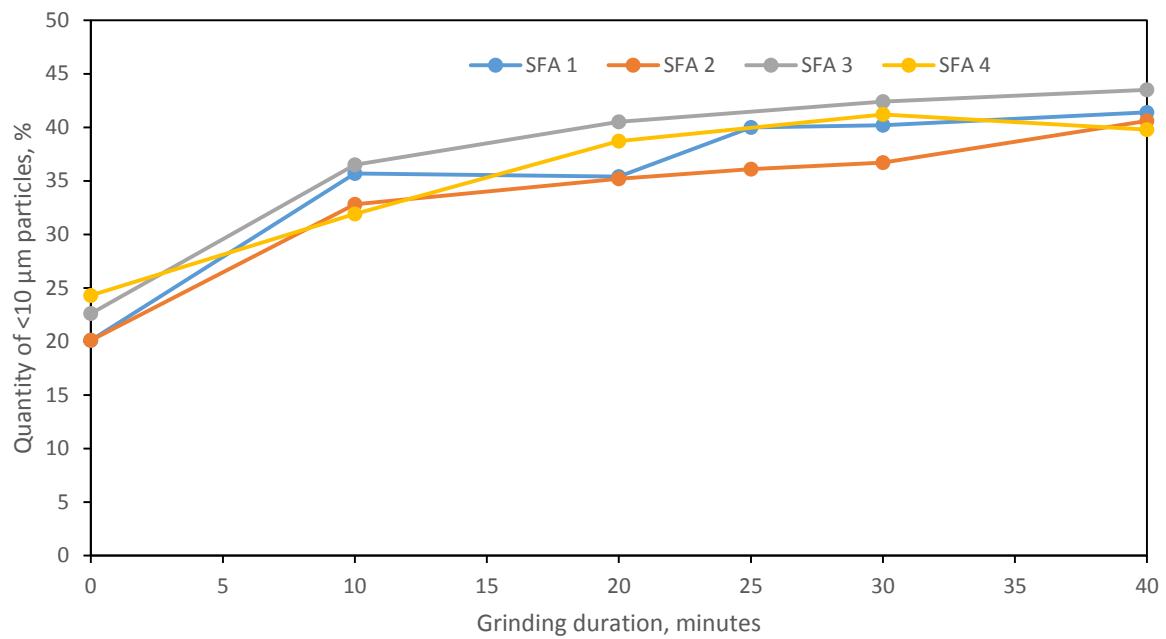
Figure 151 - Change in quantity of<10 µm particles with ball milling duration for various on-site wet-stored materials in 125 g batches
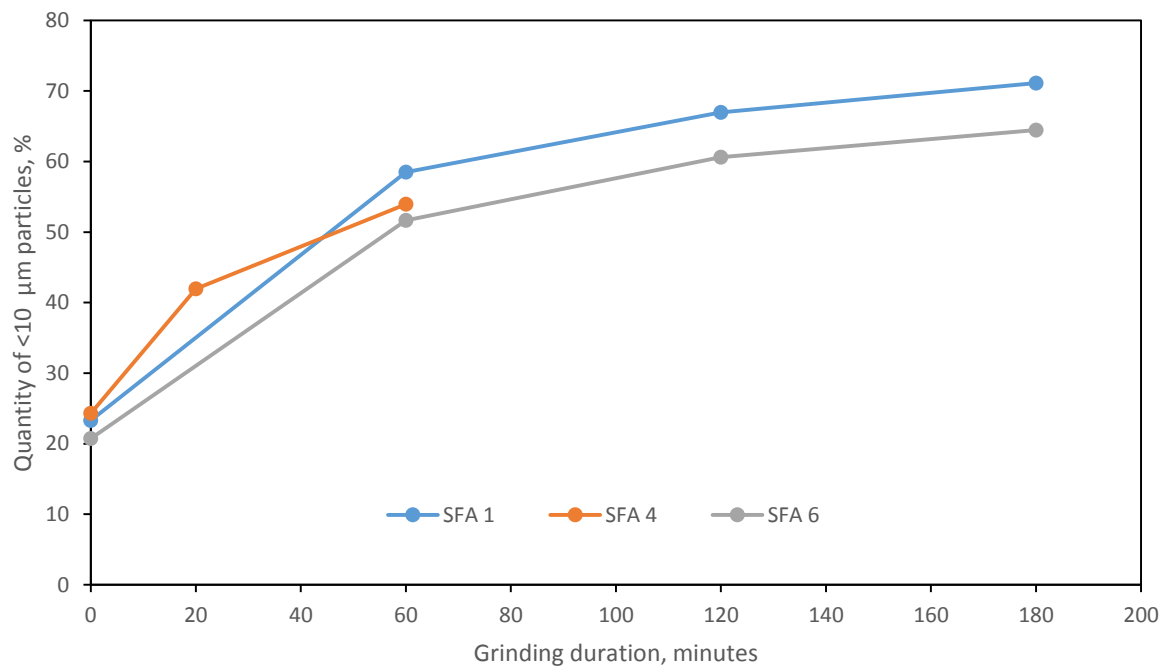
Figure 152 - Change in quantity of <10 µm particles of select on-site wet-stored materials after ball milling in 100 g batches
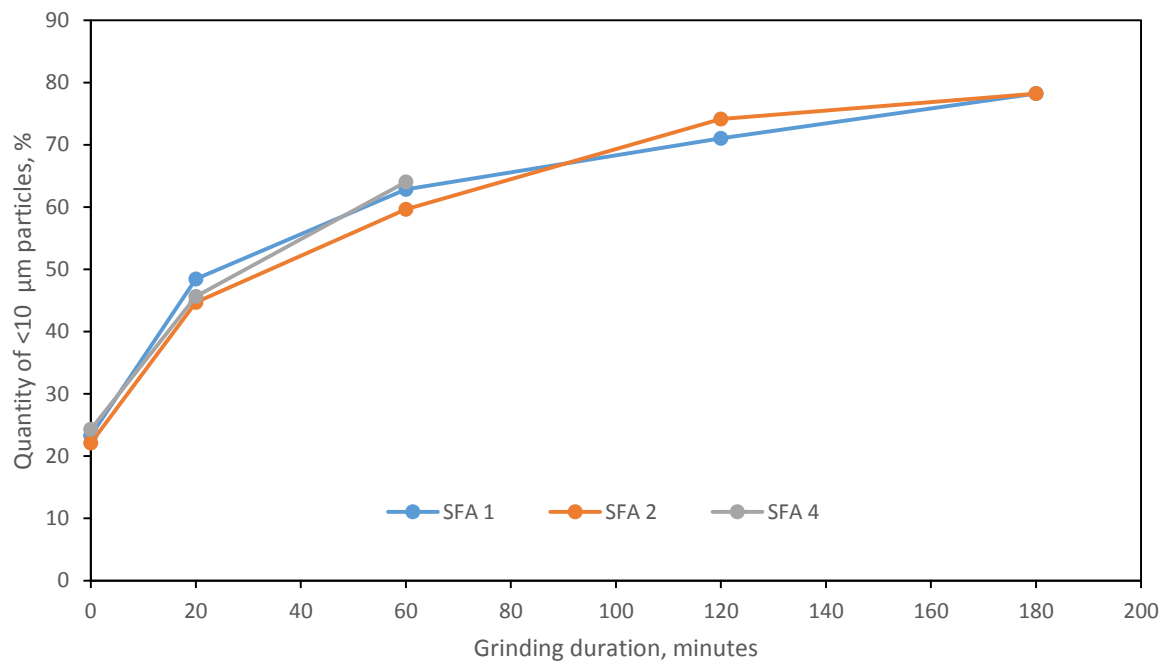
Figure 153 - Change in quantity of <10 μm particles of select on-site wet-stored materials after ball milling in 50 g batches
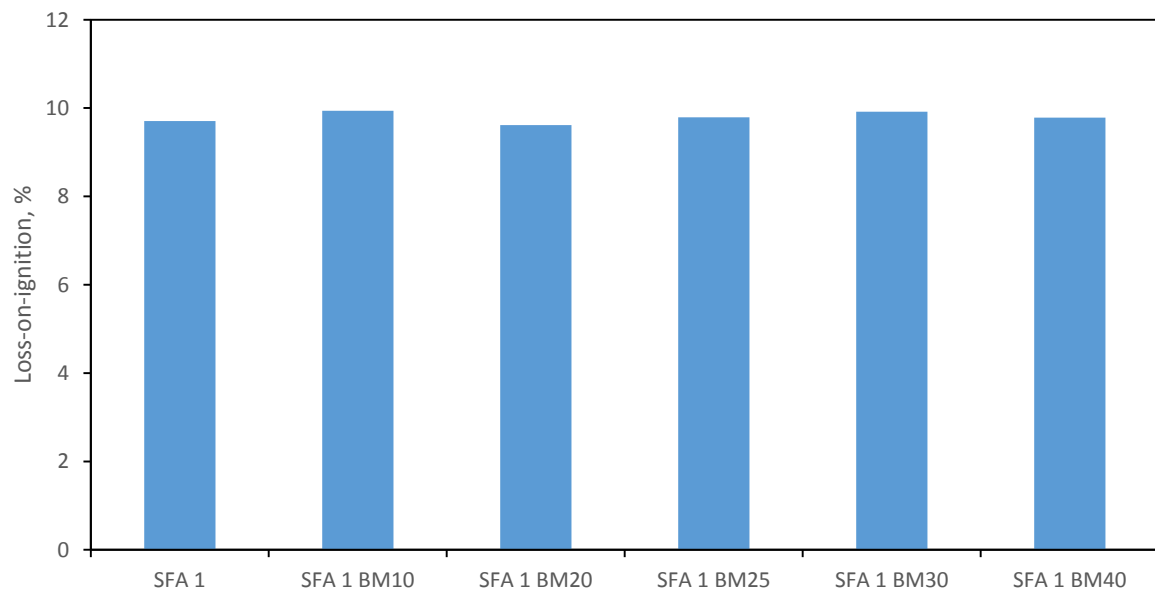
Figure 154 - Change in loss-on-ignition of SFA 1 after ball milling for 20 minutes in 125 g batches

197

Surface products between fly ash particles

Fly ash particles

Surface products on particles

Unburned carbon particle
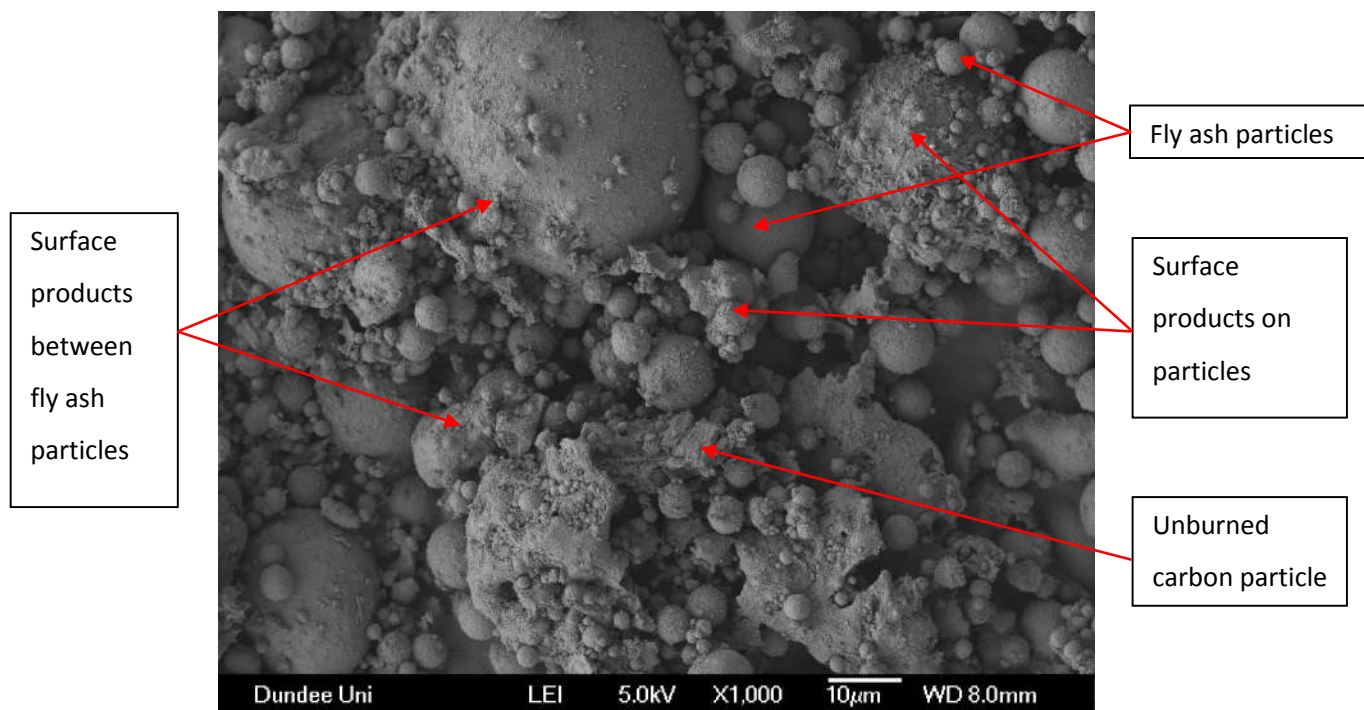
Figure 155 - Scanning Electron Microscopy image of SFA 1 (x1000)

Surface products between fly ash particles

Ground, broken fly ash particles

Fly ash particles

Surface products on particles

Unburned carbon particle
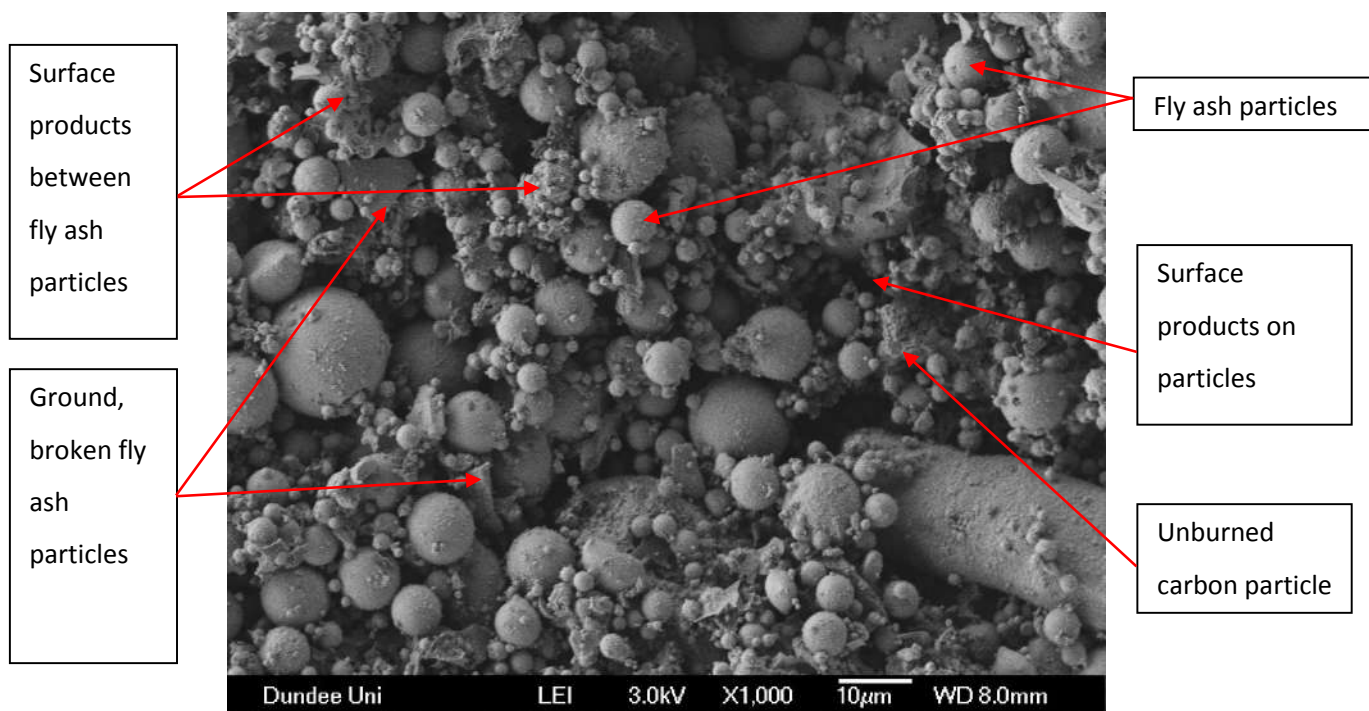
Figure 156 - Scanning Electron Microscopy image of SFA 1 ball milled for 10 minutes (x1000)
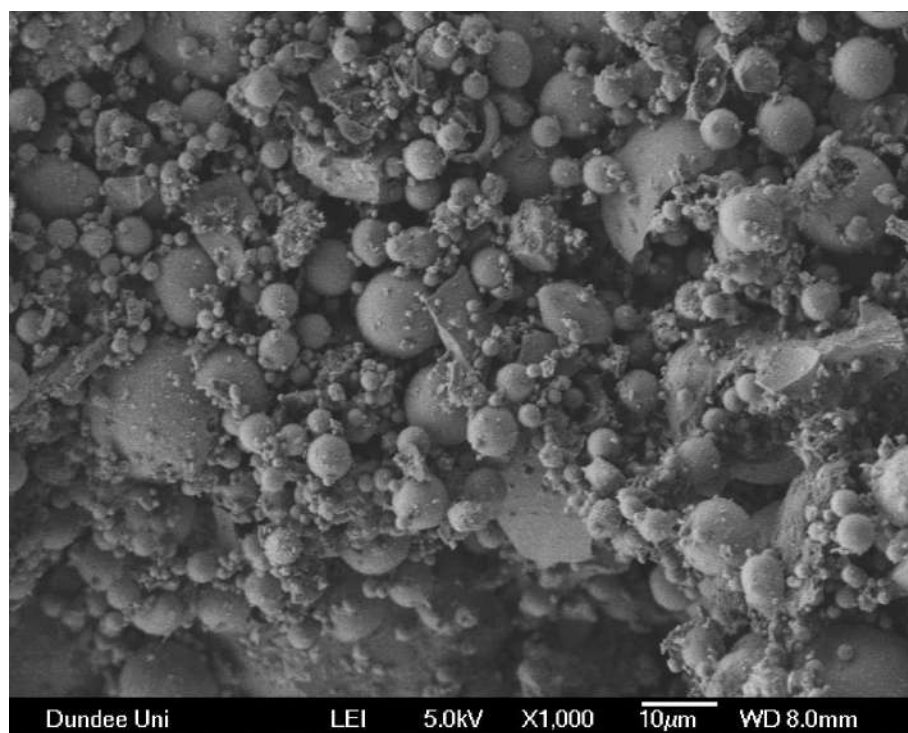
Figure 157 - Scanning Electron Microscopy image of SFA 1 ball milled for 20 minutes (x1000)
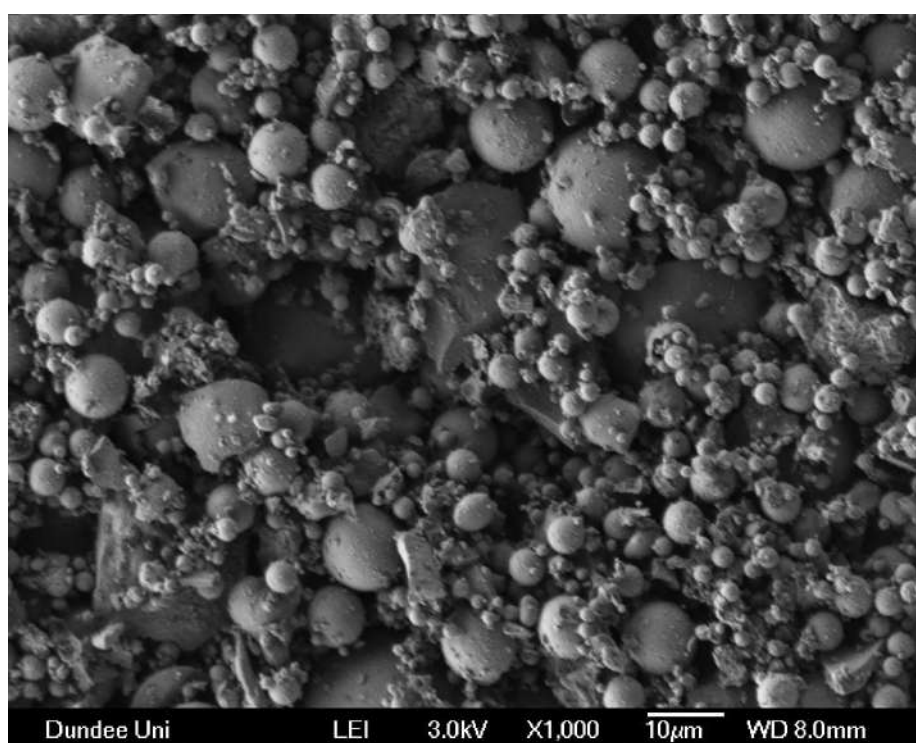
Figure 158 - Scanning Electron Microscopy image of SFA 1 ball milled for 30 minutes (x1000)
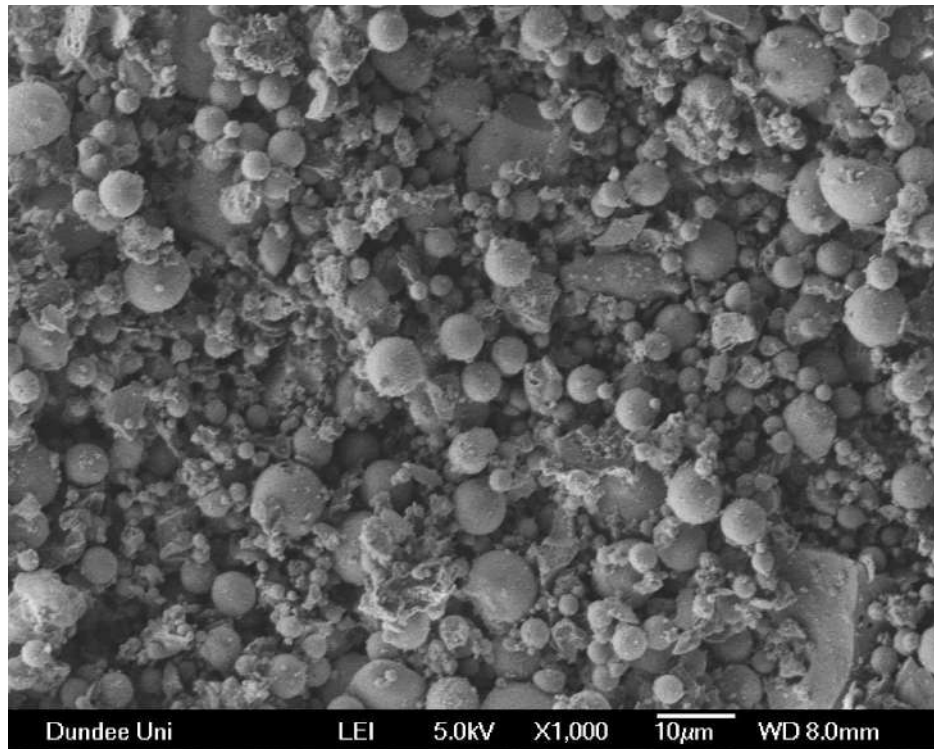
Figure 159 - Scanning Electron Microscopy image of SFA 1 ball milled for 40 minutes (x1000)
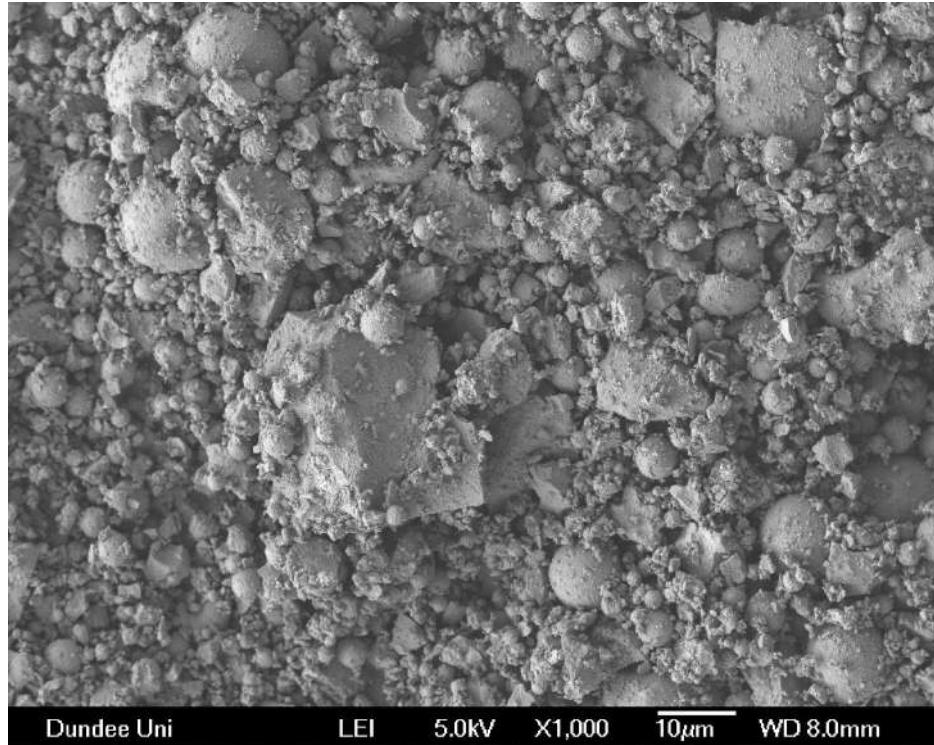
Figure 160 - Scanning Electron Microscopy image of SFA 1 <600 µm BM120 (x1000)

200
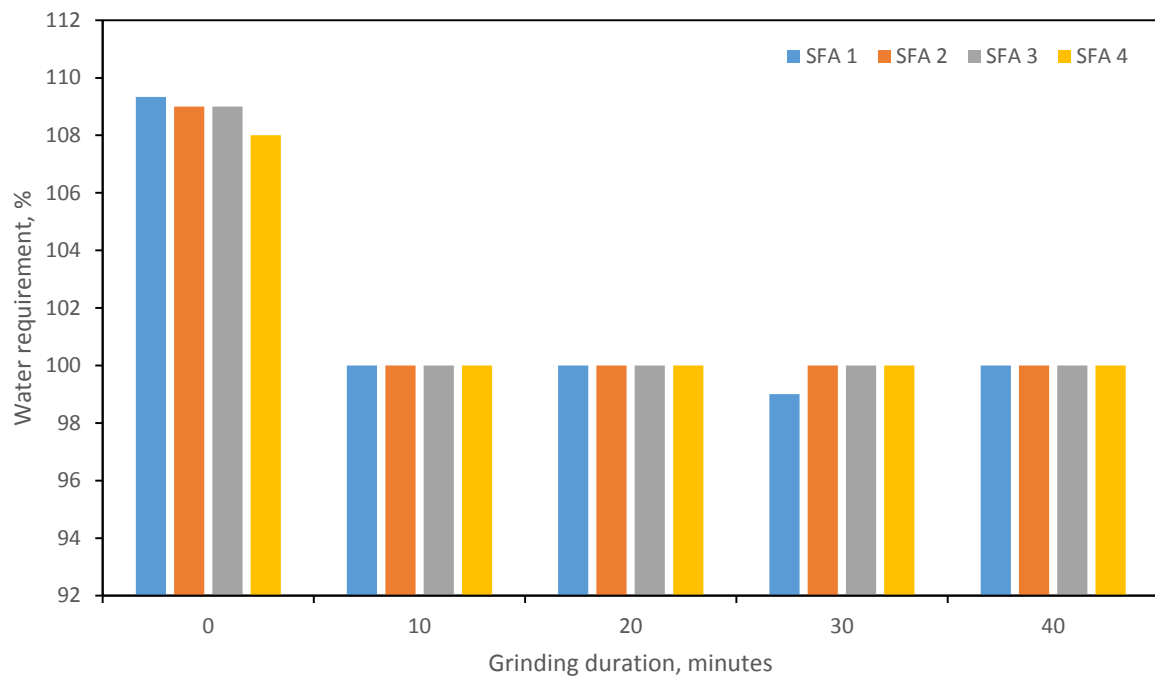
Figure 161 - Change in water requirement of select on-site wet-stored materials after ball milling in 125 g batches
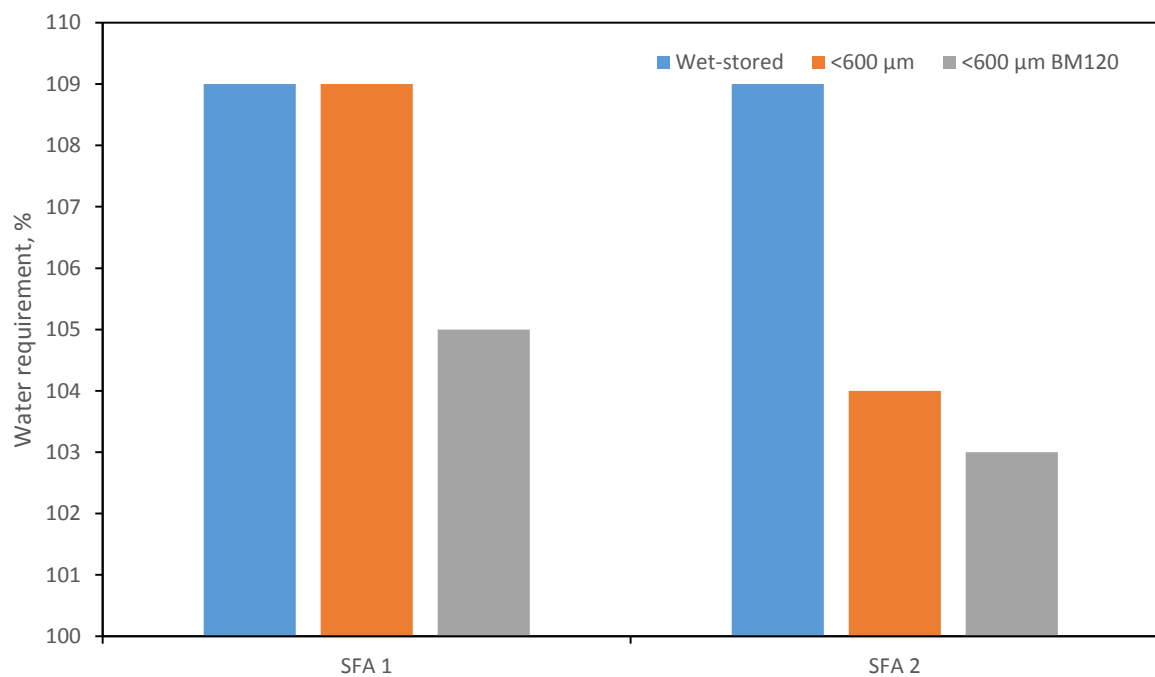
Figure 162 - Change in water requirement of SFA 1 and SFA 2 after screening at 600 μm and ball milling for 120 minutes in 50 g batches
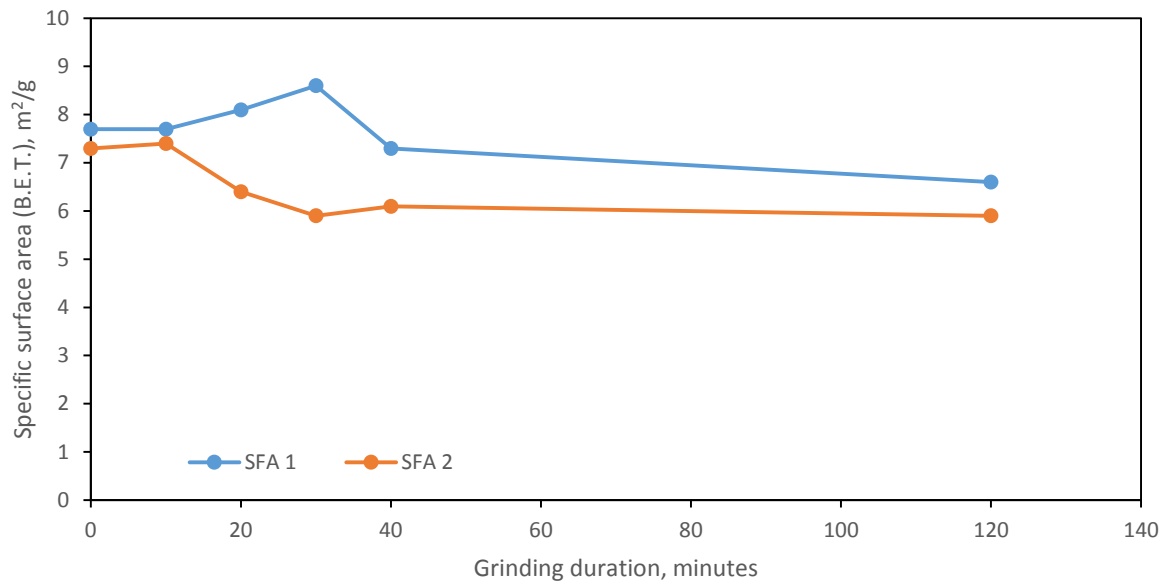
Figure 163 - Relationship between specific surface area (B.E.T.) and ball milling duration for SFA 1 and SFA 2
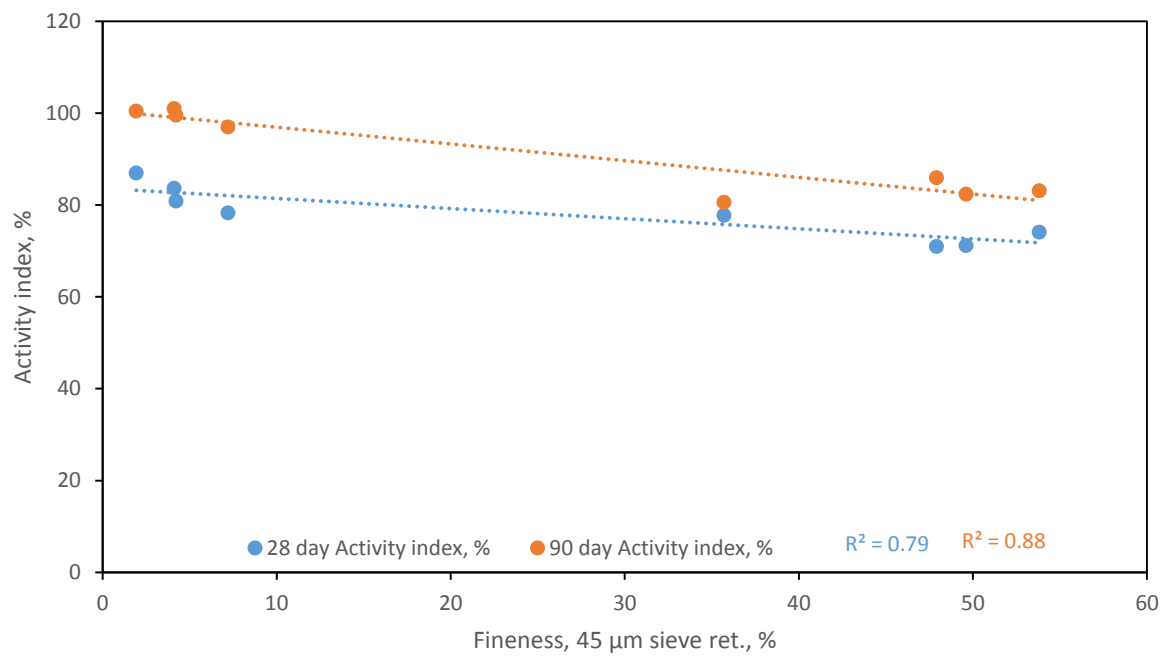
Figure 164 - Relationships between activity index, at 28 and 90-days, and fineness for on-site wet-stored material ball milled for 20 minutes in 125 g batches
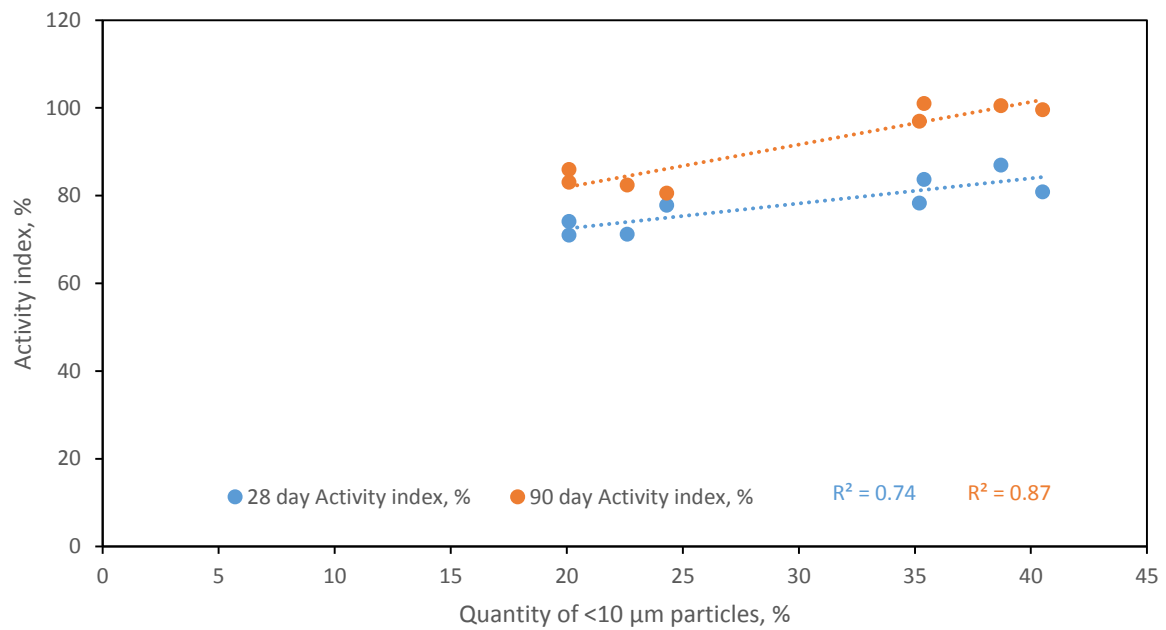
Figure 165 - Relationships between activity index, at 28 and 90-days, and quantity of<10 µm particles for on-site wet-stored material ball milled for 20 minutes in 125 g batches
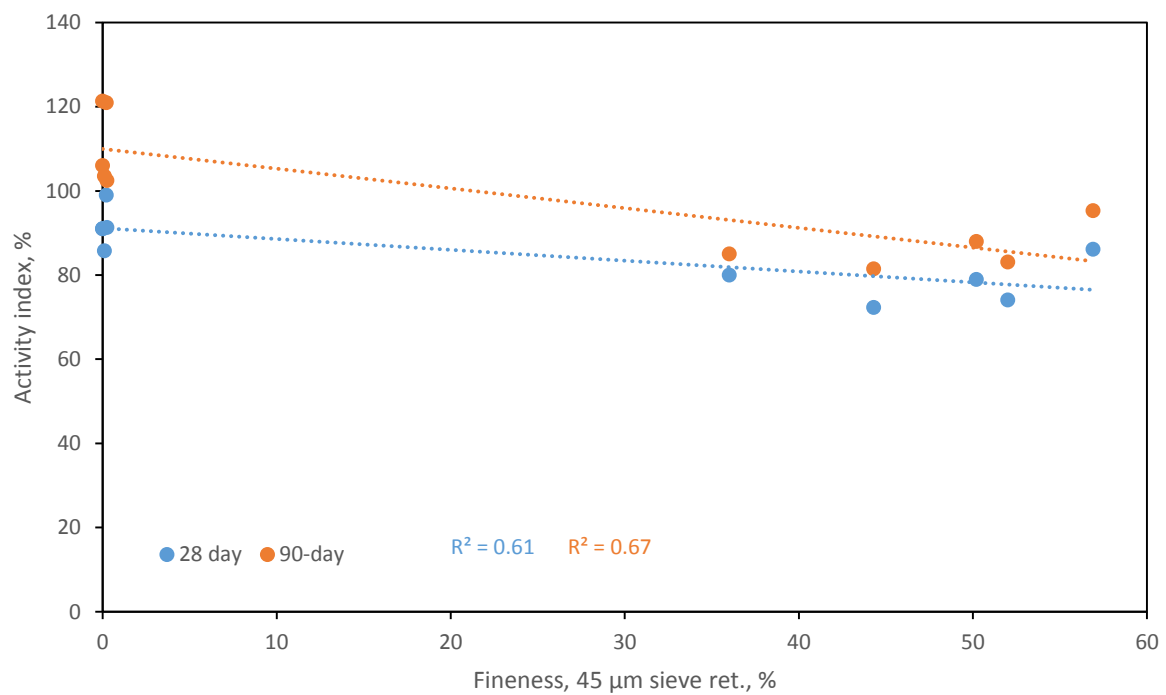
Figure 166 - Relationship between activity index, at 28 and 90-days, and fineness for on-site wet-stored materials ball milled for 60 to 120 minutes

Figure 167 - Relationship between activity index, at 28 and 90-days, and quantity of <10 µm particles for on-site wet-stored materials ball milled for 60 to 120 minutes
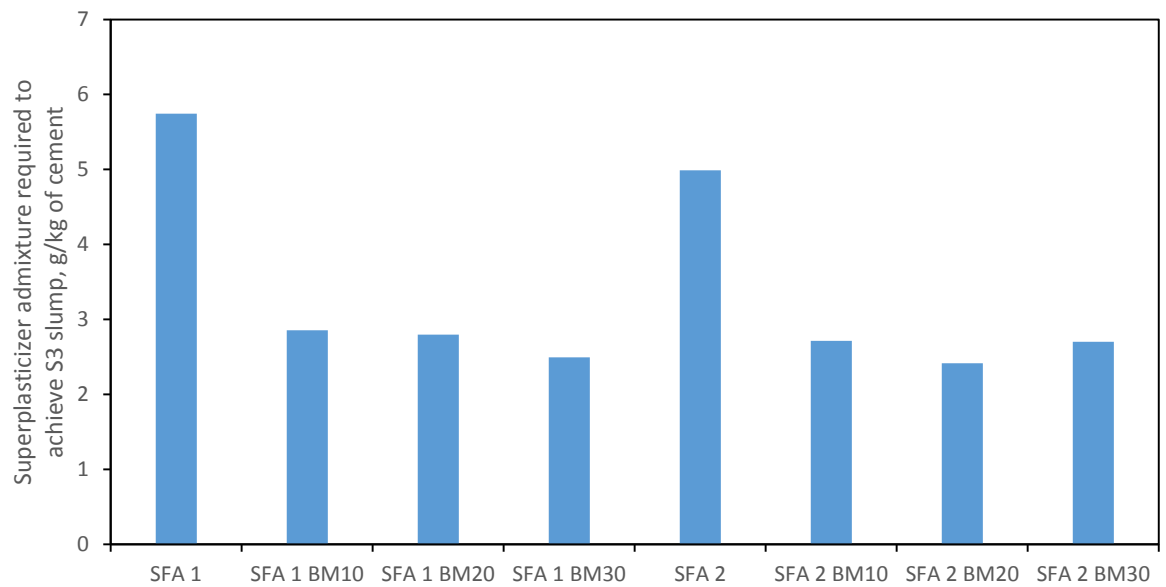
Figure 168 – Change in superplasticizer admixture dose required to achieve S3 slump in SFA 1 and SFA 2 after ball milling in 125 g batches
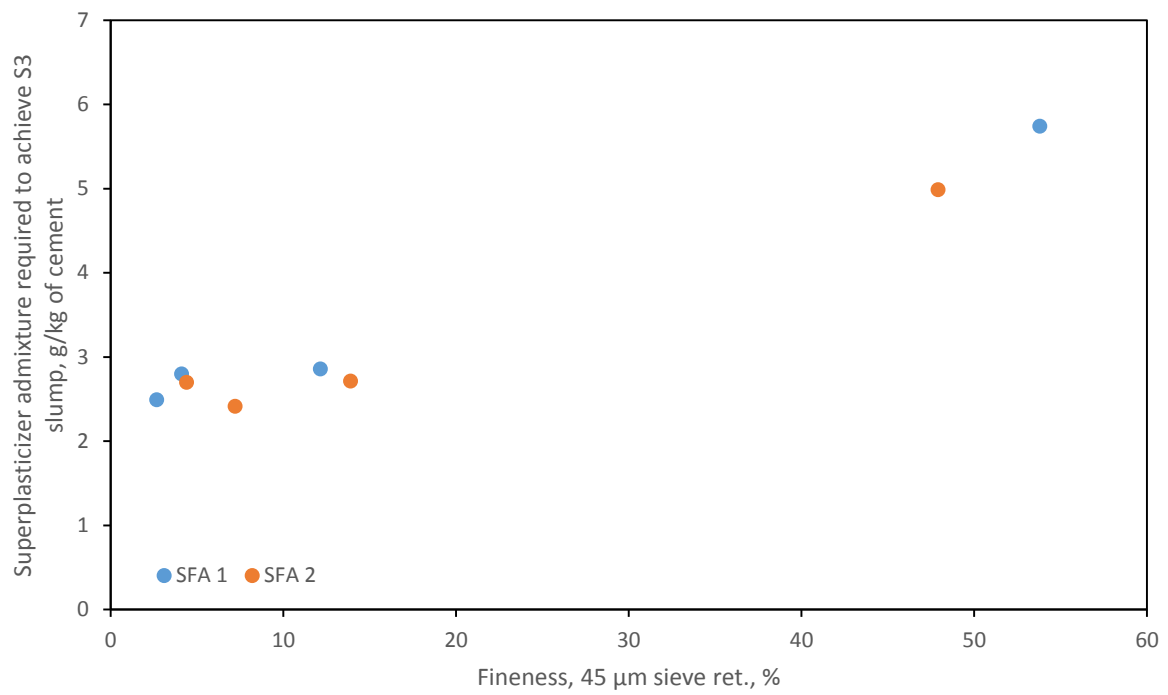
Figure 169 - Relationship between superplasticizer admixture dose required to achieve S3 slump and 45 µm sieve retention of SFA 1 and SFA 2 before and after ball milling
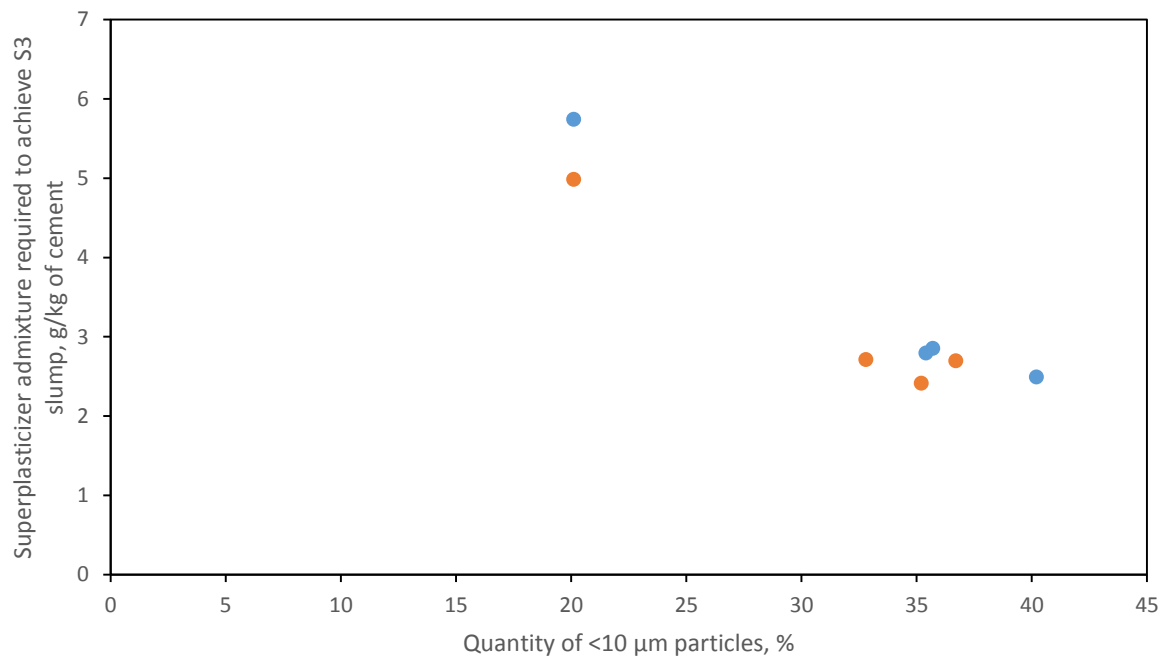
Figure 170 - Relationship between superplasticizer admixture dose required to achieve S3 slump and <10 µm content of SFA 1 and SFA 2 before and after ball milling

Figure 171 – Change in superplasticizer admixture dose required to achieve S3 slump in select on-site wet-stored materials before and after ball milling for 120 minutes in 50 g batchers
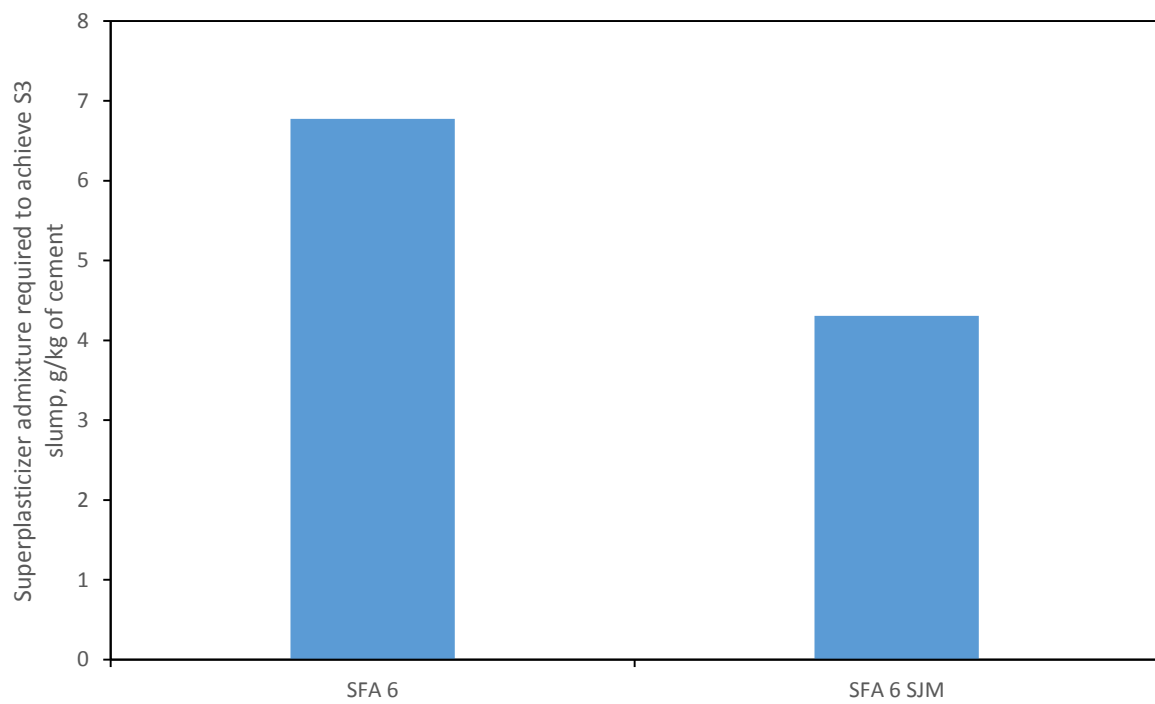
Figure 172 - Change in superplasticizer admixture requirement of SFA 6 after a single pass through the microniser
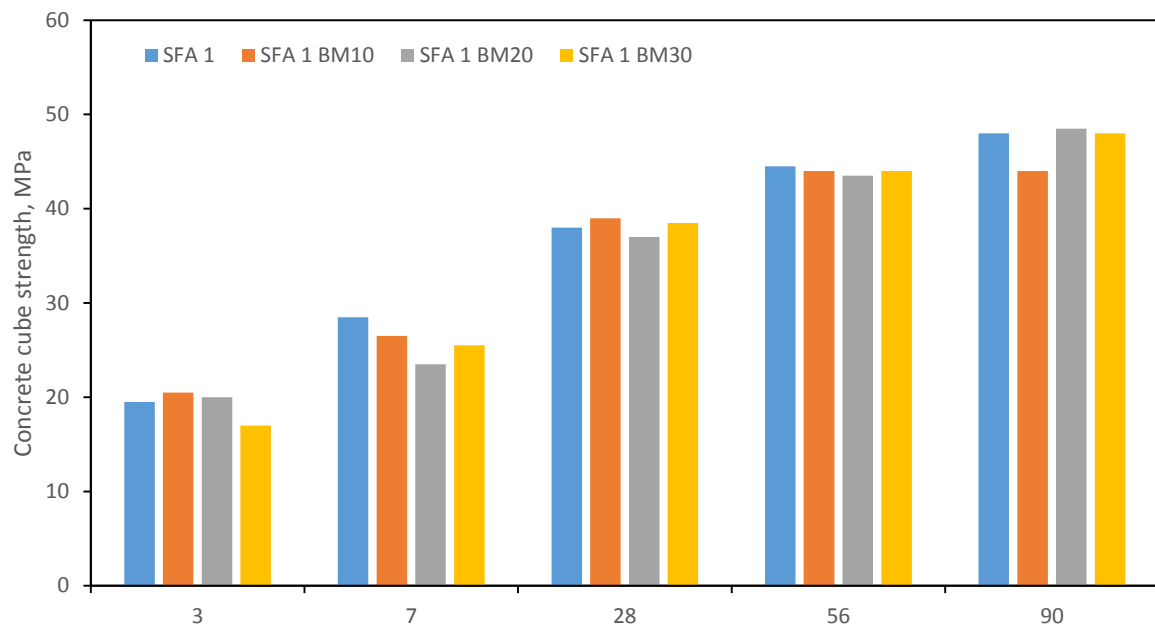
Figure 173 - Concrete strength of SFA 1 after ball milling in 125 g batches
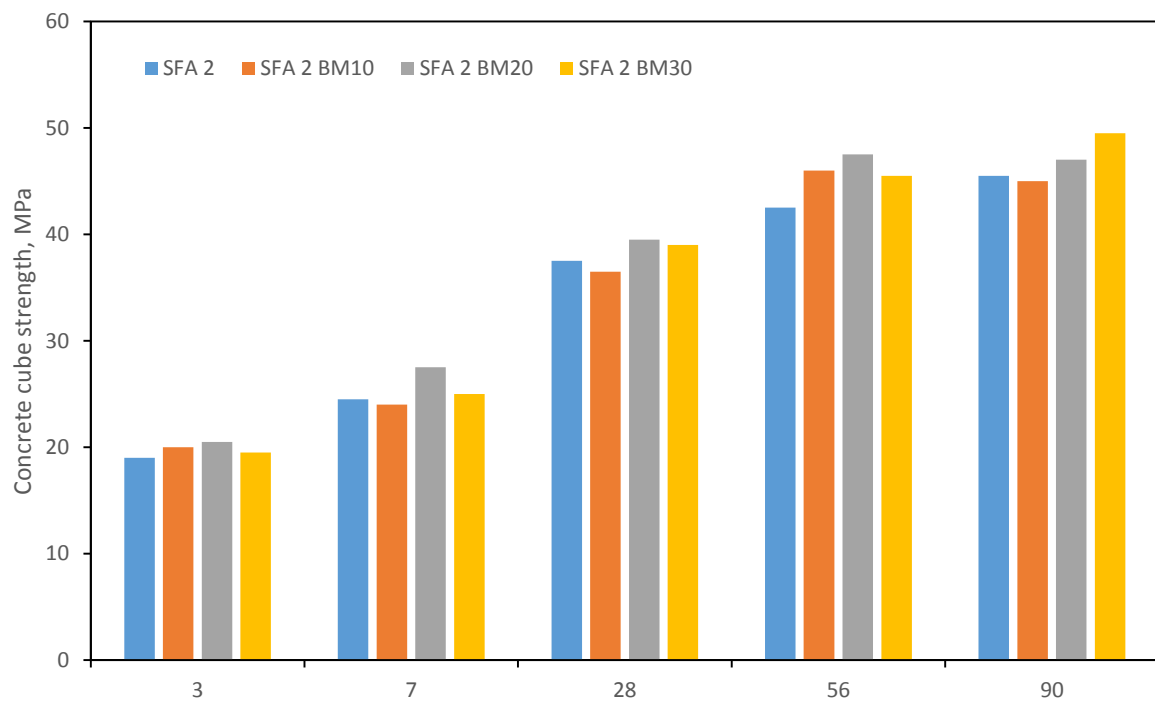
Figure 174 - Concrete strength of SFA 2 after ball milling in 125 g batches
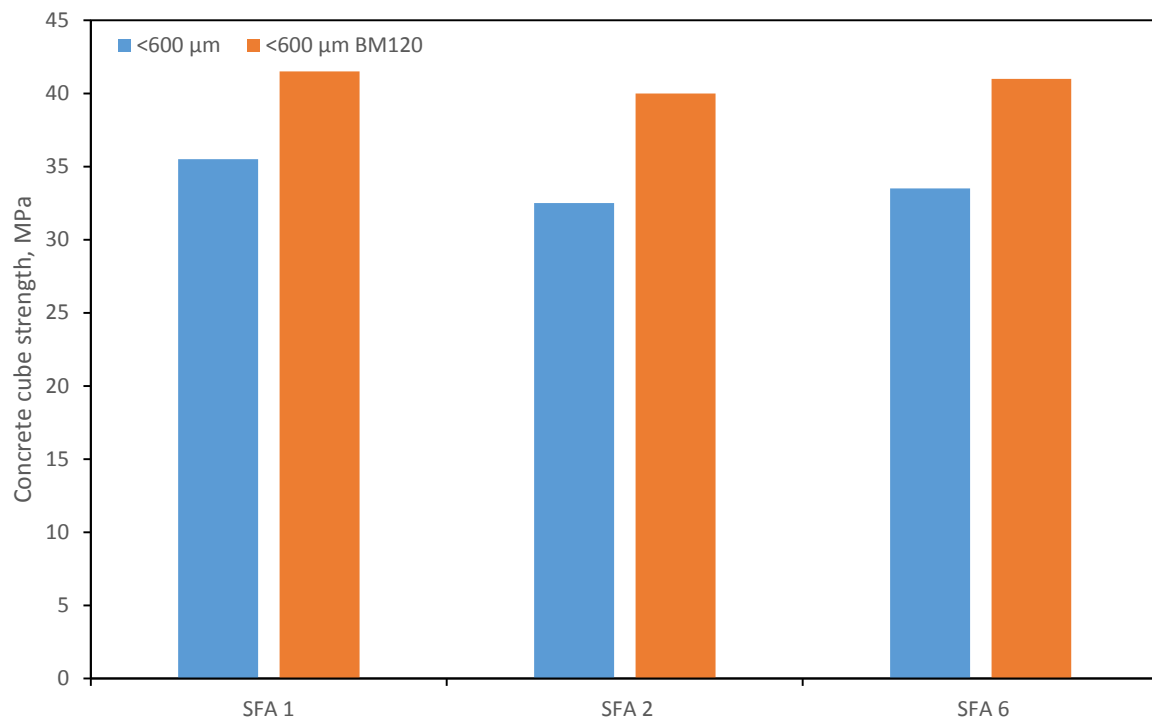
Figure 175 - Change in 28-day concrete strength of select on-site wet-stored materials after ball milling for 120 minutes in 50 g batches
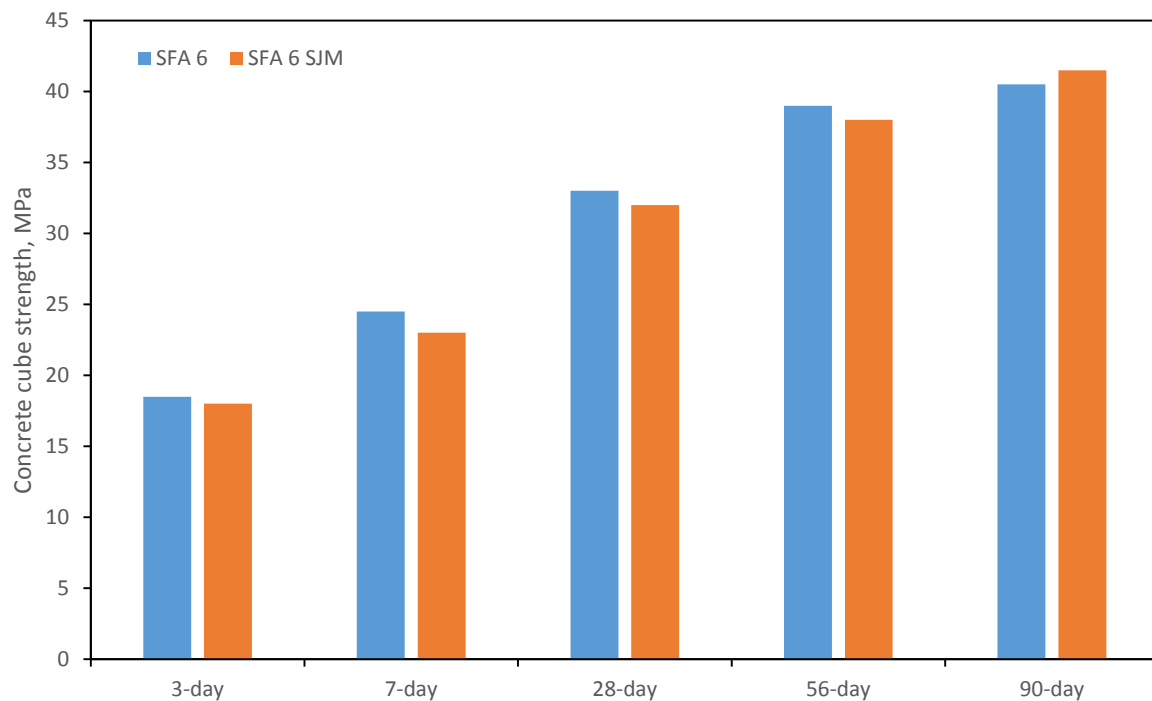
Figure 176 - Concrete cube strength of SFA 6 before and after a single pass through the microniser

18.4.4. Carbon removal
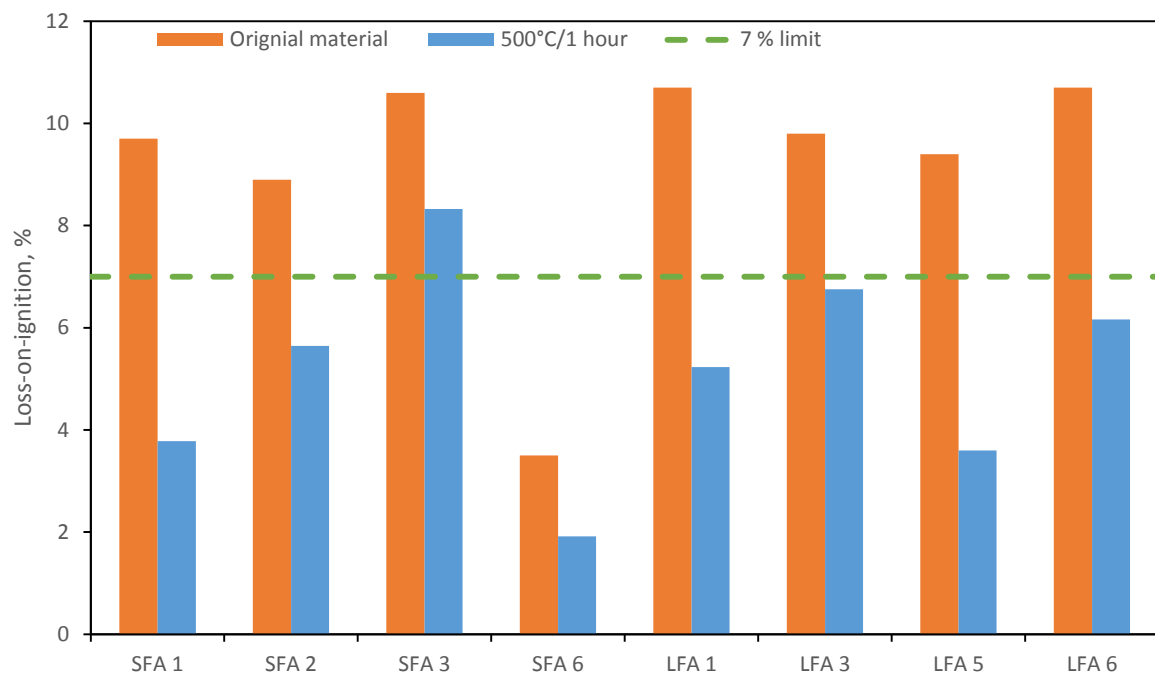
Figure 177 – Loss-on-ignition of wet-stored materials before and after carbon removal at 500°C for 1 hour
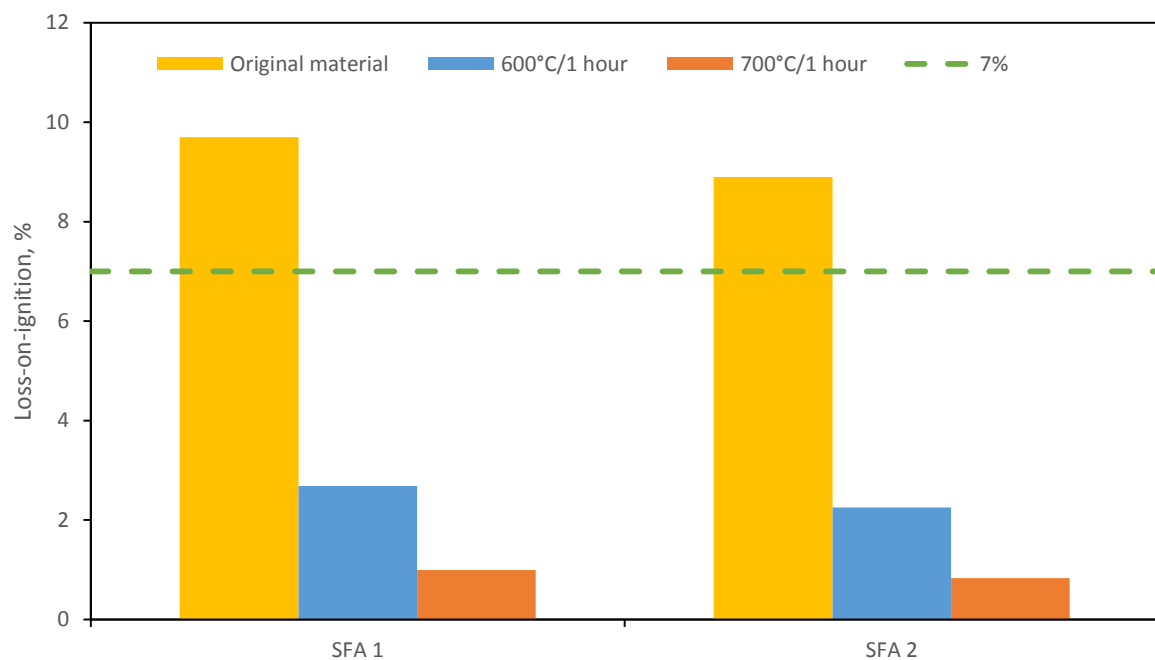
Figure 178 – Loss-on-ignition of wet-stored materials after carbon removal at 600 and 700°C for 1 hour
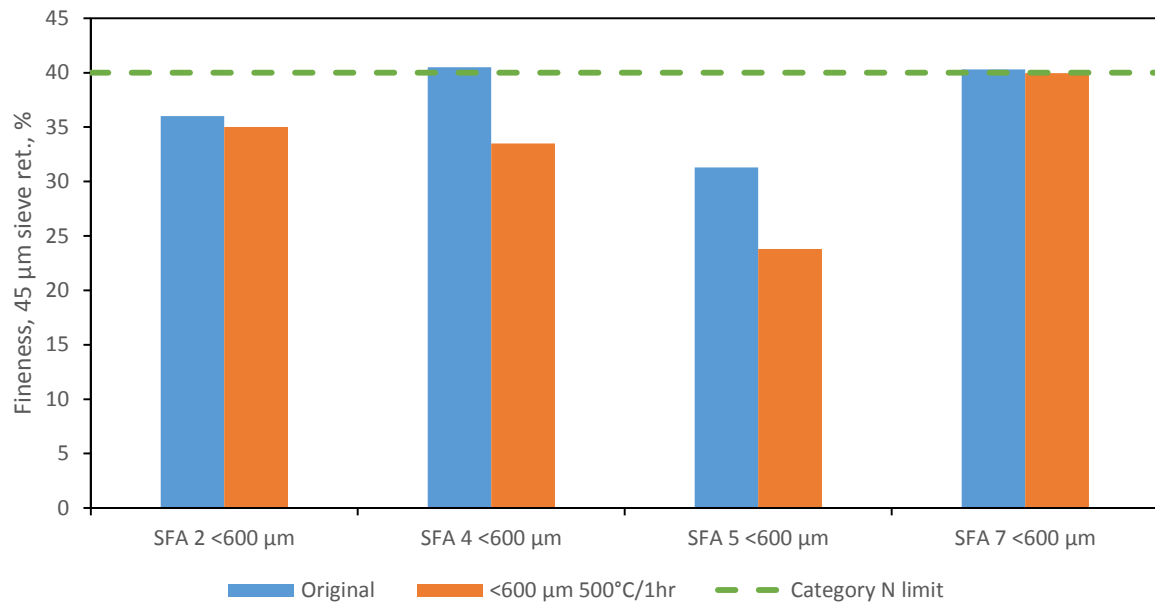
Figure 179 - Change in fineness in select wet-stored materials after screening at 600 μm and carbon removal at 500°C/1hr
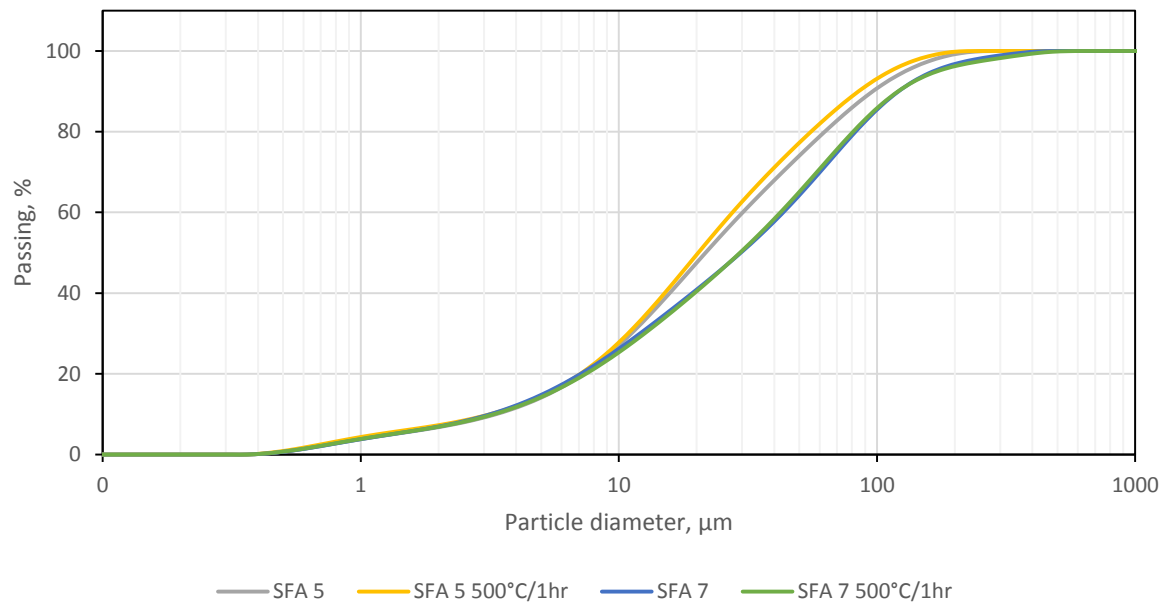
Figure 180 - Particle size distribution of on-site wet-stored materials before and after carbon removal at 500°C for 1 hour
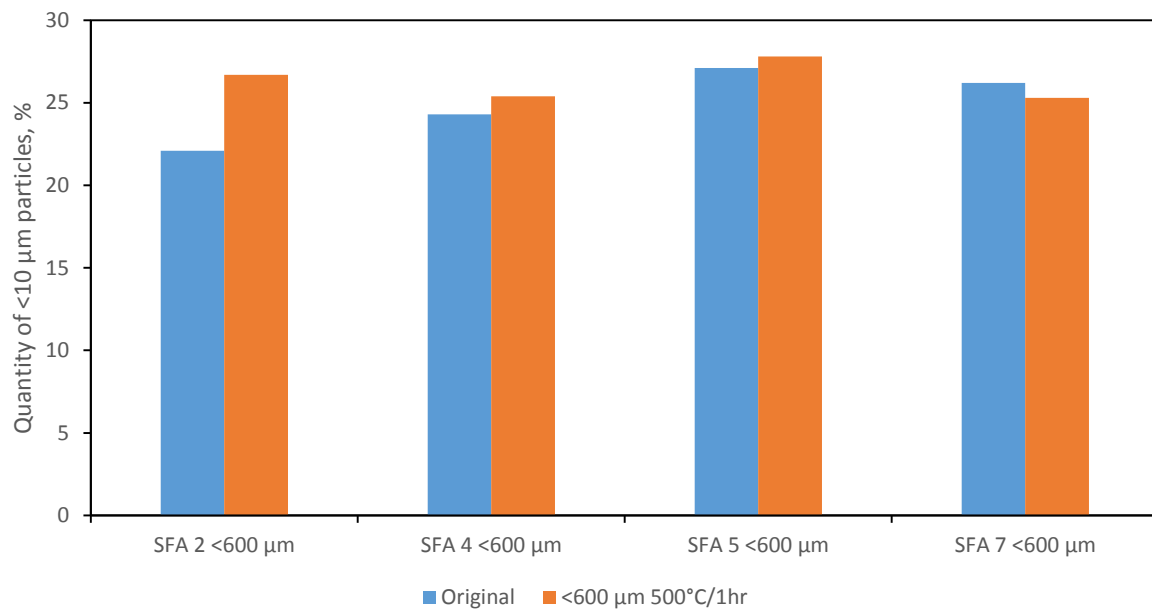
Figure 181 - Change in quantity of <10 μm particles in select wet-stored materials after screening at 600 μm and carbon removal at 500°C/1hr
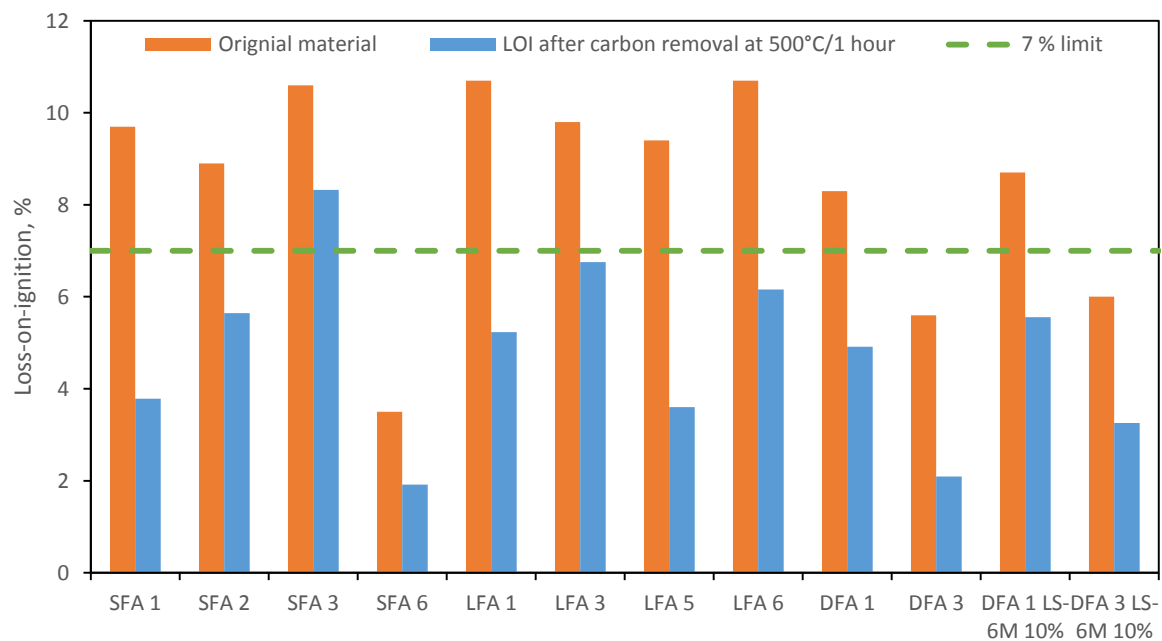
Figure 182 - Change in loss-on-ignition in various wet-stored materials after carbon removal at 500°C/1hr
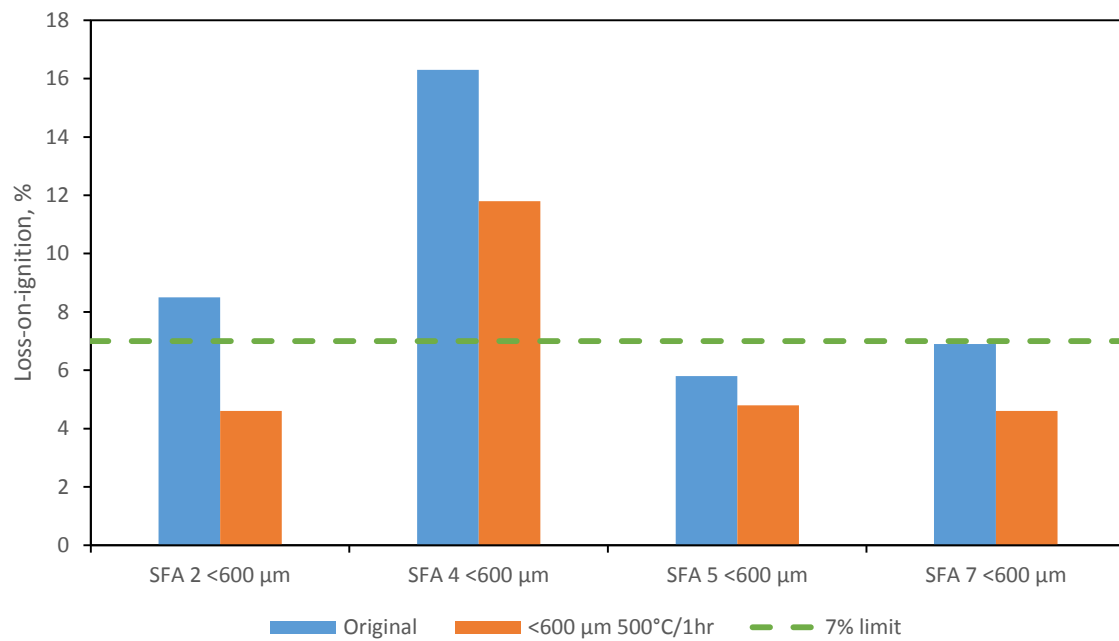
Figure 183 - Change in loss-on-ignition of select on-site wet-stored materials after screening at 600 µm and carbon removal at 500°C/1hr
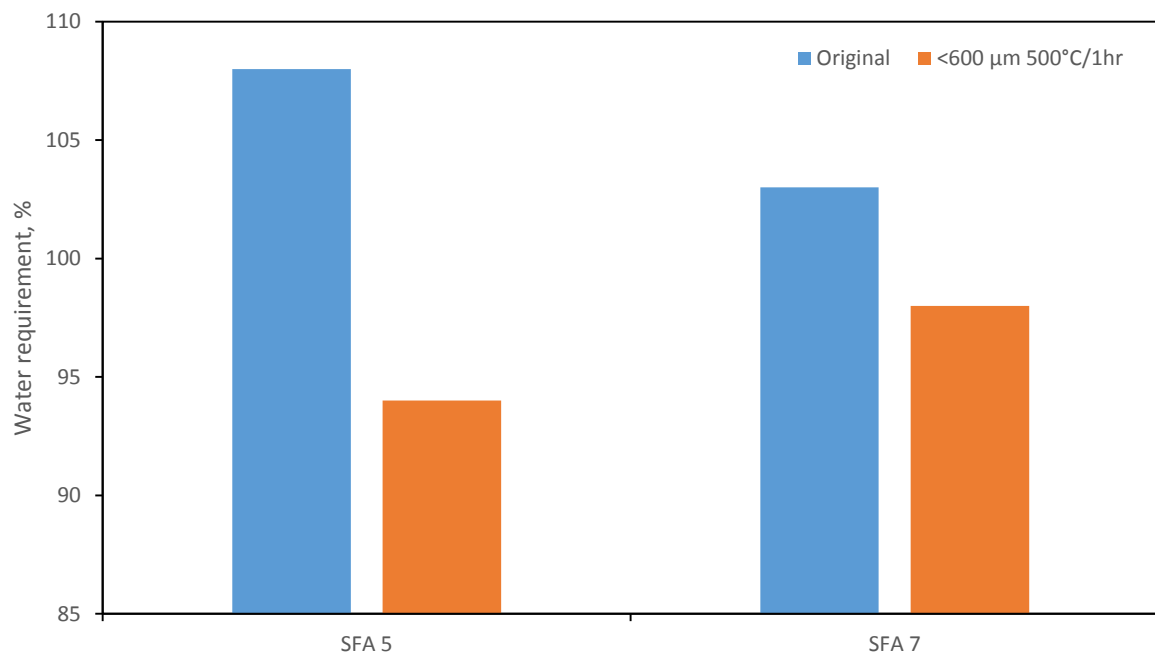
Figure 184 - Change in water requirement of SFA 5 and SFA 7 after screening at 600 µm and carbon removal at 500°C/1hr
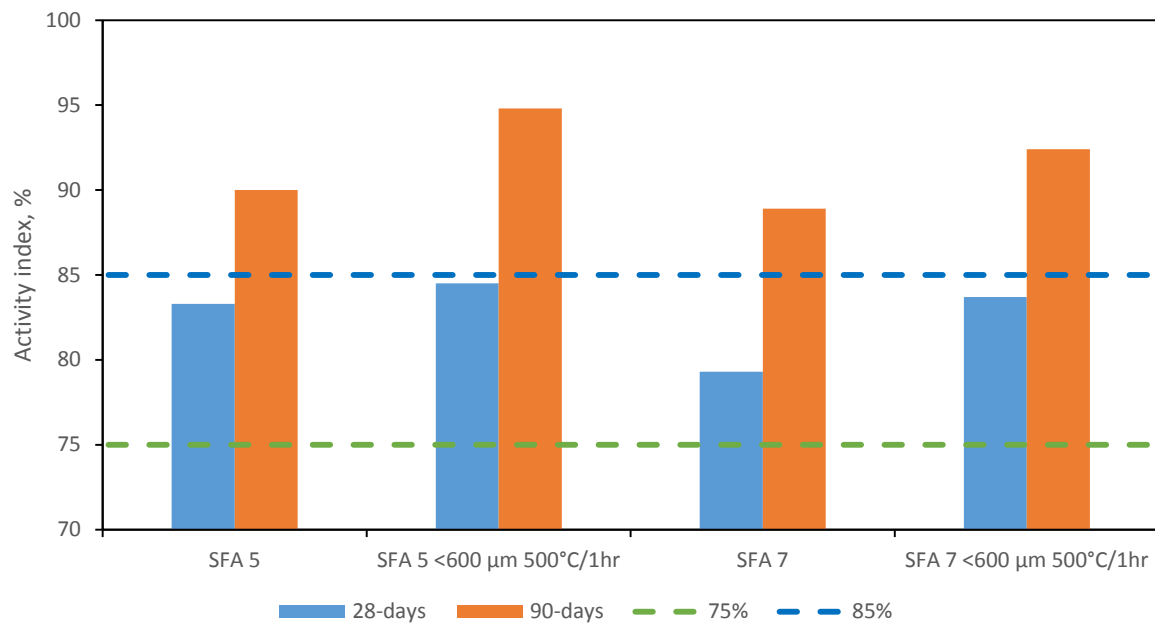
Figure 185 - Change in activity index of SFA 5 and SFA 7 after screening at 600 μm and carbon removal at 500°C/1hr
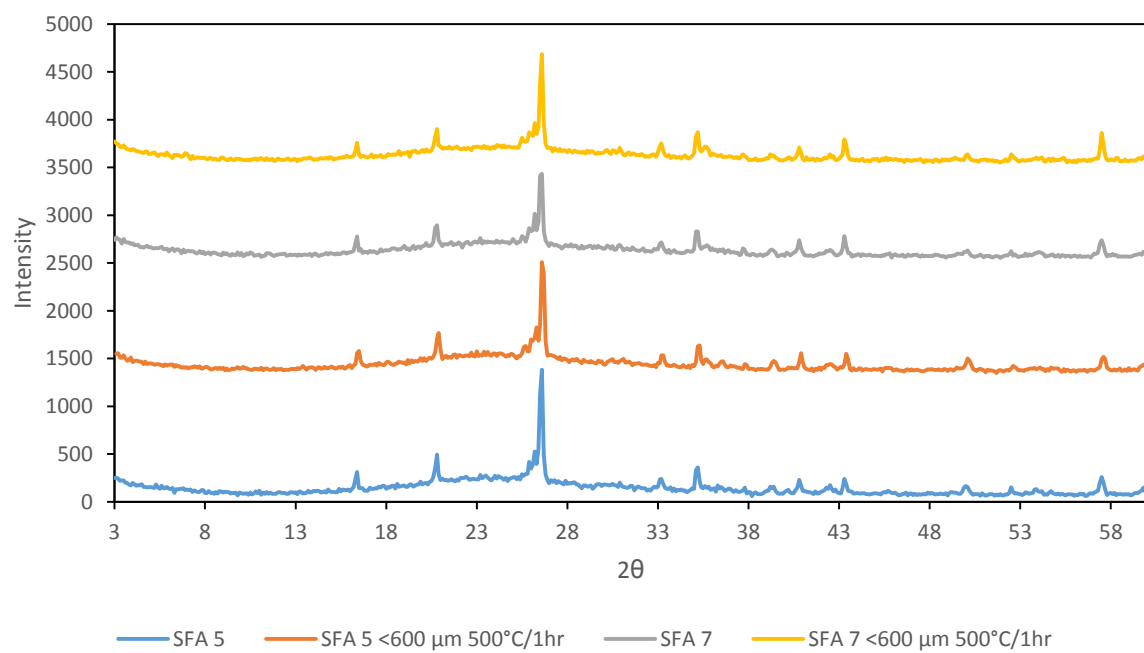
Figure 186 - X-ray diffractogram of on-site wet-stored materials before and after carbon removal at 500°C for 1 hour

213
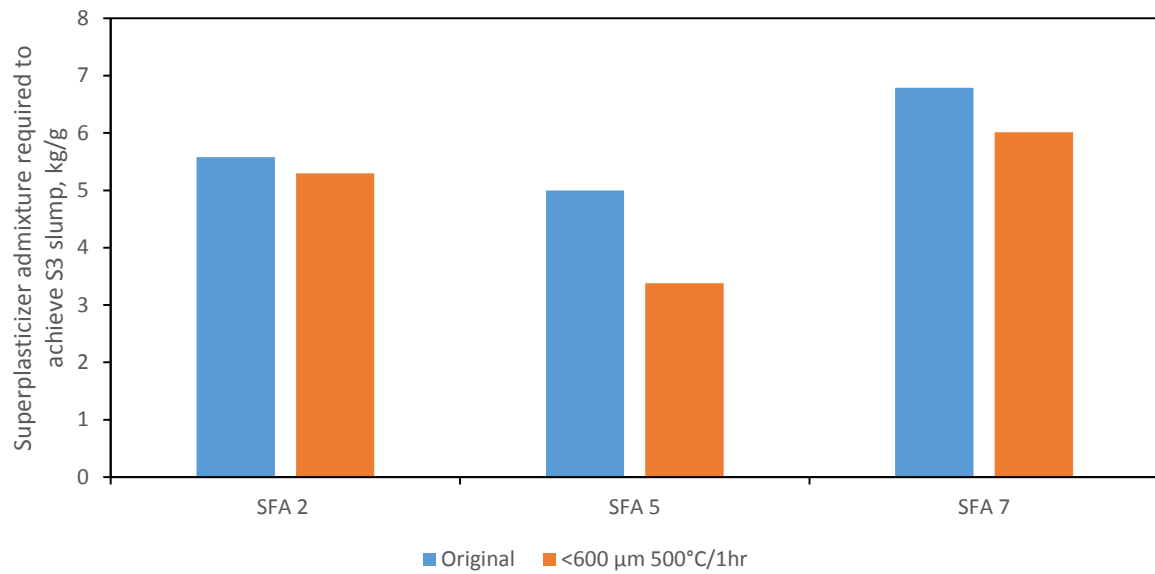
Figure 187 - Change in superplasticizer admixture dose required to achieve S3 slump in select on-site wet-stored materials before and after screening at 600 µm and carbon removal at 500°C/1hr
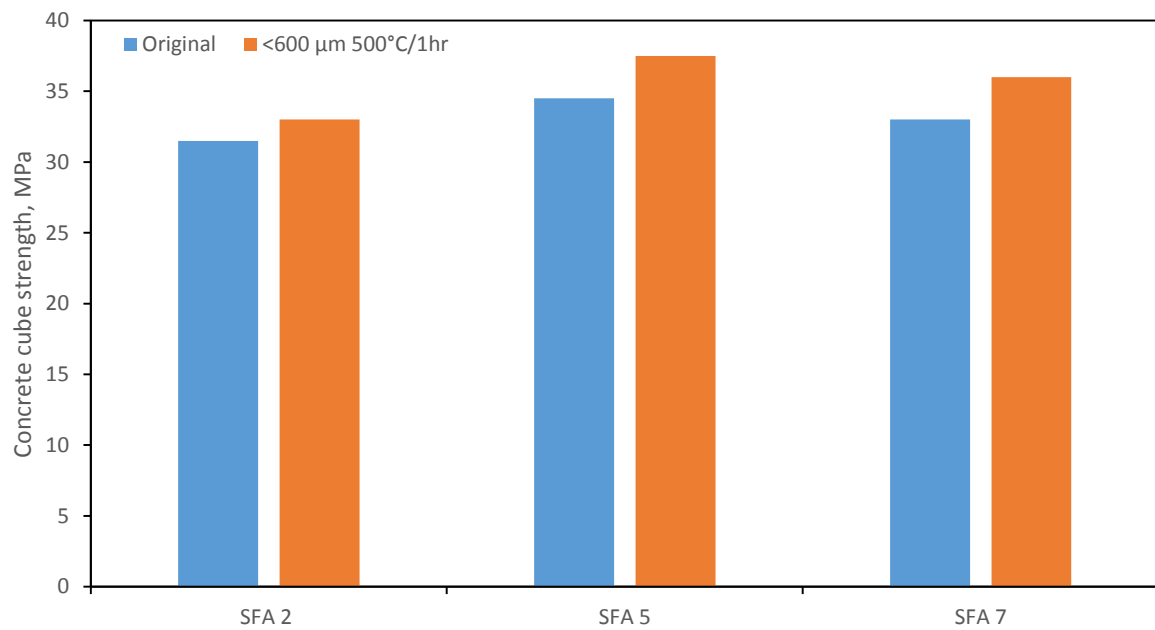
Figure 188 - Change in 28-day concrete strength of select on-site wet-stored materials after screening at 600 µm and carbon removal at 500°C/1hr

18.5. Pilot-scale processing
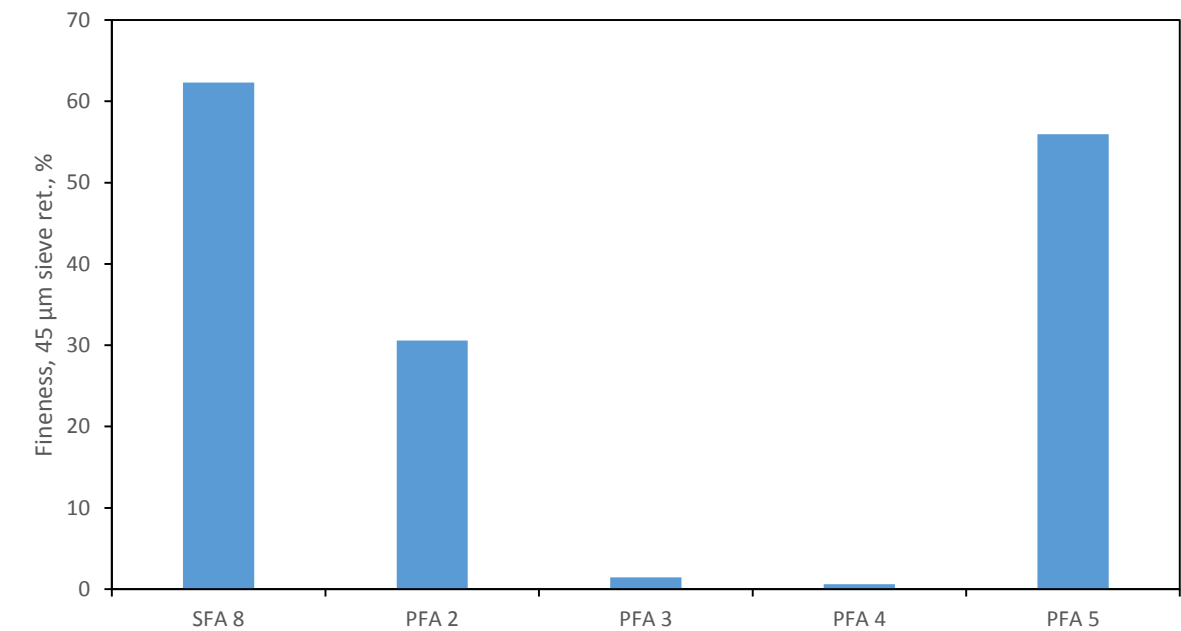
Figure 189 - Comparison of fineness values of pilot-scale processing materials
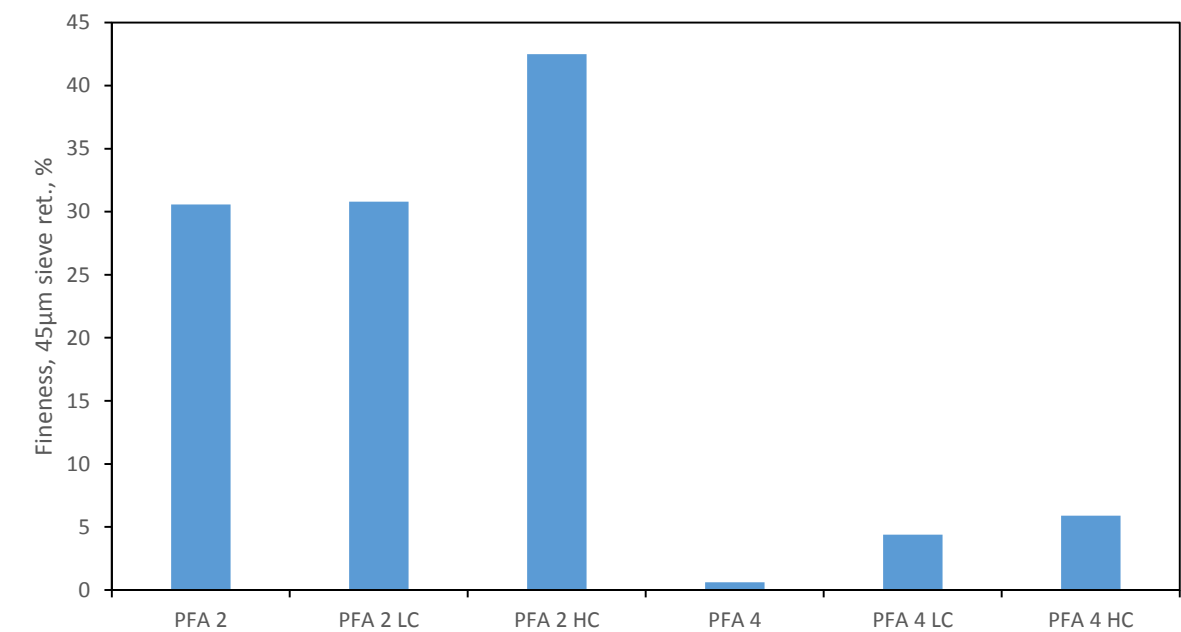
Figure 190 - Comparison of fineness values of pilot-scale processing materials after carbon removal at STET
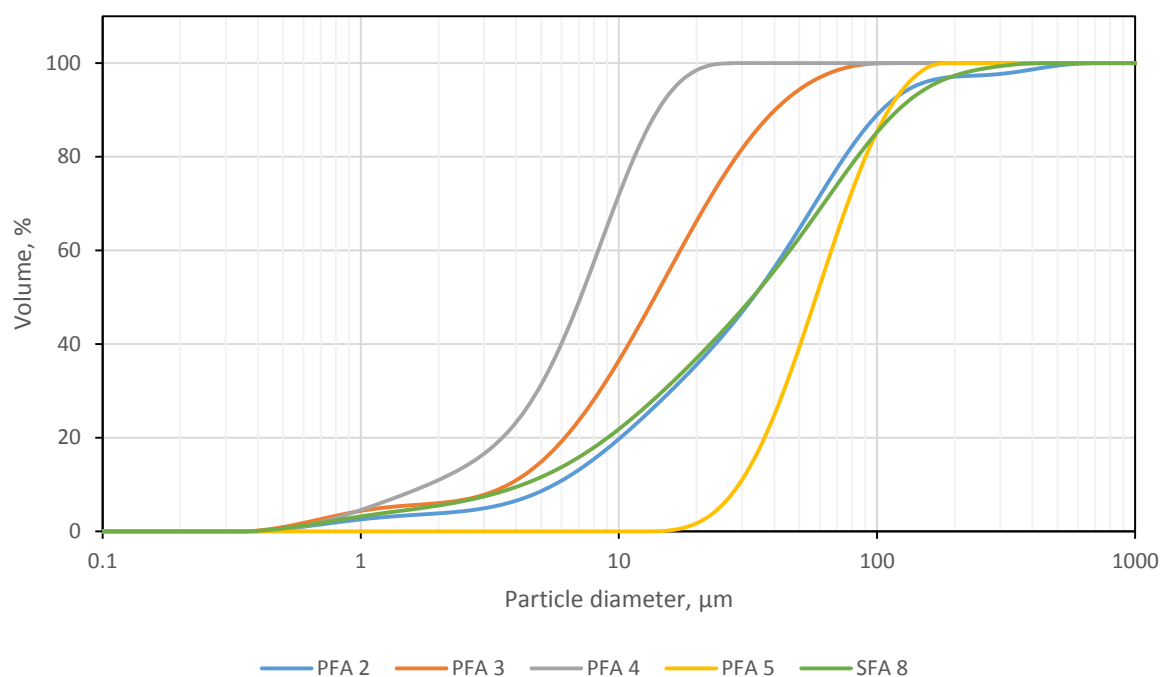
Figure 191 - Particle size distribution of pilot-scale processing materials
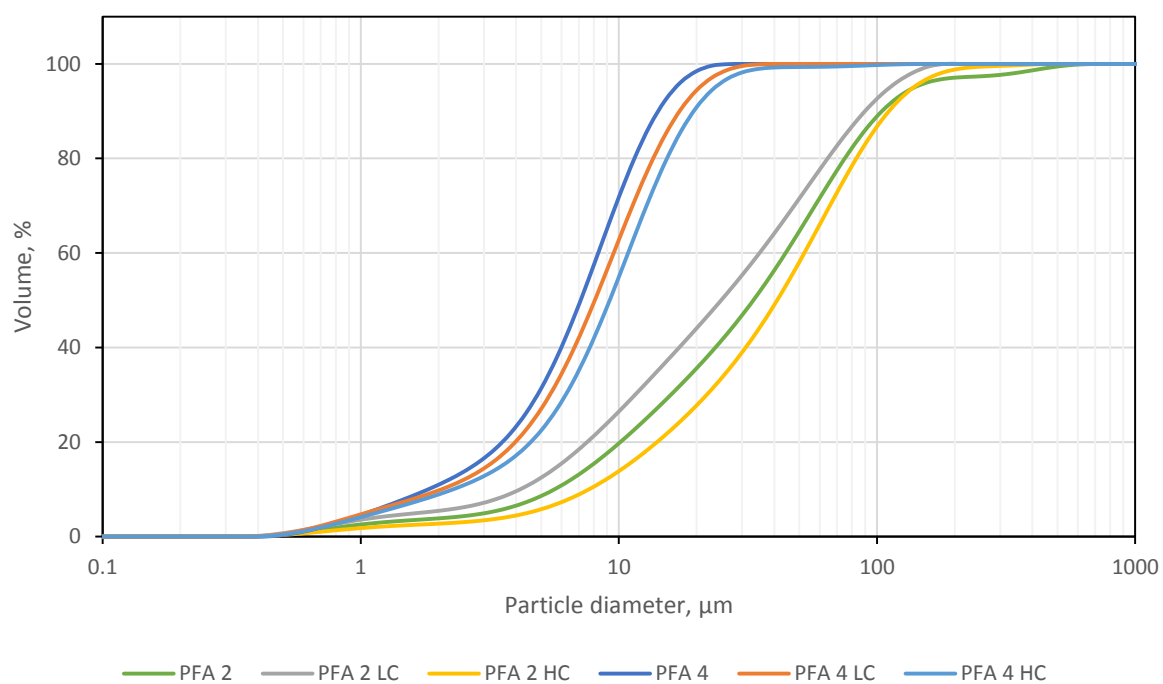
Figure 192 - Particle size distribution of pilot-scale processing materials after electrostatic carbon removal
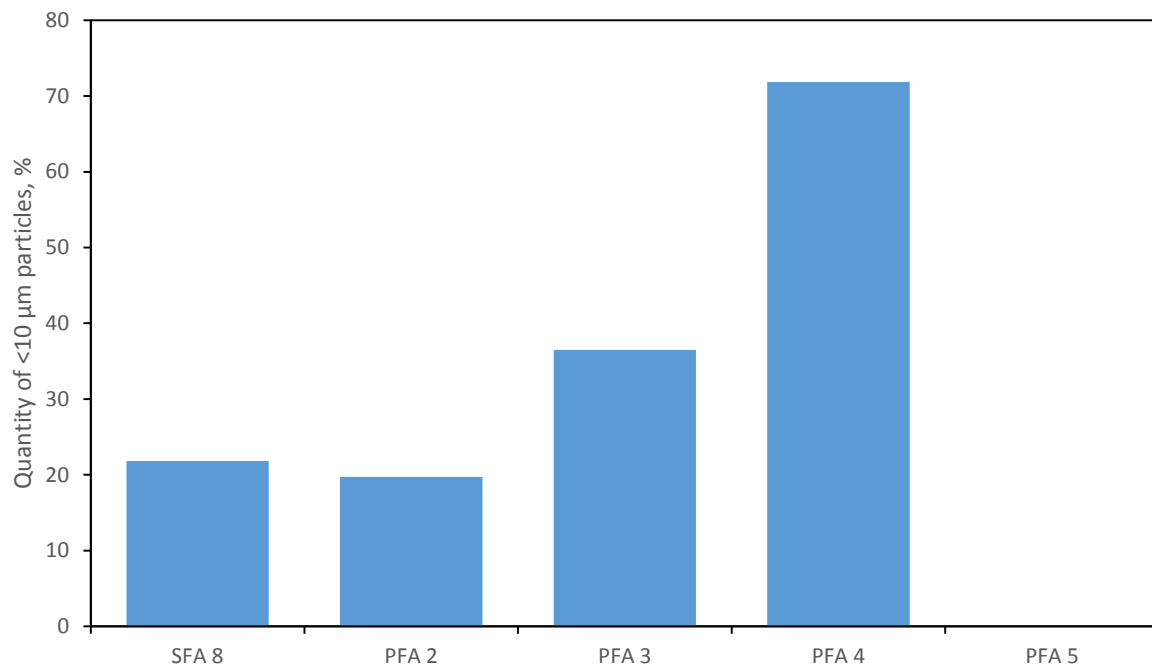
Figure 193 - Comparison of quantity of <10 μm particles of pilot-scale processing materials
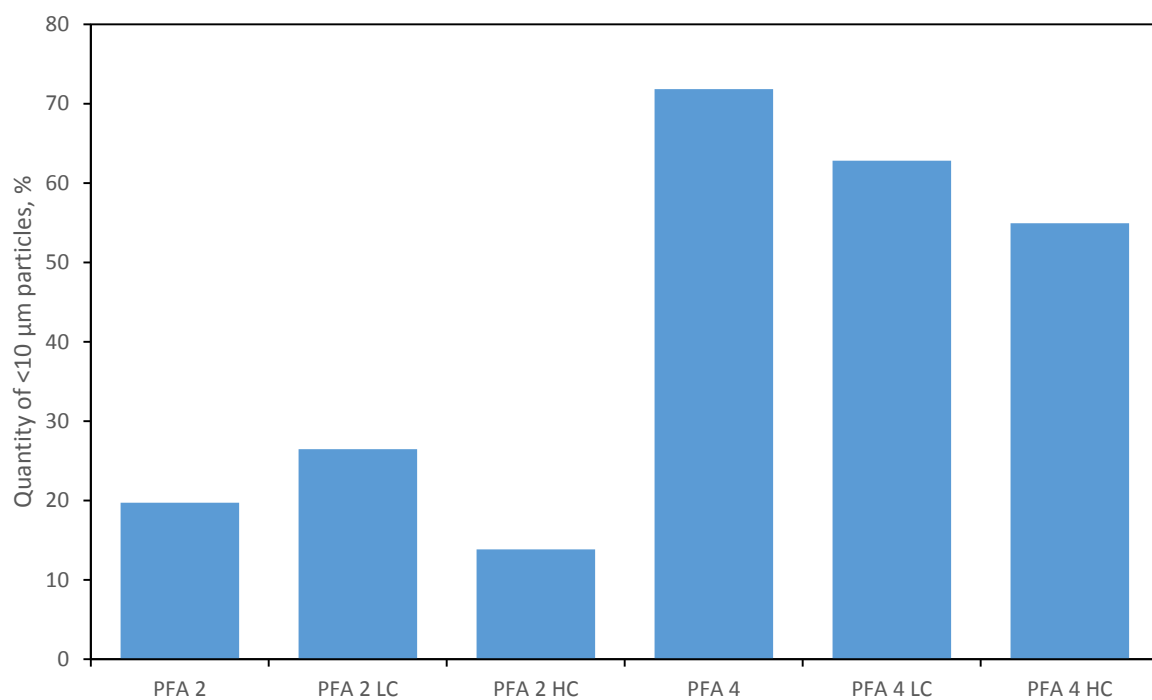
Figure 194 - Comparison of quantity of<10 μm particles of pilot-scale processing materials after carbon removal at STET
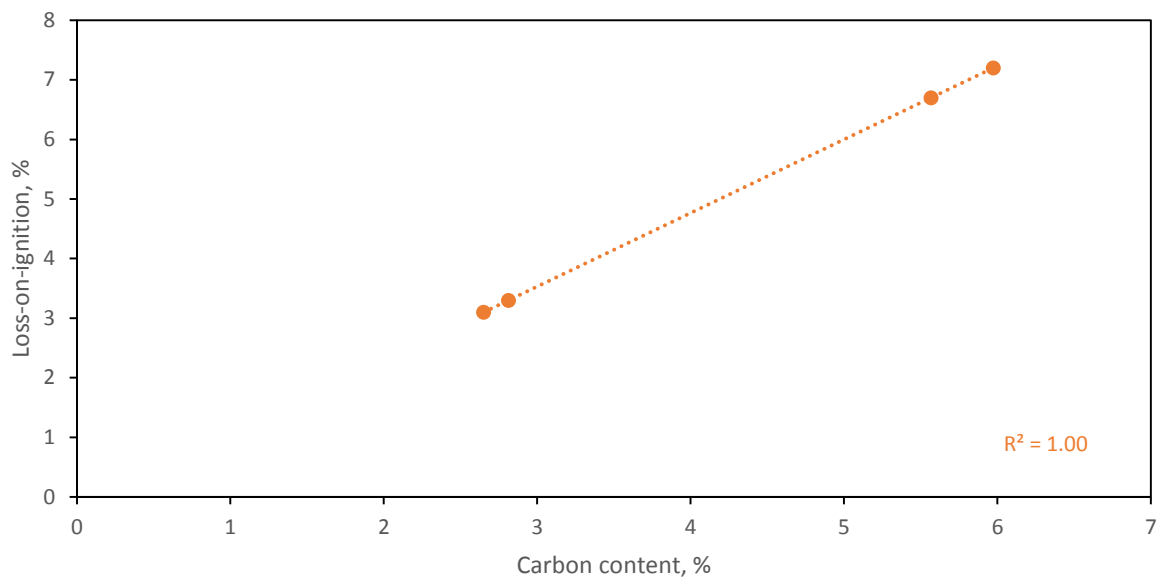
Figure 195 - Relationship between carbon content and loss-on-ignition for pilot-scale trial materials
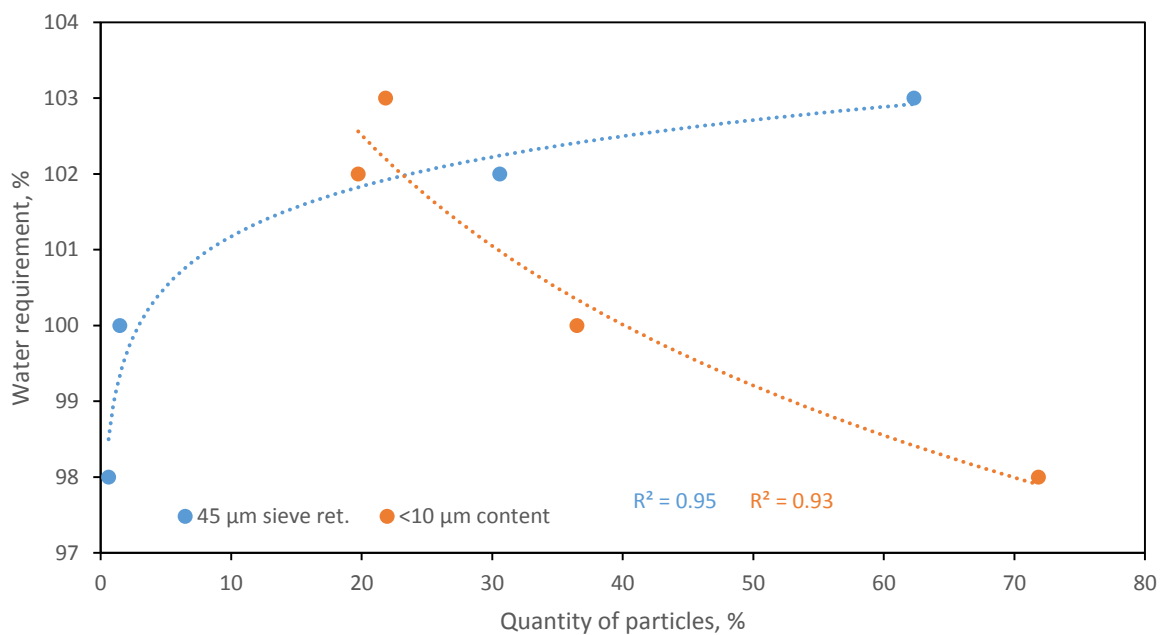
Figure 196 - Relationship between water requirement and fineness and <10 µm content for pilot-scale trial materials
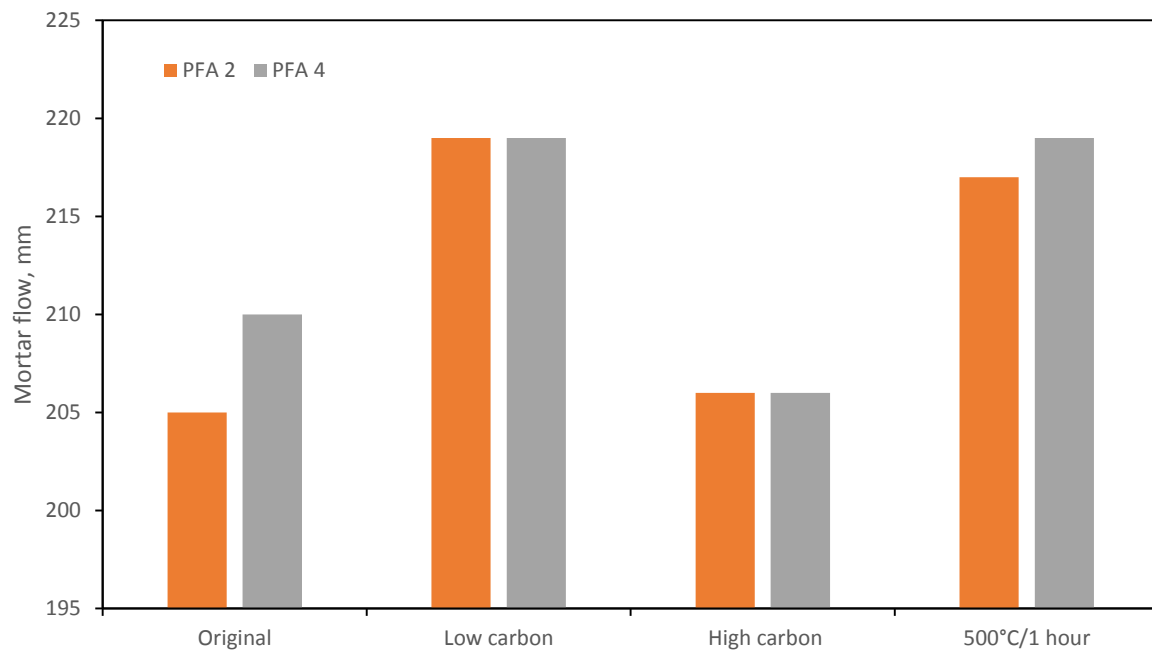
Figure 197 - Mortar flow of pilot-scale processing materials before and after carbon removal
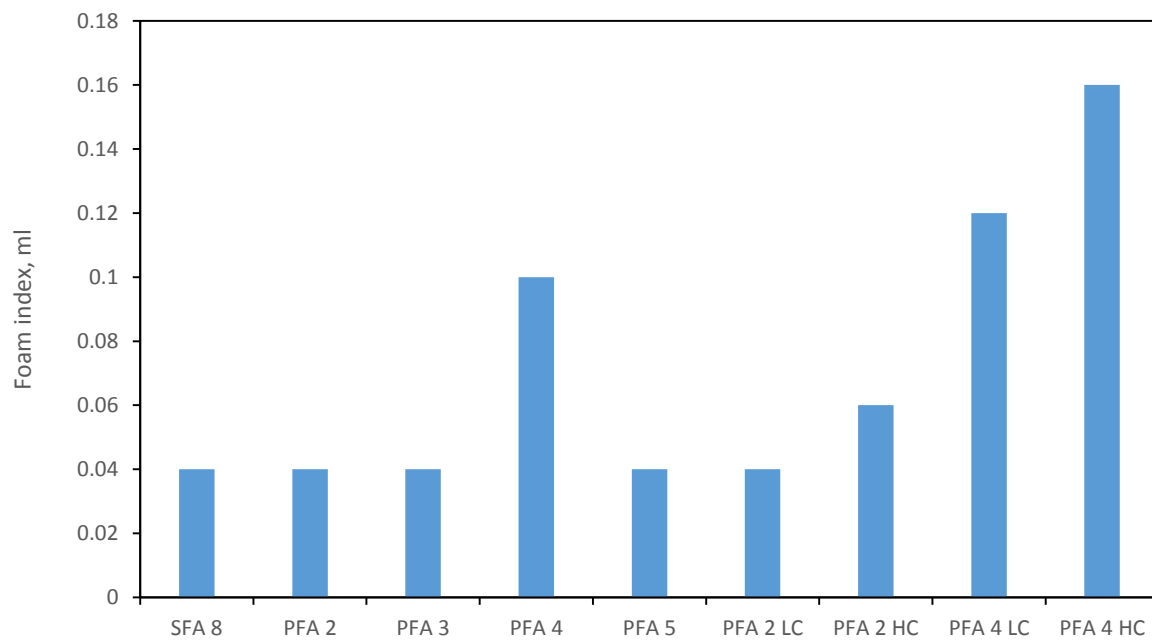
Figure 198 - Foam index of pilot-scale trial materials
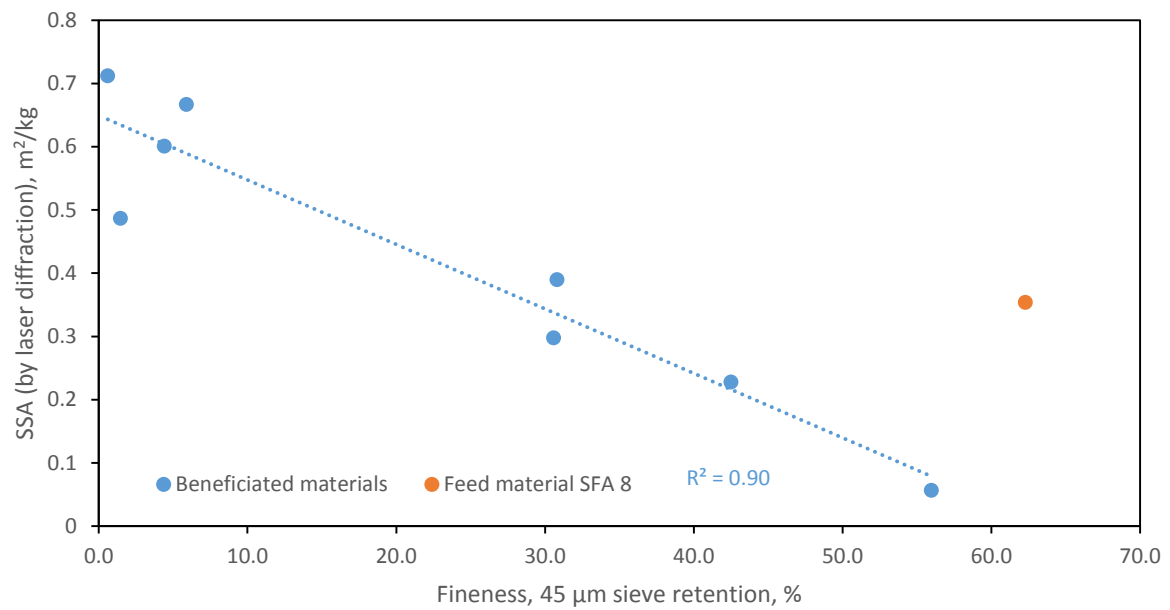
Figure 199 - Relationship between specific surface area (by laser diffraction) and fineness for the pilot-scale trial materials
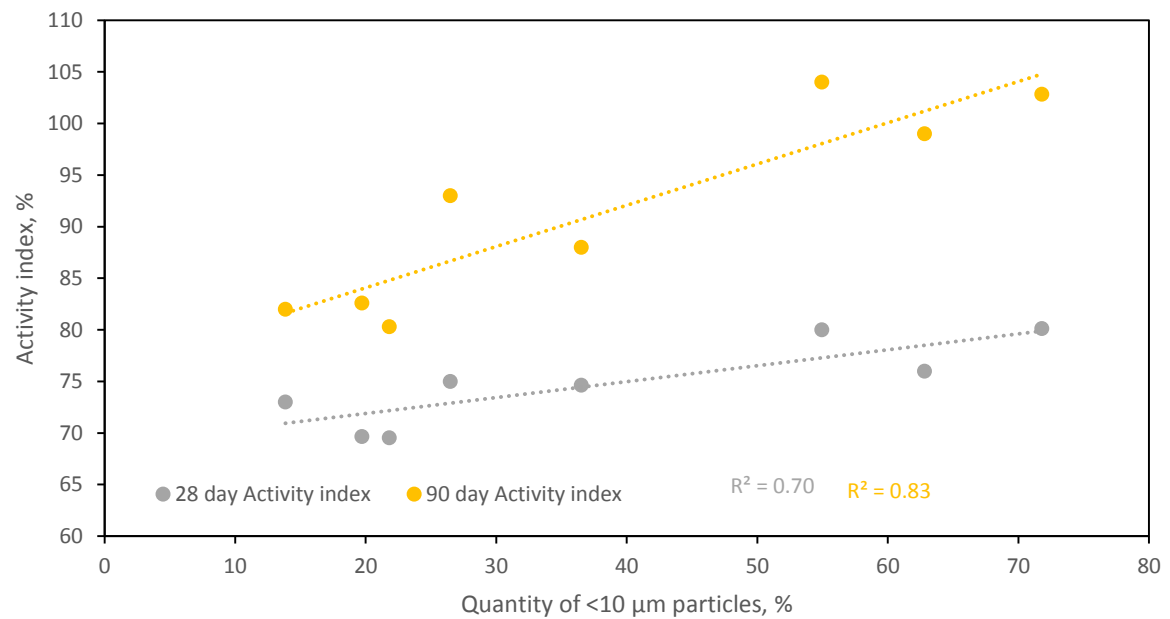
Figure 200 - Relationship between activity index, at 28 and 90-days, and quantity of <10 μm particles for pilot-scale trial materials
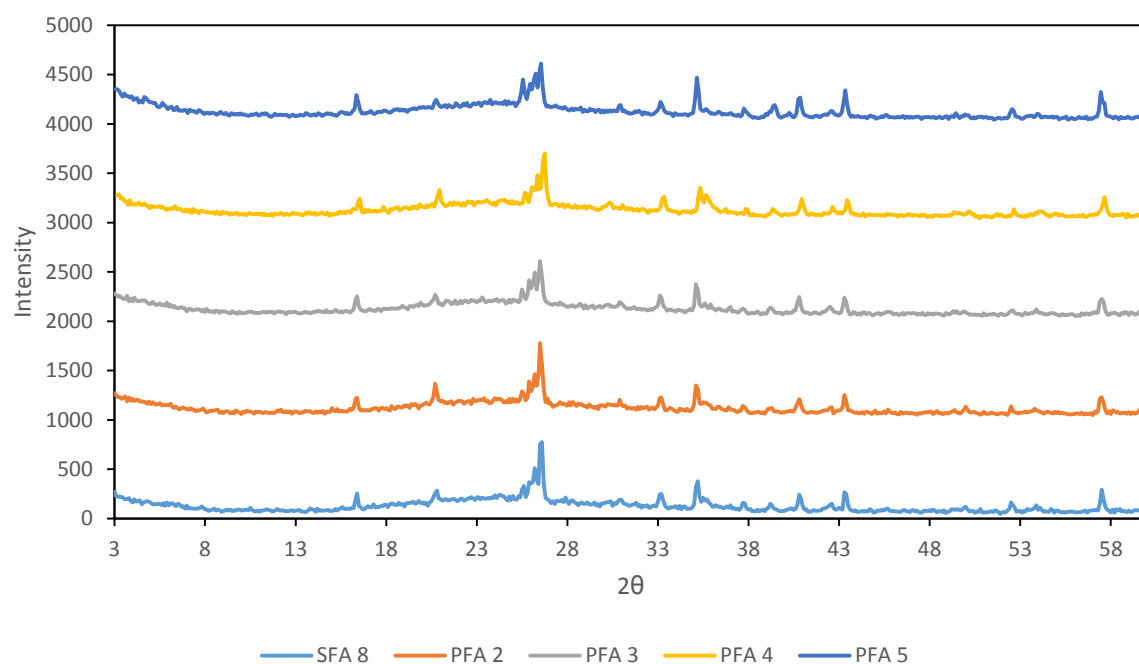
Figure 201 - X-ray diffractogram of pilot-scale processing materials
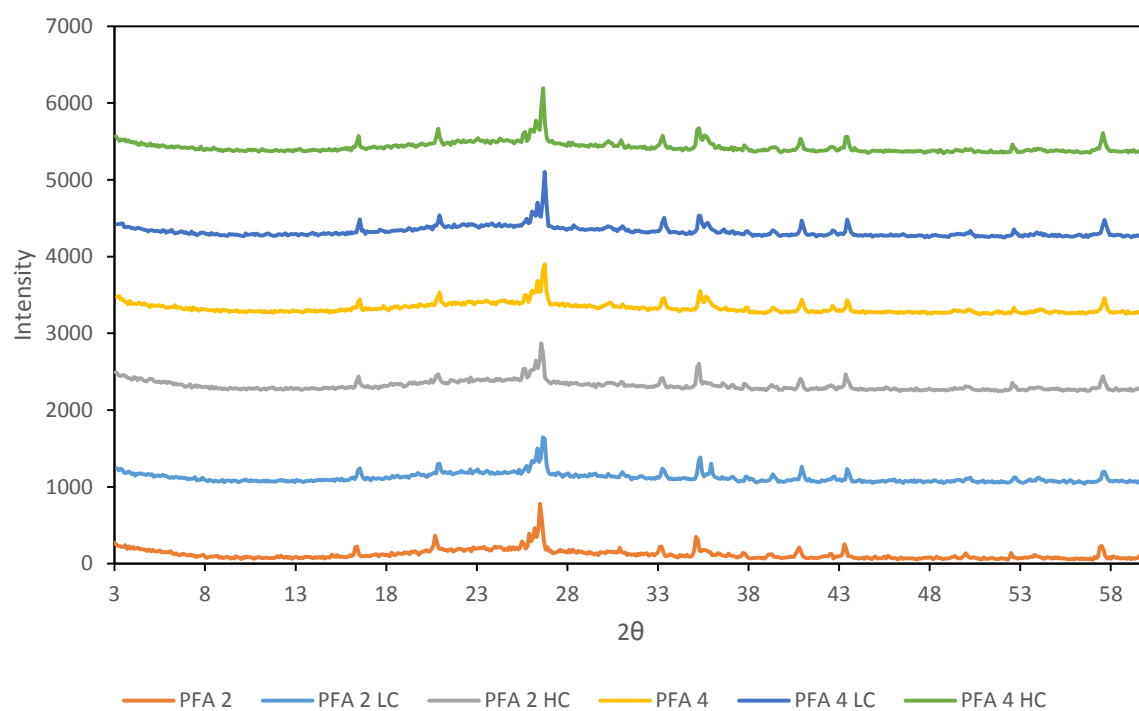
Figure 202 - X-ray diffractogram of pilot-scale processed materials after carbon removal
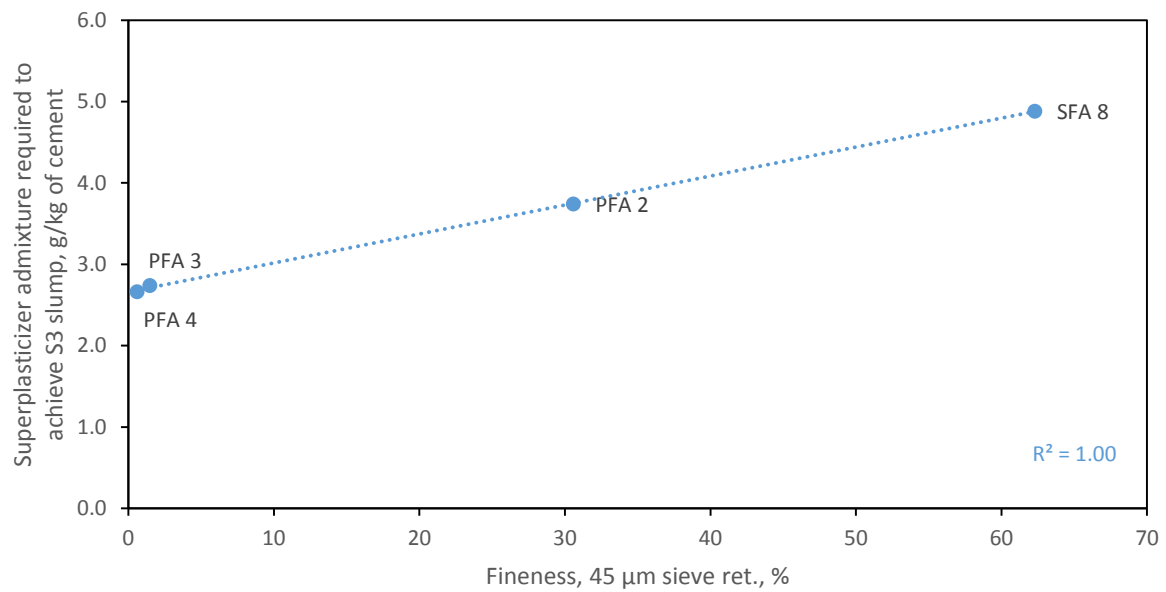
Figure 203 - Relationship between superplasticizer admixture requirement to achieve S3 slump and fineness of pilot-scale trial materials
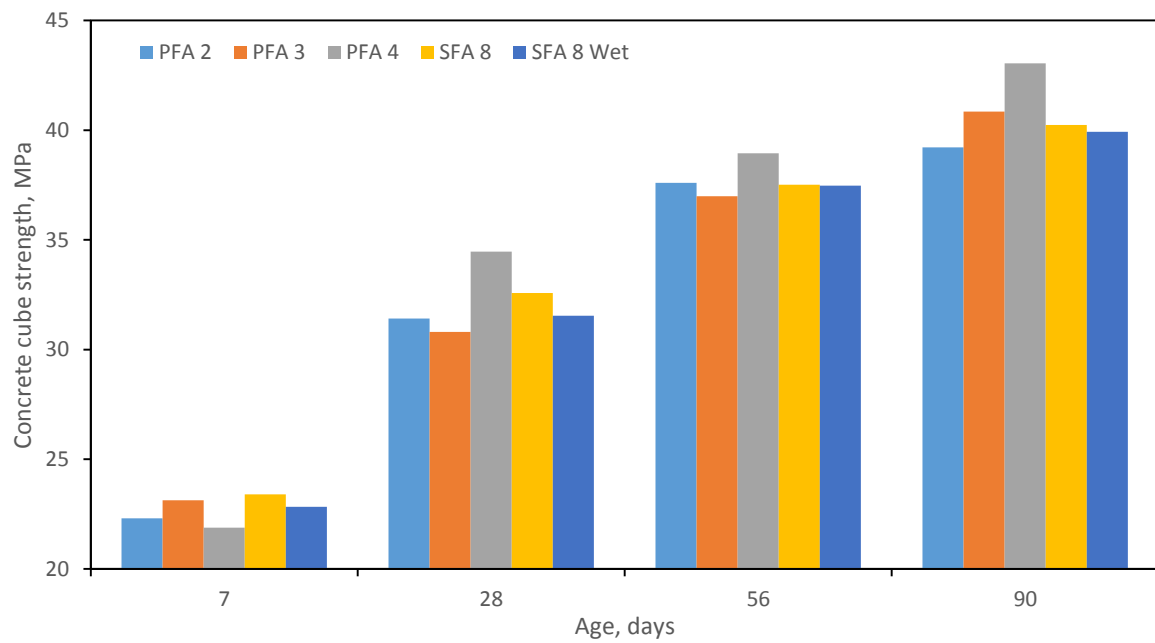
Figure 204 - Concrete strengths of pilot-scale trial materials
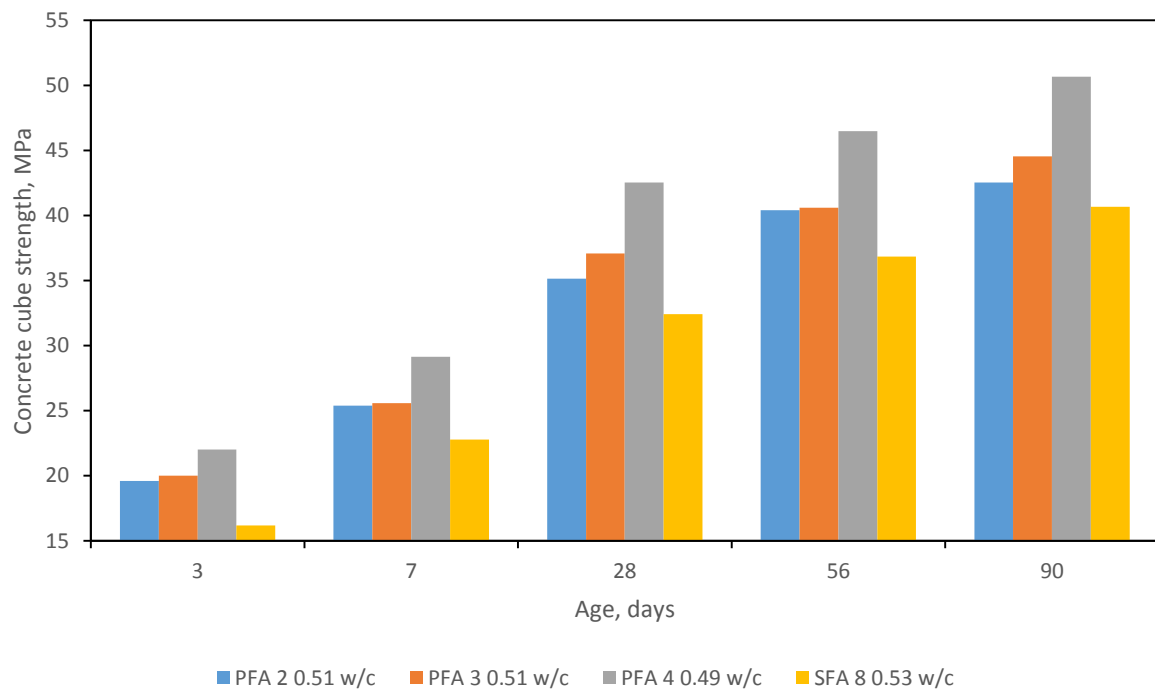
Figure 205 - Concrete strengths of the pilot-scale trials with adjusted water/cement ratios for equal admixture dose

18.6. Durability
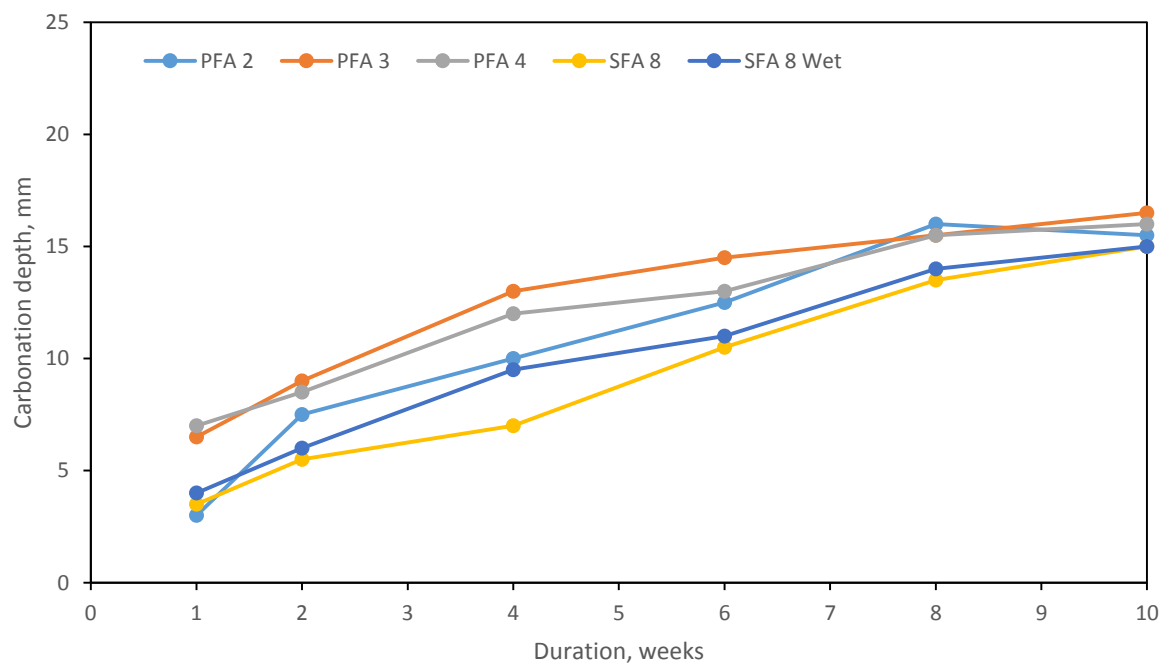
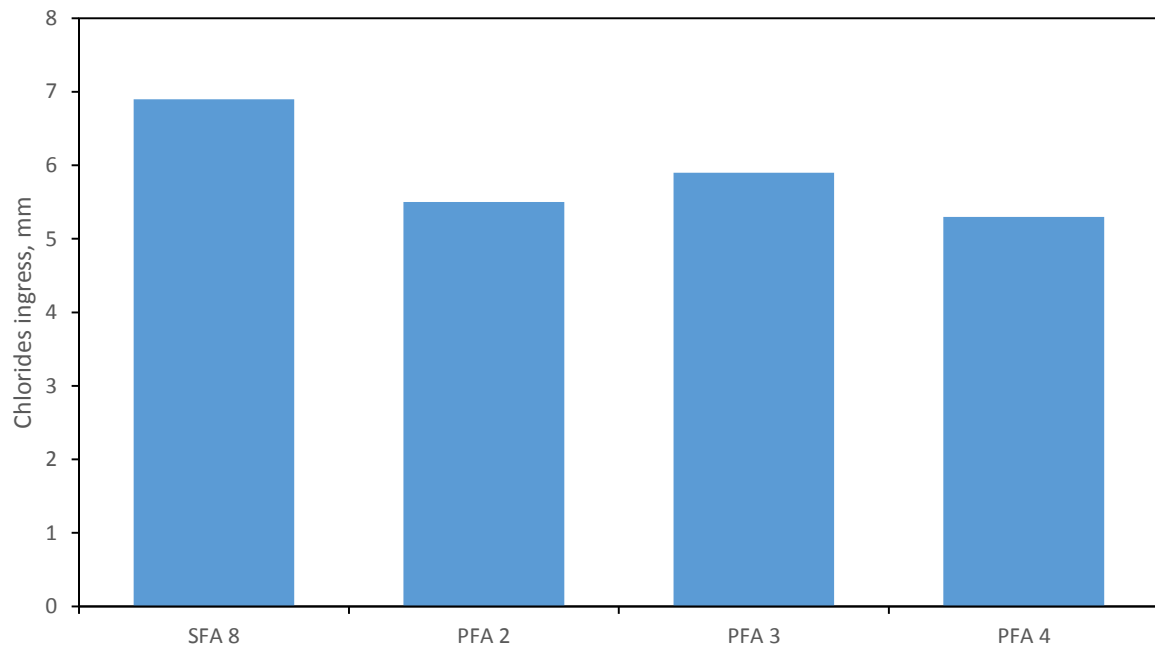*Figure 206 – Accelerated carbonation ingress of pilot-scale trial materials over 10 weeks*

Figure 207 - Accelerated chloride ingress of pilot-scale trial materials after 90 days
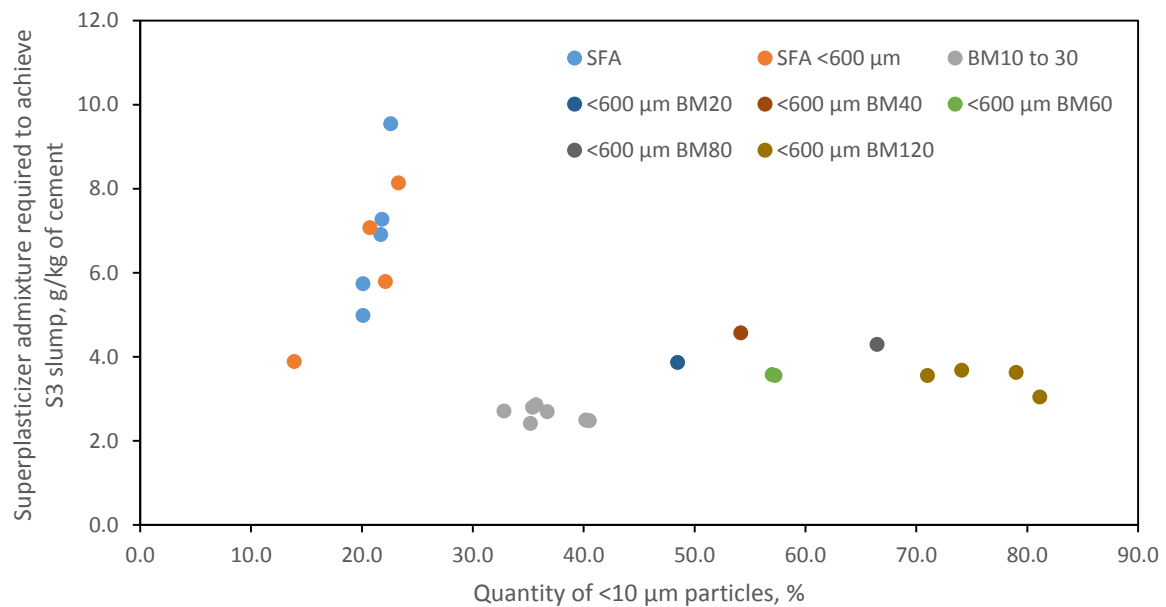
18.7. Collective analysis of materials

Figure 208 – Superplasticizer admixture required to achieve S3 slump for various on-site wet-stored and ball milled materials against quantity of <10 μm particles
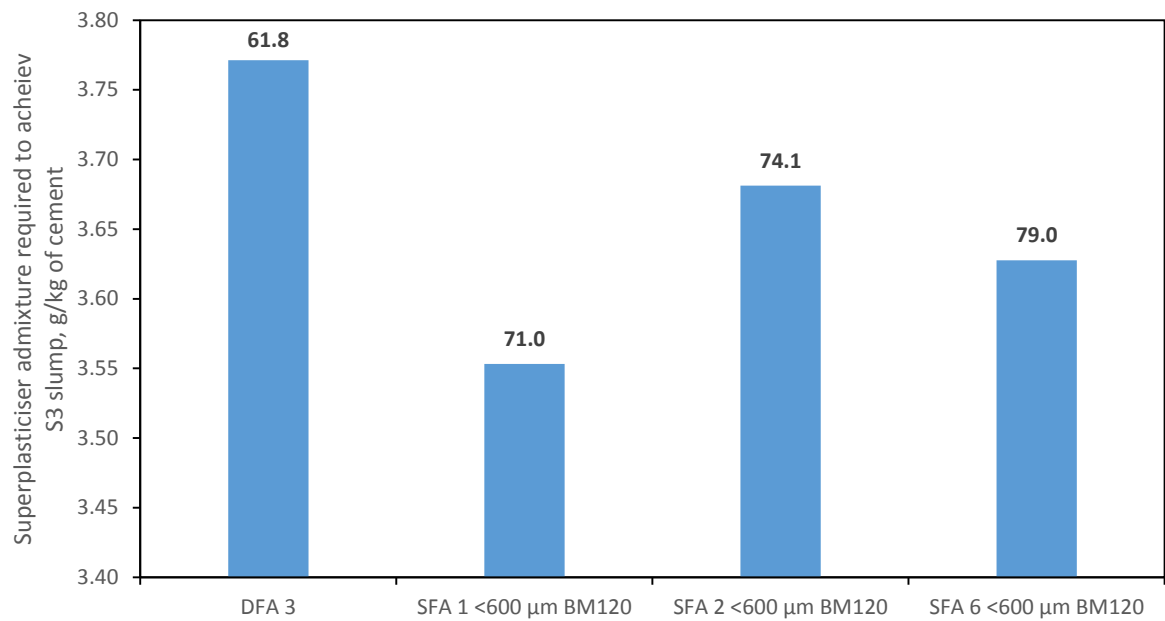
Figure 209 - Comparison between superplasticizer admixture requirement to achieve an S3 slump between DFA 3 and wet-stored materials ball milled for 120 minutes
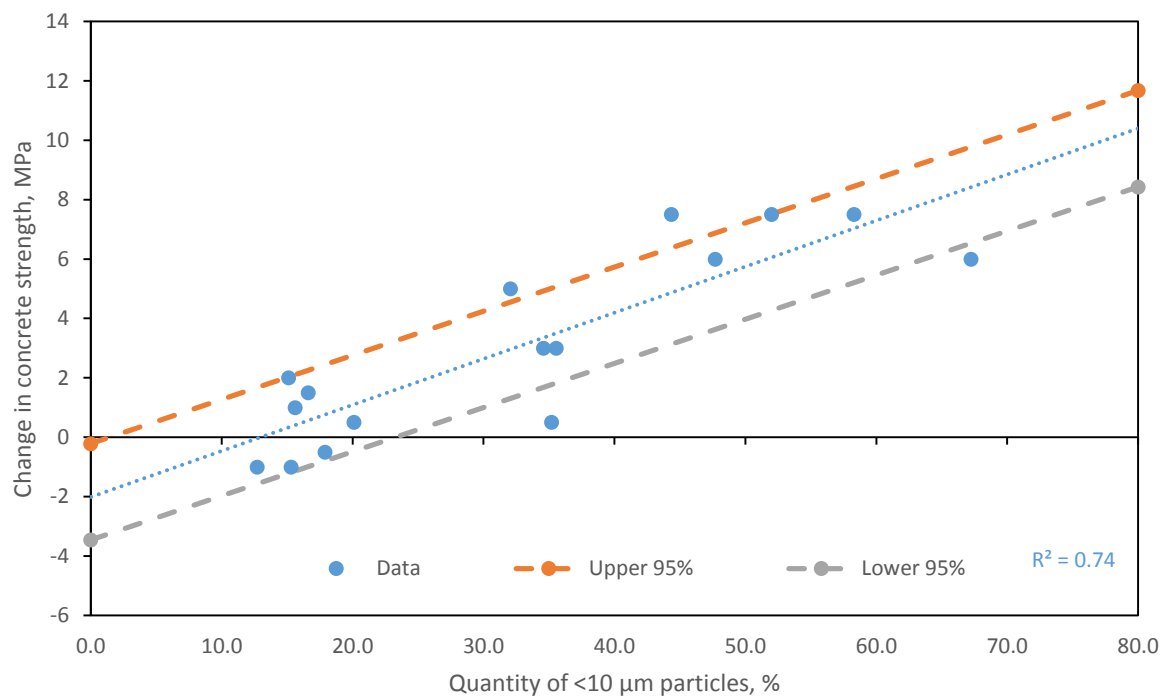

Figure 210 – Relationship between quantity of <10 µm particles and change in concrete strength at 28 days before and after particle size reduction
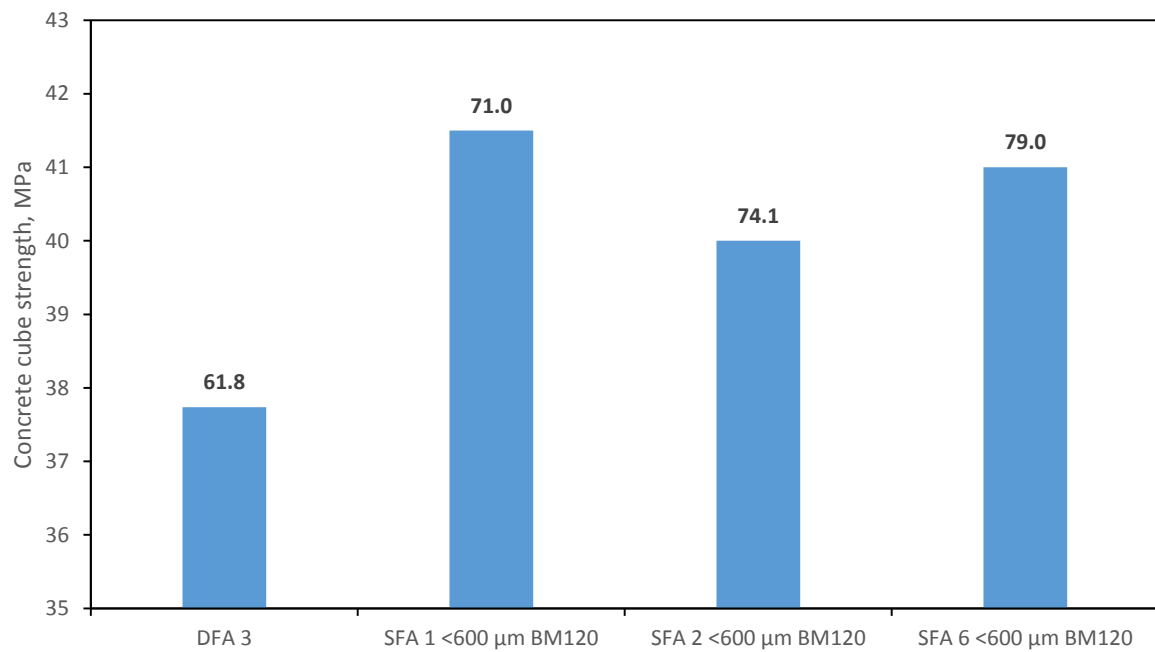
Figure 211 - Comparison between 28-day concrete strength of DFA 3 and wet-stored materials ball milled for 120 minutes, with the quantity of <10 μm particles of each material also given

18.8. Photos

Figure 212 - SFA 8, the feed wet-stored material for the pilot-scale trial

Figure 213 - Internal view of dryer-pulveriser used to dry and de-agglomerate feed material during the pilot-scale trial

Figure 214 - Air-classifier used to produce PFA 3 from PFA 2 during the pilot-scale trial

Figure 215 - Internal view of the microniser used to produce PFA 4 from PFA 2 during the pilot-scale trial