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Sulphate Attack Resistance of Selected Cement Brands in Nigeria

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Abstract

Sulphate attack is a major threat to any concrete structure. While the environment of the concrete structure could aggravate the attack, material constituent also plays significant role to either permit or resist the attack. In this paper, sulphate resistance potential of selected cement brands in Nigeria was investigated. The cement brands studied were Dangote, Lafarge, Purechem and Sokoto. Mortar of mix ratio 1:3 was prepared from each cement brand with water cement ratio (w/c) of 0.5. Thereafter, mortar prisms of size 160 x 40 x 40 mm were cast for flexural and compressive strength tests. Cement paste bars (40 x 10 x 10 mm) made from each cement brand were also cast to measure expansion in sulphate solution. Each specimen was immersed in sulphate solutions of sodium, calcium, potassium, and magnesium for 7, 14, 28, and 56 days. Strength properties were determined at the end of each period, while expansion of the mortar specimens was monitored for 9 months. The results showed that the strength of the mortar reduced with increase in period of exposure to sulphate solutions for all the cement brands, but the reduction was more pronounced with mortar made from Sokoto cement. This indicates that it has the lowest residual strength, followed by Dangote and then Purechem. Lafarge appeared to have the highest residual strength. The expansion test results showed that there was no significant expansion observed from each cement brands. Perhaps, there is need to increase the days of monitoring or increase the concentration of the sulphate to be able to generalize performance. Magnesium sulphate was discovered to cause more degradation of the mortar samples followed by Sodium sulphate, while calcium sulphate was least aggressive. The study concluded that mortar sample made from Lafarge cement resisted sulphate attack better than those from other cement brands. It is therefore recommended that cement type should be carefully selected for the sulphate-ridden environment and/or the concrete structure is protected from direct contact with sulphate.

Keywords: Cement paste, concrete structure, expansion, mortar and sulphate attack.

1.0 INTRODUCTION

Sulphate attack on concrete is one of the durability challenges both to reinforcing steel and concrete materials. Most concrete structures have contact with soil and underground water, which may contain ions of sulphate. Worst affected are hydraulic structures built in marine environment and concrete sewers (Olonade, 2016). Sulphate attack causes cracking, spalling, loss of strength and other negative effects on concrete (Neville, 2014). It equally attacks reinforcing steel bars in concrete, if sulphate solution percolates through the concrete (Bentur *et al*., 1998). Most concrete structures attacked by sulphate often require repair or complete rehabilitation, which gulp substantial investment that could have been deployed to build new structures. Not only that, man-hour is lost, while operation would be grossly affected during repair. Thus, cost associated with sulphate attack on concrete is heavy to bear.

Mechanism for sulphate attack remains subject of discourse among researchers with different theories put forward. The first theory is that recrystallization of ettringite orchestrated by external source of sulphate is responsible for volume changes in concrete, leading to cracking (Wee *et al*., 2000). In the second theory, sulphate attack is attributed to formation of additional gypsum due to cations exchange reactions with any substance rich in sulphate (ACI, 1997). Decalcification of calcium silicate hydrate was another explanation given to the mechanism of sulphate attack, though the theory was not popular among scientists as decalcification is more attributed to more acidic attack than sulphate attack (Trinh *et al*., 1997). In these cases, the deterioration observed appears to be related to the reaction of phases in the concrete and the additional chemical reactions caused by infiltration of sulphate along with other counter-ions, such as calcium, magnesium, sodium or potassium.

One thing that is certain in the proposed theories of sulphate attack mechanism is that material composition of the concrete plays significant roles in determining the severity of attack. Most importantly, cement that is binding other constituents' cement-based products is a first suspect. If cement is prone to sulphate attack, may be due to its chemical composition or other physical properties, it is likely that the concrete or mortar made from it will be equally affected. Therefore, knowing the sulphate resistance capacity of cement types is fundamental to building the concrete structures. Different author has equally studied the use of supplementary cementitious materials (SCMs) to fortified cement against sulphate attack (Ikotun and Ikotun, 2014; Merida and Kharchi, 2015). Corral *et al*. (2011) studied the potential of incorporating fly ash and silica fume to increase sulphate resistance of recycled aggregate concrete. Their results indicated that inclusion of fly ash and silica fume reduced weight loss to sulphate attack. Contrarily, if the SCMs are not well integrated with cement, they could lead to greater ingress of sulphate through the pore structure of the concrete matrix (Whittaker and Black, 2014). Jianhe *et al*. (2019) suggested that geopolymer cement based could also provide better sulphate resistance compared to normal concrete made from ordinary Portland cement (OPC).

However, there are a few cement brands found in Nigerian markets and virtually nothing is known about their sulphate resistance capacity. These cements are used in the environment indiscriminately. The thrust of this study, therefore, is to investigate sulphate resistance capacity of common cement brands in Nigeria, with a view to characterizing them. The results of this study will add to the existing knowledge of Nigerian cements and serve as guide for users of cement on the choice of cement for an environment, especially sulphate prone environment.

2.0 MATERIALS AND METHOD

2.1 Materials

Four common OPC brands studied were Dangote, Lafarge, Purechem and Sokoto cements. River sand was used as fine aggregate, while potable water was used for mixing.

2.2 Preparation of sulphate solution

Sulphate solutions of sodium ion (Na^+), Calcium ion (Ca^{2+}), Magnesium ion (Mg^{2+}) and Potassium ion (K^+) were prepared by dissolving 50 grams of each of the sulphate in a litre of distill water.

2.3 Preparation of Mortar Samples

Mortar constituents (sand, cement, and water) were batched by weight in the ratio of 1:3 with water-cement ratio of 0.5. The constituents were mixed in an electric mixer for a total period of 5 minutes until a uniform and consistent mortar paste was formed. Mortar samples were poured in moulds of size 40 x 40 x 160 mm. These were then covered with polythene for 24 hours before the mortar beams were removed from the moulds and then placed in respective sulphate solutions of Ca^{2+}, Na^+, Mg^{2+} and K^+ for 7, 14, 28 and 56 days, respectively while samples cured in water were taken as reference samples. Similarly, samples of sizes 10 × 10 × 60 mm were cast from cement pastes for expansion.

2.4 Methods

2.4.1 Determination of the Physical and Chemical Properties of the Cements

Chemical composition of Dangote, Lafarge, Purechem and Sokoto cements were determined using X-ray florescence spectroscopy. The surface areas of the cements were determined with Blain meter cell, while their densities as well as their specific gravities were equally determined in accordance to the provisions of BS 196 (2000) standard. Other properties that were determined were refractive index, absorption index and uniformity. Particle size distribution of the cements were determined using Mastersizer 300 following the standard described in ASTM E2651 (2019). All the tests were conducted in the physical and chemical laboratories of Lafarge Cement Plc, Ewekoro, Nigeria.

2.4.2 Aggregate Characterization

Properties of the aggregate (sand) such as specific gravity, bulk density, water absorption and total moisture content were some of the properties determined. Sieve analysis was carried out and the particle size distribution curve for the aggregate was plotted and its corresponding grading properties: coefficients of uniformity, coefficient of curvature and fineness modulus were determined. The characterization of the aggregate was conducted in accordance with the standard procedure of BS EN 1097 (2010). From the particle size distribution curve of the sand, coefficients of uniformity (C_u) and curvature (C_v) were determined using Equations 1 and 2 respectively as specified by ASTM D2487 (2017).

$$C_u = \frac{D_{30}}{D_{60}} \tag{1}$$

$$C_v = \frac{(D_{30})^2}{D_{10} \times D_{60}} \tag{2}$$

Where,

D_{10} = Diameter corresponding to 10% finer in the grain size distribution
D_{30} = Diameter corresponding to 30% finer in the grain size distribution
D_{60} = Diameter corresponding to 60% finer in the grain size distribution

2.4.3 Determination of strength

A. Flexural strength

At the end of each curing age, mortar samples were removed from the sulphate solution. Each specimen was inspected for any physical disintegration before tested for strength. Flexural strength was first tested using 3-point load method. The beam was placed on two supports and load was applied at the centre of the beam until it broke into two halves. The load that caused the beam to break into halves was noted and flexural strength was determined from Equation 3. Average of three tests was determined. The same approach was followed to test all the beams exposed to different sulphate solutions at their specified ages. The detail of the procedure for the test is described in ASTM C78 (2018). Figure 1 shows the flexural strength set-up.

$$f_s = \frac{1.5Fl}{b^3} \tag{3}$$

Where,

f_s = flexural strength, N/mm^2
F = flexural force, N
b = side of prism square section, mm
l = span between supports, mm

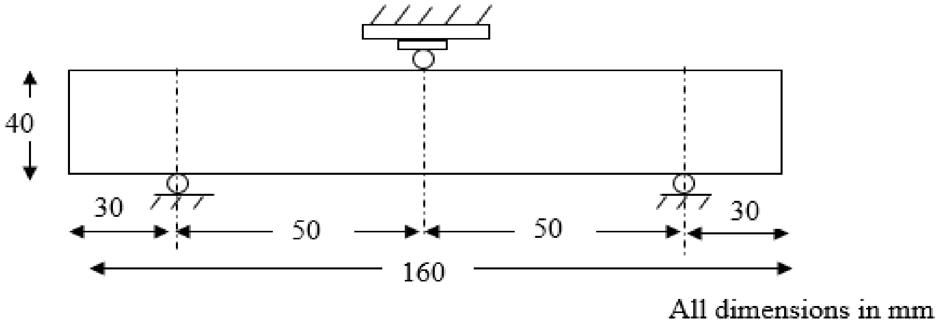

Figure 1: Set-up for flexural strength testing of mortar specimen

B. Compressive strength

Each half of the samples obtained from flexural strength test was used for compressive strength. The sample was placed under compression machine and load was exerted until the sample shattered such that it could not resist any load. The load at this point was recorded and compressive strength was calculated from Equation 4. Average of six readings was determined and taken as average compressive strength. This test was conducted also in line with the provisions of ASTM C78 (2018).

$$P = F/A \tag{4}$$

Where,
P= Compressive load (N/mm^2)
F= Applied force (N)
A= Area of the cube (mm^2)

For each of the flexural and compressive strength, loss or gain in strength was estimated due to sulphate attack from Equation 5.

$$\%Loss\ or\ gain\ in\ strength = [(A - B)/A] \times 100 \tag{5}$$

Where,
A is the average strength of specimens cured in water, MPa.
B is the average strength of specimens exposed to sulphate solution, MPa.

2.4.4 Expansion Test

Expansion test was performed in accordance with ASTM C1012 (2018). Mortar bar specimens of size 10 mm × 10 mm × 60 mm were first immersed in limewater for 24 hours before they were immersed in 50g/l sulphate solutions of calcium, potassium, magnesium and sodium sulphate. The expansions of the samples were monitored every seven (7) days for a total period of 9 months by measuring the length of the sample, using digital Vernier caliper of precision 0.001 (Figure 2).

Figure 2: Expansion measurement with the Digital Venier Caliper

The expansions of the samples were then calculated, using Equation 6.

$$\Delta L = \frac{L_x - L_i}{L_g} \times 100 \qquad (6)$$

Where,

ΔL = change in length at age x,

L_x = Venier caliper reading of specimen at age x (mm)

L_i = Initial Venier caliper reading of the specimen (mm)

L_g = gauge length considered as the nominal length (mm), measured when the mould was constructed.

2.5 Mineralogical Characterization of Mortar in Sulphate Solution by X-Ray Diffraction

The XRD analysis was carried out on finely crushed sulphate attached samples, collected from the surface of the mortar, which was prepared with four brands of cements. The mineralogical phases were identified with a POWDILL powder diffractometer, using a Cu Kα radiation of wavelength = 1.54 Å, operating at 40 kV and 30 mA, with a step size 0.01 ° (2θ).

3.0 RESULTS AND DISCUSSION

3.1 Aggregate Characterization

The properties of the aggregate (sand) were determined for proper classification. The results obtained from the tests are summarized in Table 1.

Table 1: Physical and grading properties of the aggregate

Properties	Sand
Specific Gravity	2.63
Total Moisture Content, (%)	0.15
Water Absorption (%)	3.8
Fineness Modulus	2.42
Coefficient of Curvature, C_v	1.25
Coefficient of Uniformity, C_u	4.60

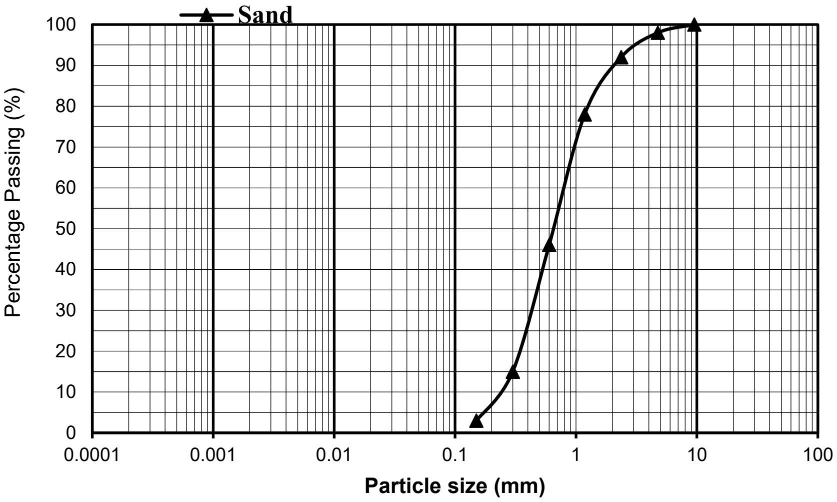

Figure 3: Grading curves for sand

The fineness modulus, which depicts percentage by mass of the aggregate retain on the 150μm falls within the recommended value for sand, while the water absorption fell within the range of 0.2 to 4% as stipulated by ASTM C70 (2013) for aggregate to be used in concrete without contributing to mixing water content.

While the uniform coefficients (C_u) of the sand was 4.60, its coefficient of curvature (C_v) was 1.25 as obtained from the gradation curve shown in Figure 3. When value C_u was greater than 4 and C_c less than 3, the sand was therefore classified as well graded based on Unified Soil Classification. About 90% of its particle size was retained on 300 μm sieve size, while less than 5% of the particle size passed 150 μm sieve size, indicating that the sand fell within fine aggregate suitable for making mortar samples (ASTM C136, 2019).

3.2 Characteristics of the cement samples

3.2.1 Physical and Grading properties

The particle size distribution (PSD) is one of the main parameters used in the characterization of a cement powder. Figure 4 shows the particle size distribution (PSD) of the cement samples.

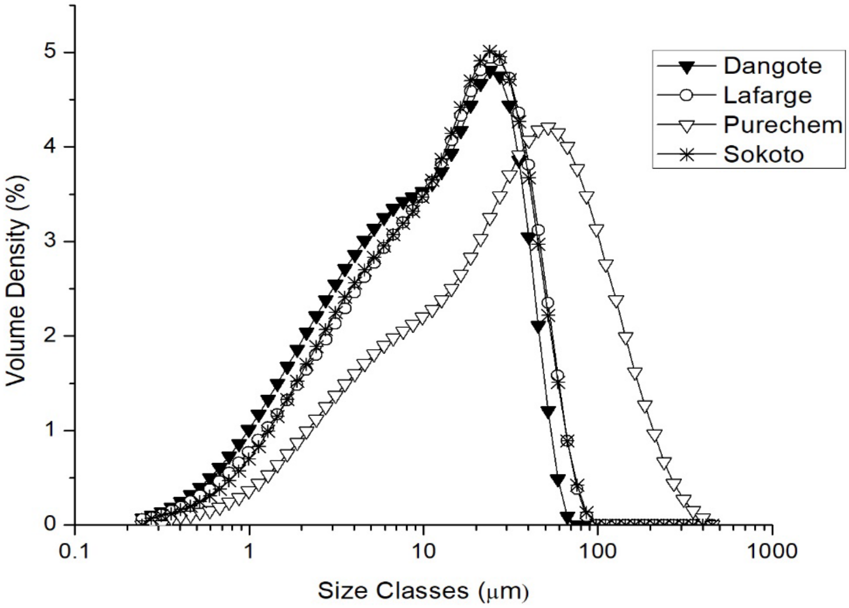

Figure 4: Particle size-distribution curve of Portland Cement Brands

Each cement particles have variety of angular shapes and a wide range of sizes. From Figure 4, it could be observed that all the cement brands were not normally distributed, as their curves were not symmetrical about the central axis, suggesting that there were more small particles than larger ones. Apart from Purechem that skewed more to the right, all other cement samples seem to have similar particle sizes as indicated by the shape of their PSD curves. Thus, the particle sizes vary in proportion against the volume density. Lafarge had 5% volume density with much of the particles around 13 µm. Dangote and Sokoto equally have much of its sizes also around 13µm. However, the volume density was lesser in Sokoto cement, which was about 4.8%. On the other hand, Purechem had sizes within the range of 80 to 95µm, indicating that it may cause late initiation of hydration process, as hydration process of a Portland cement depends on fineness (Shetty, 2005). Meanwhile, hydration process may likely start earlier in Lafarge cement compared to other cement brands.

PSD analysis also showed that Dangote cement had the highest specific surface area of 473.7m^2/kg, which may suggest that it will take up more water for hydration reaction. Nevertheless, all the cements studied had surface areas within the recommended values of between 300 and 500m^2/kg for cement (ASTM C204, 2011). Similarly, the absorption index of all the cement samples was 0.01, suggesting that the laser diffraction light was constant during the interaction with the particles. Thus, it is expected that the cement brands would likely perform differently under sulphate attack.

3.3 Chemical Analysis of the Cements

Performance of any Portland cement is highly influenced by its chemical composition. In Table 2, it can be seen that the dominant oxides in all the cement samples were CaO, SiO_2, Al_2O_3 and Fe_2O_3, with other minor oxides. Of particular interest is the suphite or trioxo-sulphate (SO_3) content of the cement. Trioxo-sulphate contributes to the formation of tri calcium silicate (C_3S), which is responsible for the initial setting and early strength. Dangote was observed to have least C_3S content (1.9%), which was marginally different from that of Lafarge, while Purechem had the highest value (2.69%).

It then depicts that Dangote may gain early strength compared to other brands. However, the silica content of Purechem and Lafarge were found to fall within the specified range of 18 – 24% (BS EN 196-2, 1995). It could be deduced that the raw material (calcium carbonate) used to produce Dangote and Sokoto cements were low in silica compared to Lafarge and Purechem. But all the cement brands contained alumina in the right amount specified (2.6 – 8.0 %). Looking at the value of the Loss on ignition (LOI), Dangote had highest value of LOI (11.15 %), representing about 150 % of that of Lafarge and Purechem cements. Sokoto cement equally had LOI that was close to Dangote. Since LOI is a measure of amount of organic and moisture present in the cement, which are burnt off, when cement is heated up to 950 °C (Olonade *et al.*, 2015), one could infer that Dangote and Sokoto cements contained more quantities of these essential substances than other cement brands. The difference could also be due to storage condition.

Table 2: Chemical composition of Ordinary Portland Cement

Oxides/ Parameters	Dangote	Lafarge	Purechem	Sokoto
SiO_2	15.77	19.06	19.08	16.77
Na_2O	0.03	0.00	0.00	0.02
K_2O	0.34	0.24	0.06	0.27
CaO	60.53	60.24	60.44	60.56
MgO	2.25	2.34	1.03	1.71
TiO	0.22	0.28	0.27	0.23
P_2O5	0.45	0.58	0.19	0.31
Al_2O_3	4.04	5.30	4.57	4.40
Fe_2O_3	3.11	3.35	3.13	2.85
SO_3	1.90	1.91	2.69	2.00
Mn_2O_3	0.05	0.13	0.05	0.06
Blaine (cm^2/g)	4501	4103	2851	4120
L.O.I	11.15	6.20	7.04	10.24
Density	2.82	3.02	3.08	2.98
R45	2.53	4.66	40.01	10.09
Specific Area (cm^2/g)	4737	3571	2107	3965
WR (%)	0.6	0.70	0.10	0.25
LO	2.41	2.66	2.52	2.15
Span	3.155	2.901	3.764	2.941
Uniformity	0.995	0.918	1.201	0.927

LO – Laser Obscuration; WR – Weighted Residual

3.4 Effect of Sulphate Attack on compressive strength of cement mortar

3.4.1 Effect of Sodium Sulphate

In the Figure 5, Dangote cement had strength of 14.12N/mm^2 at 7 days in Na_2SO_4 but in water it was 17.22 N/mm^2. This shows a strength loss of 3.1 N/mm^2. It was further observed that there was increase in the strength loss of Dangote cement over the curing days from 8.3 N/mm^2 at 14 days to 9.7 N/mm^2 at 56 days. Mortar samples made from Purechem cement was also observed having gradual declination in the strength. At 7days, it attained strength of 12.3 N/mm^2 and 7.94 N/mm^2 in Na_2SO_4, representing a loss of about 35% (4.36 N/mm^2). However, at 14 days, it had strength of 17.13 N/mm^2 in water and 13.79 N/mm^2 in Na_2SO_4, with close to 30% loss in strength. While at 56days, the strength loss was observed to decrease by 1.4 N/mm^2. Loss of strength in each case could be attributed to the effect of sulphate attack, depending on the resistance capacity of each of the cement brand to sulphate attack. Lafarge cement showed higher resistance to sulphate attack with a residual strength of 6.58 N/mm^2 at 7 days (16.4 – 9.82) N/mm^2 while at 56 days, it was observed that there was a strength loss of about 7.21 N/mm^2 (19.45 – 26.66) N/mm^2. Furthermore, mortar samples made from Sokoto cement also showed the same characteristic strength loss as Purechem i.e., gradual declination in strength. At 7days, residual strength of 9.44 N/mm^2 (20.44 – 11) N/mm^2, while at 14days, the strength loss was observed to be 14.27 N/mm^2 (26.1 – 11.83) N/mm^2. Similarly, at 28days it was 12.19 N/mm^2 (26.3 – 14.11) N/mm^2, which further decreased to 8.55N/mm^2 (28.55 – 20) N/mm^2 at 56 days. The chemistry of attack indicated that there was cation exchange reaction between the portlandite and the Na_2SO_4 solution resulting in formation of NaOH (Equation 7). Presence of the NaOH in the mortar matrix increased the pH value of the system, causing dissolution of portlandite. On the other hand, formation of calcium sulphate that precipitated enhanced volume change in the cement microstructure leading to expansion and subsequently deterioration of the mortar matrix (Equation 7). Thus, the strength of the mortar prism is impaired with different degree of reduction, depending on the type of cement used. From the above results, it showed that Lafarge cement had the highest resistance to sodium sulphate attack. These results are comparable with what Al-Dulaijan *et al.* (2003) reported, though with different cements.

$$C_3A \cdot Ca(OH)_2 \cdot 12H_2O + 3Na_2SO_4 + 2Ca(OH)_2 + 20H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O + 6NaOH \quad (7)$$

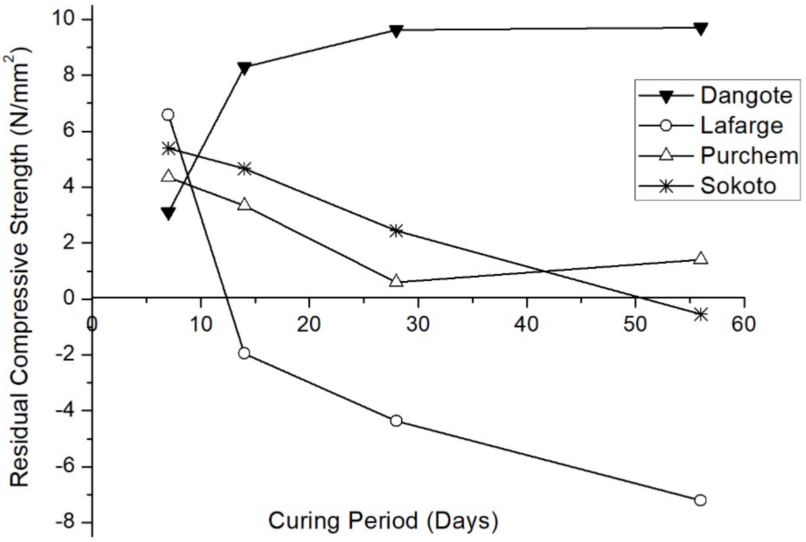

Figure 5: Residual strength of mortar samples of cement brands exposed to Na_sSO_4

3.4.2 Effect of Calcium Sulphate

At 7days in $CaSO_4$, Dangote cement had a residual strength of 1.65N/mm^2 i.e. 17.22 N/mm^2 in water and 15.57N/mm^2 in calcium sulphate solution. The residual strength continues to increase till 28days (9.27 N/mm^2), where the strength in water was 27.5 N/mm^2 and the strength in sulphate was 18.23 N/mm^2. There was a little drop at 56 days, which could be ascribed to the starting of the attack on the mortar. The strength was further found to have dropped to 7.2 N/mm^2 (28.3 – 21.1) N/mm^2. Purechem was also observed to follow the same trend as Dangote cement except at 28 days, where there was slight increase in strength. The strength was observed to be 17.5 N/mm^2 in water while it was 18.22 N/mm^2 in the sulphate solution. Lafarge cement, on the other hand, was observed to have been attacked by the calcium sulphate causing reduction in strength at all the ages of exposure. (7days until 56 days). At age 7 days, it had a residual strength of 5.27 N/mm^2 (16.44 – 11.13) N/mm^2, while it further reduced to 1.05 N/mm^2 at 14 days. At 28 days and 56 days respectively, the residual strengths were observed to be 4.19 N/mm^2 and 4.95 N/mm^2, respectively. However, Sokoto cement showed resistant to an appreciable degree, where its residual strength was 5.5 N/mm^2 (20.44 – 10.9) at 7 days and 4.93 N/mm^2 at 14 days. It further reduced to 2.76 N/mm^2 at 56 days. The summary of these results suggested that Dangote cement showed more resistant to calcium sulphate, while Lafarge was the least resistant to the attack (Figure 6).

Generally, exposing hydrated cement to $CaSO_4$ solution does not have detrimental effect on the hydrated product because it only involved in synthesis of ettringite as portlandite did not have direct reaction with calcium sulphate. There is also no cation exchange as shown in Equation 8. Similarly, calcium sulphate has low solubility and thus less reaction (Piasta *et al.*, 2014).

$$C_3A \cdot Ca(OH)_2 \cdot 12H_2O + 3CaSO_4 + 20H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O + Ca(OH)_2 \qquad (8)$$

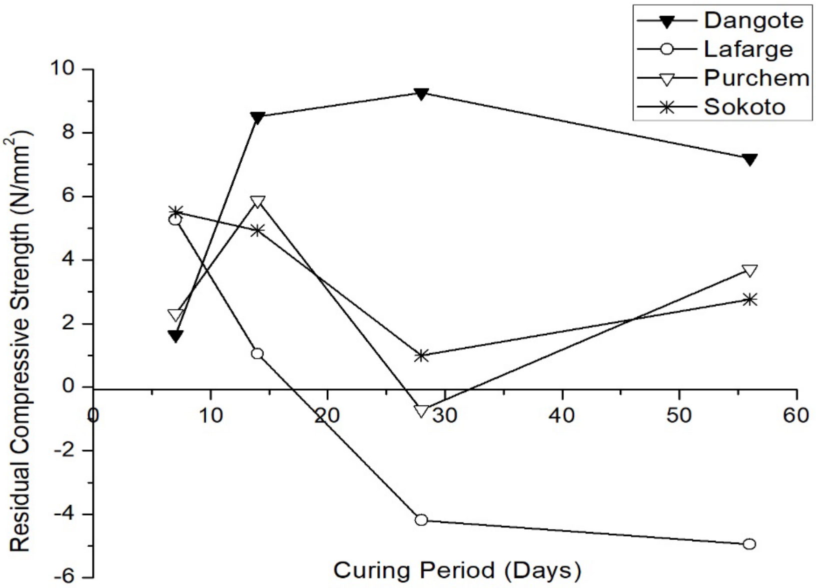

Figure 6: Residual Compressive Strength of Portland Cement Brands in $CaSO_4$ solution with curing age

3.4.3 Effect of Magnesium Sulphate

In magnesium sulphate solution, Dangote cement was observed to be resistant to the attack with an increase in the residual strength of 5.52 N/mm^2 (17.22 – 11.7) at 7days to 5.91 N/mm^2 (25.2 – 19.29) at 14days (Figure 7). However, there was a slight decrease in the residual strength at 28 days 5.3 N/mm^2 (27.5 – 22.2) then afterwards, an increase in the strength to 5.6N/mm^2 (28.3 – 22.7) at 56 days. In the general, Dangote cement proved to show relative resistant to the magnesium sulphate attack throughout the curing ages. Purechem also depicted the capacity to be resistant to the attack having attained a gradual increase in the residual strength over the curing ages. At 7 days, the residual strength was observed to be 1.82N/mm^2 (12.3 – 10.48) while at 14days, it was 5.38N/mm^2 (17.13 – 11.75), while at 56 days, the strength was 7.2 N/mm^2 (22.2 – 17.2) which showed a higher resistance to the attack.

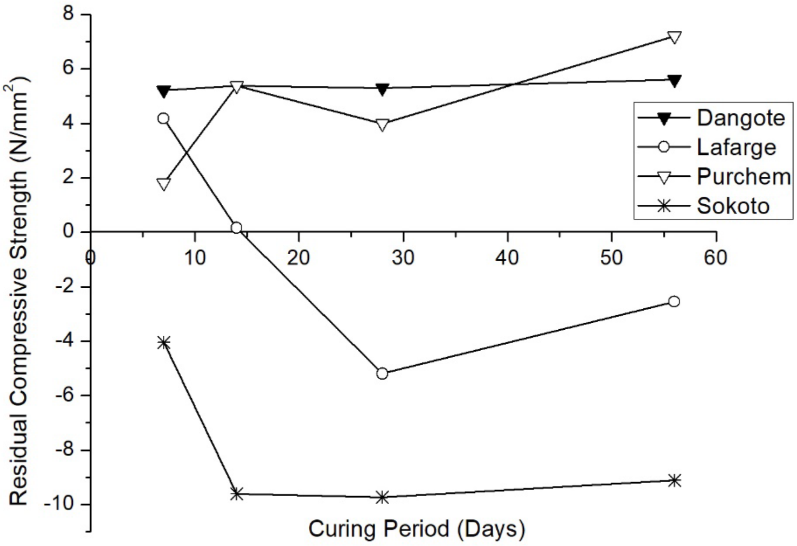

Figure 7: Residual Compressive Strength of Portland Cement Brands in $MgSO_4$ solution with curing age.

Whereas Lafarge cement seemed to be relatively less resistant to Magnesium Sulphate as shown by the consistent decrease in residual strength from 4.18N/mm^2 at 7 days to a strength of 0.16

N/mm^2 at 14 days. Further decrease was observed at 28 and 56 days due to attack on the mortar. The observed residual strength was -5.19N/mm^2 at 28 days and -2.55 N/mm^2 at 56 days, respectively. The attack was found to be more severe on Sokoto cement having lower residual strength from 7 days to 56 days. The residual strength was 4.04 N/mm^2 at 7 days, 9.60 N/mm^2 at 14days, -9.74 N/mm^2 at 28 days and -9.1 N/mm^2 at 56 days.

The likely reason for the aggressive nature of magnesium sulphate is its high solubility and high acidic salt, which tends to neutralize the alkali medium of hydrated cement (Piasta *et. al.,* 2014). When it reacts with cement hydrated product, it produces hydroxyl of magnesium, which precipitated in the hydrated cement medium leading to expansion (Equation 8). Acidic nature of the product due to magnesium sulphate attack caused dissociation of calcium ions and accelerated formation of gypsum.

$$C_3A \cdot Ca(OH)_2 \cdot 12H_2O + 2MgSO_4 + 2Ca(OH)_2 + 20H_2O \rightarrow$$
$$C_3A \cdot 3CaSO_4 \cdot 32H_2O + 2Mg(OH)_2 \downarrow \qquad (9)$$

3.4.4 Effect of Potassium Sulphate

Curing all the mortar samples in potassium sulphate, Dangote cement was observed to be the most resistant to the sulphate, showing a residual strength of 4.89N/mm^2 (17.22 – 12.33) at 7 days and a further increase in the residual strength of 7.83 N/mm^2 (25.2 – 17.37) at 14 days (Figure 8). The residual compressive strength continues to increase until 56 days. The recorded strength for 28days was 8.26 N/mm^2 while 9.06 N/mm^2 (28.3 – 19.25) was recorded for 56 days.

Mortar made from Purechem cement also exhibited the same characteristics, giving a strength of 4.98 N/mm^2 (12.3 -10.82) at 7 days, 4.80N/mm^2 at 14 days, 5.11 N/mm^2 at 28 days and 7.7 N/mm^2 at 56 days (Figure 8). However, Lafarge cement showed resistance to the attack at early age i.e. 7 and 14 days before it responds to the attack after 28days. The observed strength for 7 days was 5.58 N/mm^2 while it gave -3.93 N/mm^2 after 28 days. A further reduction was observed at 56 days -2.33 N/mm^2. This showed that only Lafarge cement responded largely to the attack while Dangote was the least responded. Sokoto cement also made a decrease in the residual compressive strength throughout the curing ages. The observed residual strength for 7 days was 7.20 N/mm^2 while 14, 28 and 56 days were 4.00 N/mm^2, -2.64 N/mm^2 and -0.75 N/mm^2 respectively. From the detailed study, it was observed that magnesium sulphate was the most aggressive followed by Sodium sulphate. The magnesium sulphate caused the highest strength loss in Sokoto cement throughout the curing ages while Lafarge cement was observed to be highly susceptible to the sodium sulphate attack.

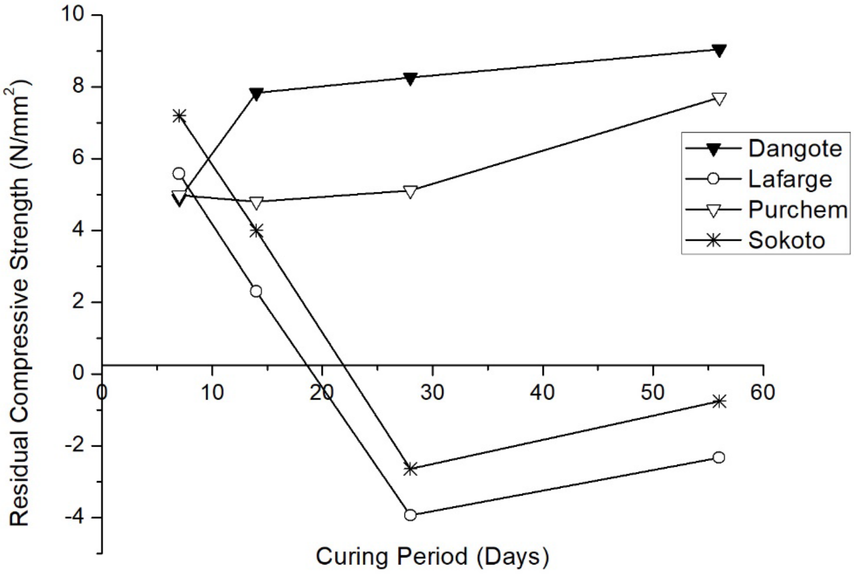

Figure 8: Residual Compressive Strength of Portland Cement Brands in K_2SO_4 solution with curing age.

However, Dangote cement was found to be the most resistant to sodium sulphate attack while Purechem was highly resistant to magnesium sulphate attack. Different sulphates can affect the concrete differently. Magnesium sulphate is the most severe because of the presence of magnesium ions. These ions can cause additional corrosive reactions through the formation of $Mg(OH)_2$ and ettringite, which has potential to decompose the C-S-H. (Atta-ur-Rehman *et al.,* 2018).

3.5 Flexural Strength

Table 4 below shows the flexural strength of the mortar samples cured in sulphate solutions.

Table 4: Flexural Strength of Portland cement Brands

Cement Brands	Flexural strength (N/mm^2)															
	NaSO4 Solution				CaSO4 Solution				MgSO4 Solution				KSO4 Solution			
	Ages (days)				Ages (days)				Ages (days)				Ages (days)			
	7	14	28	56	7	14	28	56	7	14	28	56	7	14	28	56
D	7.4	7.6	7.9	7.9	7.5	7.7	8.3	8.5	7.3	7.9	8.3	8.4	7.3	7.4	8.2	8.8
P	7.2	7.4	7.6	8.2	7.0	7.1	7.3	7.4	7.2	7.2	7.6	7.8	7.1	7.2	7.4	7.5
L	7.1	7.2	8.1	8.3	7.3	7.3	7.7	7.7	7.5	8.0	8.1	8.2	7.3	7.4	7.9	7.9
S	7.2	7.5	7.8	7.9	7.3	7.3	7.5	7.5	7.7	7.7	7.8	7.9	7.2	7.4	7.4	7.5

From the detailed observation of the flexural strength, it was observed that there is no defined pattern and that the flexural strength of the mortar samples made from all the cements studied were not different. Similarly, type of sulphate solution did not also influence the flexural strength of the mortar. Generally, flexural strength is not an intrinsic property of cement-based products, unlike compressive strength because they are brittle in nature and do not resist flexural stresses (Shetty, 2006). Thus, flexural strength is not adequate property to measure loss or gain due to sulphate attack.

3.6 Physical Damage of Mortar Samples by Sulphate Solution

The mortar samples were cured in sulphate solutions in order to examine the physical damage caused by the solutions. Figure 9a-b below shows the resistance of different brands of cements to different solutions and also the degree of deteriorations caused on the brands.

Figure 9: Apperance of cement paste prism exsposed to sulphate attack (a) Other sulphate attack (b) $MgSO_4$ attack

3.7 Mineralogical Characterization of Mortar in Sulphate Solution by X-Ray Diffraction

The diffraction patterns of the paste made from each of the cement brands immersed in the solution of $MgSO_4$ and $CaSO_4$ at 22 °C for a period of 56 days are shown Figures 10 and 11 respectively.

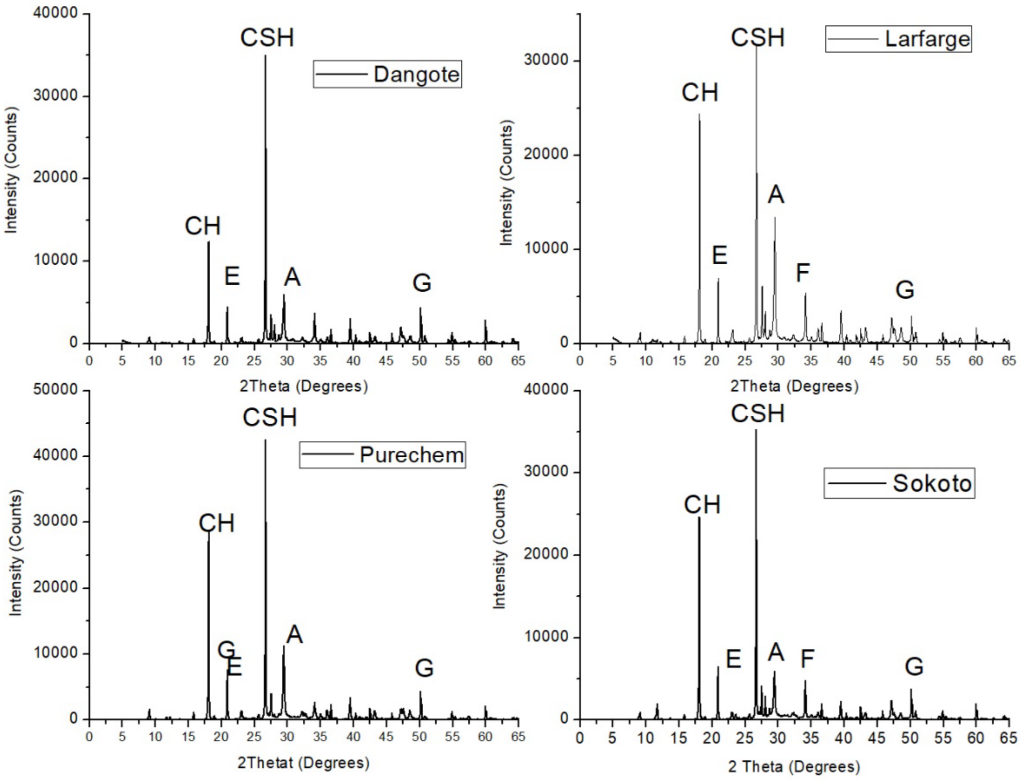

Figure 10: XRD Patterns of Pastes immersed in $MgSO_4$ solution for 56 days. Identified Phases: Portlandite (CH), Ettringite (E), Aluminate (A), Calcium silicate hydrate (CSH) and Ferrite (F)

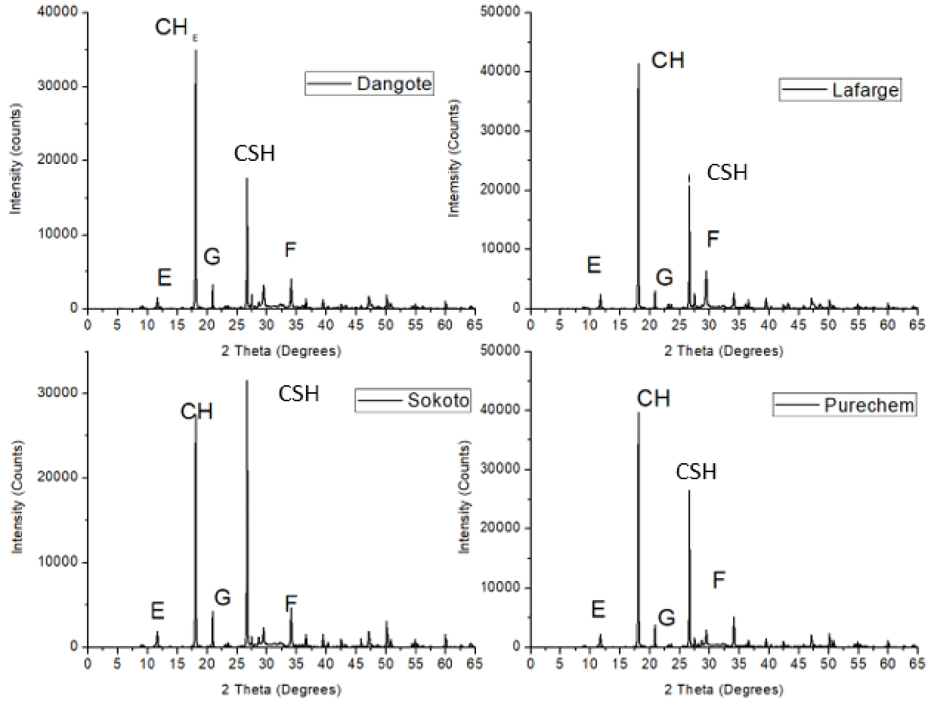

Figure 11: XRD Patterns of Pastes immersed in $CaSO_4$ solution for 56 days. Identified Phases: Portlandite (CH), Ettringite (E), Aluminate (A), Calcium silicate hydrate (CSH) and Ferrite (F)

From the XRD patterns, major phases identified were CSH, CH, gypsum (G) and ettringite (E). It is observed that portlandite (CH) was more pronounced in the hydrated cement paste exposed to calcium sulphate because of additional CH formed as shown in Equation 8. There seem not to be much difference in the other phases identified in each of the cement paste. Important to note that more CSH is formed in addition with substantial aluminate hydrae (A) in the Lafarge cement cured in $MgSO_4$ (Figure 10) compared to other cements, which could be responsible for higher residual strength observed in the mortar made from it. As for $CaSO_4$ solution, the patterns are similar for all the cements. This may be due to less damaging effect of $CaSO_4$ on cement composite.

4.0 CONCLUSION

Effect of selected sulphate solutions on the mortar made from some cement brands in Nigeria has been studied. Residual strength and physical deterioration of the samples as well as phase formation were determined. It is concluded that Mortar cured in the sulphate solution gave an increment in strength at the initial days (7 days) after it decreased, depending on the sulphate solution type. Calcium sulphate solution had mild effect on the mortar samples, while magnesium sulphate solution had severe effect as the residual strength reduced by an average of 50% at age 56-day exposure. While mortar made from Purechem cement showed greater resistant to the magnesium sulphate, Sokoto showed the least resistance. It is therefore, suggested that cement brands should be selected based on the intended environment exposure, especially sulphate rich environment.

REFERENCES

ACI Code Detailing Manual (1997). *ACI Special Publication SP-66*. American Concrete Institute, Farmington Hills,

Al-Dulaijan, S. U., Maslehuddin, M., Al-Zahrani, M. M., Sharif, A. M., Shameem, M. and Ibrahim, M. (2003). "Sulphate resistance of plain and blended cements exposed to varying concentrations of sodium Sulphate." *Cement and Concrete Composites*, 25 (4-5): 429-437.

ASTM C1012 / C1012M-18b, Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution, ASTM International, West Conshohocken, PA,

ASTM C136 (2019). Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates, ASTM International, West Conshohocken, PA.

ASTM C204 (2011). Standard Test Methods for Fineness of Hydraulic Cement by Air-Permeability Apparatus, ASTM International, West Conshohocken, PA.

ASTM C70 (2013). Standard Test Method for Surface Moisture in Fine Aggregate. ASTM International, West Conshohocken, PA.

ASTM C78 (2018). Standard Test Method for Flexural Strength of Concrete (Using Simple Beam with Third-Point Loading), ASTM International, West Conshohocken, PA.

ASTM D2487-17, Standard Practice for Classification of Soils for Engineering Purposes (Unified Soil Classification System), ASTM International, West Conshohocken, PA.

ASTM E2651-19, Standard Guide for Powder Particle Size Analysis, ASTM International, West Conshohocken, PA, 2019

Atta-ur-Rehman, Abdul Qudoos, Hong Gi Kim and Jae-Suk Ryou (2018). Influence of Titanium Dioxide Nanoparticles on the Sulphate Attack upon Ordinary Portland cement and Slag-Blended Mortars. *MDPI Materials,* 11: 1-17.

Bentur, B., Cohen, M.D. (2000). Expansion of alite paste caused by gypsum formation during Sulphate attack, *J. Mater. Civ. Eng*. 12 (1): 24 – 25.

BS 196 (2000). Cement. Composition, specifications and conformity criteria for common cements, British Standard Institution (BSI), London

BS EN 1097 (2010): Tests for mechanical and physical properties of aggregates. Methods for the determination of resistance to fragmentation, British Standard Institution (BSI), London

Corral-Higuera, R., Arredondo Rea, S. P., Neri Flores, M. A., Gómez Soberón, J. M., Almeraya Calderón, F., Castorena González, J. H. and Almaral Sánchez, J. L. (2011). Sulfate attack and reinforcement corrosion in concrete with recycled concrete aggregates and supplementary cementing materials*. Int. J. Electrochem. Sci,* 6: 613 – 621.

Ikotun, B. D. and Ikotun, A. G. (2014). Effect of a Modified Pozzolan on the Sulphate Attack Resistant of Mortar, *IACSIT International Journal of Engineering and Technology*, 6(1): 55 – 59.

Jianhe, X., Jianbai, Z., Junjie, W., Chonghao, W., Peiyan, H. and Chi, F. (2019). Sulfate Resistance Of Recycled Aggregate Concrete With Ground granulated blast slag and Fly Ash-Based Geopolymer, Materials (Basel), 12(8): 1247.

Merida, A. and Kharchi, F. (2015). Pozzolan concrete durability on sulphate attack, *Procedia Engineering* 114: 832 – 837.

Neville, A. M. (2014). *Properties of Concrete*, 5th Ed. Pearson Publisher, London, UK.

Olonade, K. A. (2016). A Review of the Effect of Wastewater on Reinforced Concrete Structure in Nigeria. *Nigerian Journal of Technology*, 35(2): 234–241

Olonade, K.A., Jaji, M.B., Rasak, S.A. and Ojo, B.A. (2015). Comparative Quality Evaluation of Cement Brands Used in South West Nigeria. *Academy Journal of Science and Engineering*, 9 (1): 53 – 63.

Piasta, W., Marczewska, J., & Jaworska, M. (2014). Some aspects and mechanisms of sulphate attack., Materials Science, 19 –24.

Shetty, M. S. (2006). *Concrete Technology: Theory and Practice*, Multicolour Ed. S. Chand and Company Ltd. New Delhi, India.

Trinh, C., Bucea, L. and Ferguson, O. (1997). Sulphate Resistance of Cementitious Materials, Mechanisms, Deterioration Processes, Testing and Influence of Binder" Proc. Concrete 97 Concrete Institute of Australia, Adelaide:263- 268.

Wee T. H., Suyavanshi, A. K., Wong, S. F., Anisur Rahman A. K. M. (2000). Sulfate resistance of concrete containing mineral admixtures. 97:536–49.

Whittaker, M., Zajac, M., Ben, H.M., Bullerjahn, F. and Black, L. (2014). The role of the alumina content of slag, plus the presence of additional sulfate on the hydration and microstructure of Portland cement-slag blends. *Cement and Concrete Research*, 66: 91–101.