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Original Article

Geo-polymerized cementitious material as a stabilizer of waste fly ash to produce green building bricks

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ABSTRACT

Fly ash (FA) and granulated blast furnace slag (GBFS) are waste materials that are readily available. The purpose of this study was to develop a cementitious material (CM) through geopolymerization and utilize it with GBFS to stabilized FA to produce sustainable building material. The strength development of CM stabilized FA was studied over the curing periods of 3, 7, 14, 28, 56 and 90 days. The specimens were evaluated for elemental composition, mineralogy, micrography and unconfined compressive strength (UCS). Stabilization of FA with GBFS yielded the highest strength of 0.24 MPa. The CM improved the strength of the specimen significantly and the strength of 8.86 MPa was attained with a mix design containing 50% FA and 50% CM. Curing for longer period up to 90 days improved the strength of the specimen to 16.03 MPa. CM proved to be the best stabilizer for the FA investigated. Stabilization of FA with a CM was successful and based on the strength attained, the specimen produced can be used to make building bricks.

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INTRODUCTION

Granulated blast furnace slag (GBFS) and fly ash (FA) are waste materials that are readily available in South Africa. Over the year's vast quantities of coal ash, generated from the steam generation coal-based process have accumulated [1]. The backbone for every developing nation and industry is coal driven power sectors. The increasing generation of coal FA is because of industry reliance on coal fueled power sectors [2]. The environmental impact due to the continuous generation of FA is a concern globally.

Disposal and landfilling of FA can no longer be an option for many companies generating FA due to environmental nuisance, challenges related to leaching, air pollution, and impact on human health, contamination of ground water and soil, and increasing costs of land. Between 2014 and 2015, the power producers in South Africa generated 34.4 million tons of coal FA [3]. Although numerous successful studies have been reported where FA was used as an additive to improve the geotechnical and geochemical properties of other materials, in this study other additives were investigated to stabilize FA as it cannot be used independently due to its characteristics and requires some modification before any application. Addi-

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tives investigated in this study were GBFS and cementitious material (CM) developed through a geopolymerisation process. The traditional manufacturing of CM such as Portland cement is energy intensive and greenhouse gases are emitted, resulting in global warming [4]. Investigating alternative solutions, other than cement for stabilization of wastes is therefore a critical area of study. Geopolymer has proven to be a developing material that can be used as an alternative to Portland cement [4]. Tchadjie et al. [5] and Samantasinghar et al. [6] stated that the term "geopolymer" refers to the inorganic aluminosilicates based on materials with geological sources that react with alkaline solution to generate a binder material via polycondensation process at ambient or elevated temperature. Geopolymers as alternative CM were first proposed by Davidovits in 1972 [7]. These materials have attracted major research interest worldwide over the past decade [7]. One of the advantages is the high potential of the materials to minimizing carbon dioxide generation [7]. When compared to Portland cement, geopolymers possess quick compressive strength development [8-9], lower permeability [10-11], lower shrinkage [12-13], and good resistance to acid and fire attack [14-15]. The other advantage with geopolymer is the ability to be developed at lower temperatures as geopolymerization reaction can be conducted at room temperature [16]. Moreover, almost no SOx, NOx, or CO are generated in the process of geopolymer preparation [17]. With the availability of FA and the growth of population in South Africa that require access to low cost housing, a solution was developed to modify the characteristics of fly and produce building blocks. Most of the research reported is on the development of geopolymers for different applications, in this study a novel solution for the synthesis of a CM from waste and using it to stabilize and improve the properties of another waste (FA) was successfully developed. The results obtained showed that the CM stabilizer significantly improved the unconfined compressive strength (UCS) of FA and the final product is suitable to be used as building blocks.

MATERIALS AND METHODS

FA and GBFS were collected from local companies in South African. 15 M Sodium Hydroxide (NaOH) was used as the alkaline activator to develop a geopolymer. To synthesize a CM, GBFS was blended with NaOH, Figure 1. The optimum conditions used to prepare CM were at liquid to solid ratio on 0.15, curing period of 5 days at 80oC, according to [18] this material together with raw GBFS were then used separately as additives to stabilize class F FA. The elemental composition, mineralogy and morphology of the materials was studied by X-ray fluorescence (XRF; model Magix Pro Phillips), X-ray diffraction (XRD, model Rigaku Ultima IV) and Scanning Electron Microscope (SEM; model Jeol JSM 5600), respectively. The significance of difference in the variable investigated was calculated using the analysis of variance (ANOVA) with a statistical significance confidence level limit of 95% [19]. The application of the GBFS and CM composites separately as stabilizer using different proportions was investigated. Ratios from 10% to 50% stabilizers to FA were investigated. The maximum dry density (MDD) and optimum moisture content (OMC) at different stabilizers to FA were determined.

RESULTS AND DISCUSSION

XRF Analysis of FA and GBFS

Table 1 shows the elemental analysis of FA, GBFS and CM. The fly ash used in this study was predominated with SiO_2 and Al_2O_3, making up 81.02 wt% relative proportion of the material. CaO was a predominant constituent in GBFS material, with a relative proportion of 49.1%. This was followed by SiO_2 with a relative proportion of 27.2%. The developed CM was predominated with CaO, with a relative proportion of 56% and followed by SiO_2 at 16.7%. This shows that developing a CM from GBFS and NaOH significantly increased the relative proportion of CaO_2 by 14%. There was also a significant increment in the relative proportion of Na_2O from 0.21 w% to 9.65 wt% due to NaOH that was used as alkaline activator. A comparison of compo-

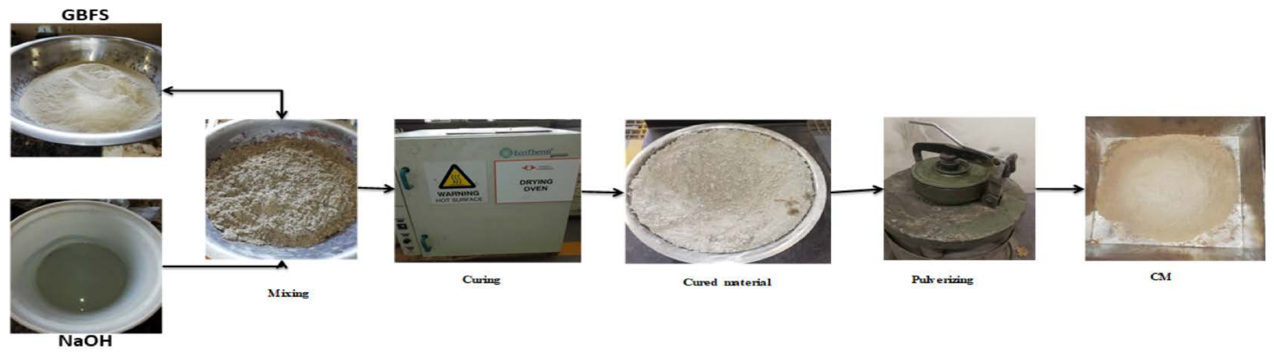

Figure 1. Preparation of cementitious material.

Table 1. Elemental composition of FA, GBFS, CM

Chemical composition (%)	FA (wt%)	GBFS (wt%)	CM (wt%)
Na_2O	ND	0.22	9.65
MgO	ND	5.48	3.52
Al_2O_3	31.77	10.7	6.95
SiO_2	50.25	27.2	16.7
P_2O_5	ND	0.01	ND
SO_3	ND	2.19	1.19
Cl	ND	0.02	ND
K_2O	1.29	0.67	0.87
CaO	8.58	49.1	56
TiO_2	2.69	0.97	ND
Cr_2O_3	ND	0.08	ND
MnO	ND	1.47	2.28
Fe_2O_3	5.42	1.22	1.41
NiO	ND	0.01	ND
SrO	ND	0.24	0.5
Y_2O_3	ND	0.02	ND
ZrO_2	ND	0.1	0.08
BaO	ND	0.3	0.85

nents in a typical constituent of a binding material Portland cement and the CM developed is showed in Table 2.

Even though the relative proportion of CaO, SiO_2 and Al_2O_3 in CM was lower than that of Portland cement, the values were not too off the range, with some components falling under blended OPC, indicating the potential binding properties in CM.

Mineralogy of FA and GBFS

The main components both in FA were Mullite, quartz, tricalcium aluminate, and periclase. GBFS was laden with Mullite, quartz, aluminium oxide, sodium oxide and periclase, as shown in Figure 2. The XRD patterns of FA show a broad "amorphous hump" between 5 °C and 13 °C which is a characteristic for this group of materials. For GBFS the hump is centered at 30 representing the partially amorphous characteristic of the slag.

Table 2. Comparison of typical Portland cement, blended OPC and developed CM

	Typical Portland cement[20]	Blended OPC [20]	CM
CaO	62–66%	42–61	59%
SiO_2	20-22%	21–30	16.7%
Al_2O_3	2.5-6%	5–10	6.97%
Fe_2O_3	0-6%		1.41%
SO_3	1.5-2.5%		1.19%

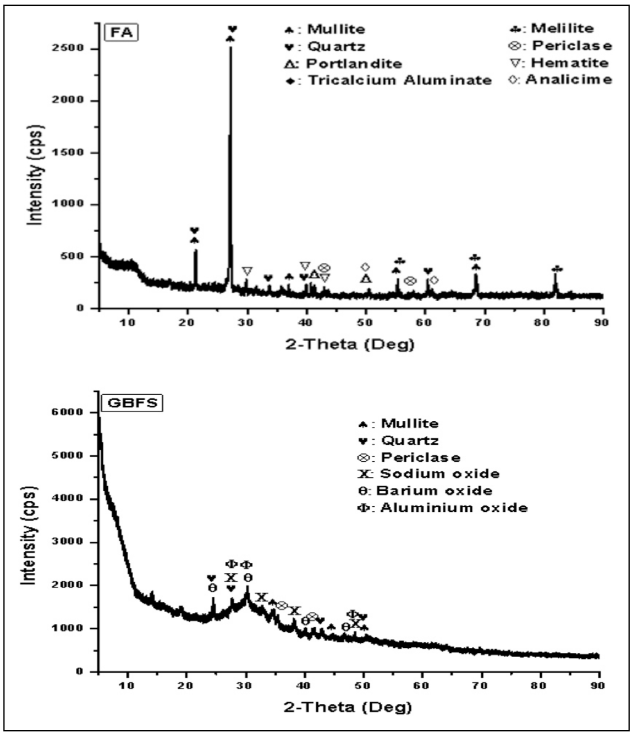

Figure 2. XRD of raw FA and GBFS.

Density and pH of the Materials

The pH and density for FA, GBFS and CM are presented in Table 3.

The results show that fly ash, GBFS and CM are alkaline materials, with pH values more than 7 and ranging between 10.45 and 13.20. A binding material Portland cement has a pH approaching 11. The density of FA was lower than that of GBFS and CM. The density of CM is closer to the density of blended cements which range between 2.9-3.15 gcm-3 [21].

STABILISATION OF FA WITH GBFS AND CM

MDD and OMC of Stabilized FA

The respective MDD and OMC with different mix designs when GBFS and CM as stabilizers are shown in Table 4, respectively.

An increment in the stabilizers content for both GBFS and CM resulted in the increment in MDD, Table 5 and 6. For GBFS as a stabilizer, MDD increased from 1581 kgm-3 to 1803 kgm-3 with GBFS: FA of 10-50% and 50:50, respectively. The MDD for CM stabilized FA increased from 1524 to 1669 kgm-3 for CM:FA of 10-50%. For both stabilizers, the mix design containing 50:50 stabilizer: FA yielded the highest MDD.

Table 3. Density and pH of FA, GBFS and CM

	Fly ash	GBFS	Cementitious material
pH	10.45	11.38	13.20
Density (gcm-3)	2.21	2.91	2.84

Table 4. MDD and OMC of GBFS stabilised FA

Ratios	MDD (kgm-3)	OMC (%)
FA90: GBFS10	1581	13.3
FA80: GBFS20	1598	14.3
FA70: GBFS30	1604	14.9
FA60: GBFS40	1679	14.7
FA50: GBFS50	1803	10.5

Table 5. MDD and OMC of CM stabilised FA

Ratios	MDD (kgm-3)	OMC (%)
FA90: CM10	1524	14.80
FA80: CM20	1584	14.30
FA70: CM30	1604	14.90
FA60: CM40	1660	14.90
FA50: CM50	1669	16:30

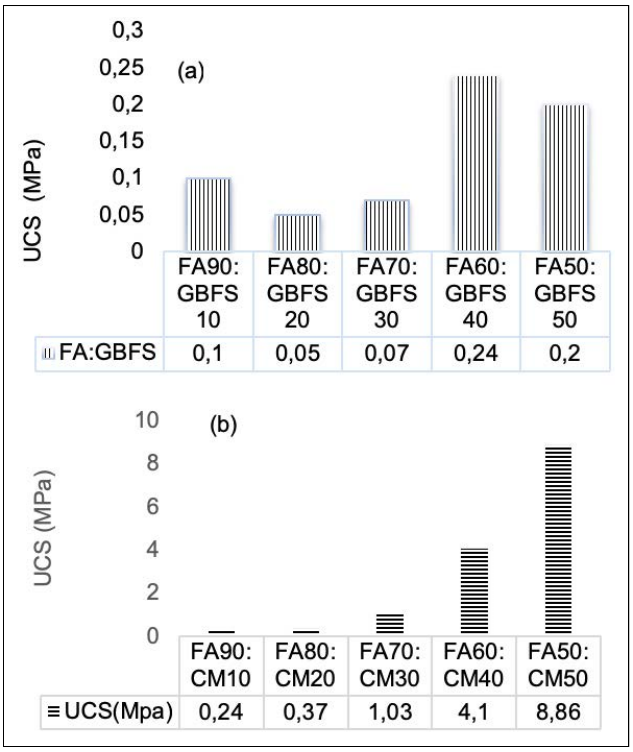

Figure 3. **(a)** UCS of GBFS stabilised FA, **(b)** UCS of CM stabilised FA.

To study if the difference in values obtained for the stabilizers investigated, analysis of variance (ANOVA) was applied as shown in Table 6. The difference was calculated at a statistical significance confidence level limit of 95%. The F value represents a ratio of two variances, which measure the dispersion, and the distance of the data from the mean. The large F value shows greater dispersion. F value is calculated by the formula (F value = variance of the group means (Mean Square Between)/mean of the within group variances (Mean Squared Error). It also represents the extent at which the variability amongst the mean exceeds the expected. F critical represents a ratio of two variances. With a test that yields F value greater than F critical value, the null hypothesis can be rejected.

A critical value of 5.3177 was obtained, a value greater than the F value of 0.6230. This shows that the difference in MDD between the two stabilizers used in all mix designs was not significant.

UCS of Stabilised FA

The results for UCS for GBFS stabilized FA and CM stabilised FA are shown in Figure 3a and Figure 3b, respectively.

The UCS for the different mix designs was measured after curing at the temperature of 80 °C for 4 days. The purpose for this test was to determine the ratio that yielded optimum strength. For GBFS material, the highest strength of 0.24 MPa was obtained with the mix design containing 60% FA and 40% GBFS. The results obtained shows that the composites developed from GBFS as a stabiliser cannot be used for the production of building blocks, as the minimum required UCS for load bearing material is 3.5 MPa. For CM, the highest UCS of 8.86 MPa was attained at the mix design containing 50% CM and 50% FA. The specimen produced with 70-80% FA yielded UCS of 1.03 MPa and 0.37 MPa, this meet the minimum requirement for the material to be used as backfill bearing material, which requires strength within a range of 0.3–2 MPa. The mix design of 60% FA and 40% CM yielded UCS of 4.1 MPa. Using the South African Burnt masonry standard, this value is within requirements for non-facing bricks [22]. Both the mix designs containing 40% and 50% GBFS and CM are applicable for building and construction material. In terms of UCS, the developed specimen meets the minimum strengths requirements to be classified as C1-C3, whereby C2/C3 class material can be used as subbase material [23]. Naganathan et al. [24] investigated the performance bricks made using fly ash and bottom ash

Table 6. ANOVA computation of MDD of GBFS and CM stabilised FA

Source	SS	% SS	df	VAR	F	p	F Critical
Between Groups (SSB)	3763.60	7.23	1	3763.60	0.6230	0.4527	5.3177
Within Groups (SSW)	48326.80	92.77	8	6040.85			
Total (SST)	52090.40		9				

*SS = Sum of squares; df = Degree of freedom; VAR=Variance; SST = Total sum of squares; SSB=Some of squares within groups.

and cement. The UCS obtained with varying of ash and OPC cement was between 7.13 MPa and 17.36 MPa. With the highest UCS of 8.86 MPa obtained in this study when CM was used, this shows that CM exhibits binding properties which may, to some extend be comparable to OPC cement.

Mineralogy of Stabilised FA

The specimen developed after stabilization were also studied for mineralogical analysis, as presented in Figure 4.

In respect to UCS results obtained, it is evident that CM performed better than GBFS. To further understand the mechanism that contributed to higher UCS, the developed composites were studied for the mineralogy. For GBFS:FA composite, an increase in the content of GBFS resulted in a decrease of Mullite and quartz peaks at 28 Theta (deg). A new hydration products, hydrated sodium aluminium silicate ($NaAlSi_2O_6 \cdot H_2O$), is observed in the composite stabilized with CM. Brykov et al. [25] observed that there is depolymerization of low polymeric silica acids, involving hydroxide ions present in the pore solution that occurs when sodium silicates with SiO_2/Na_2O ratio of about 2 and higher are added to the paste before, or simultaneously with, the precipitation of calcium hydrosilicates [25]. This depolymerization has been reported to significantly accelerates the hydration process [25], which contributes to strength development.

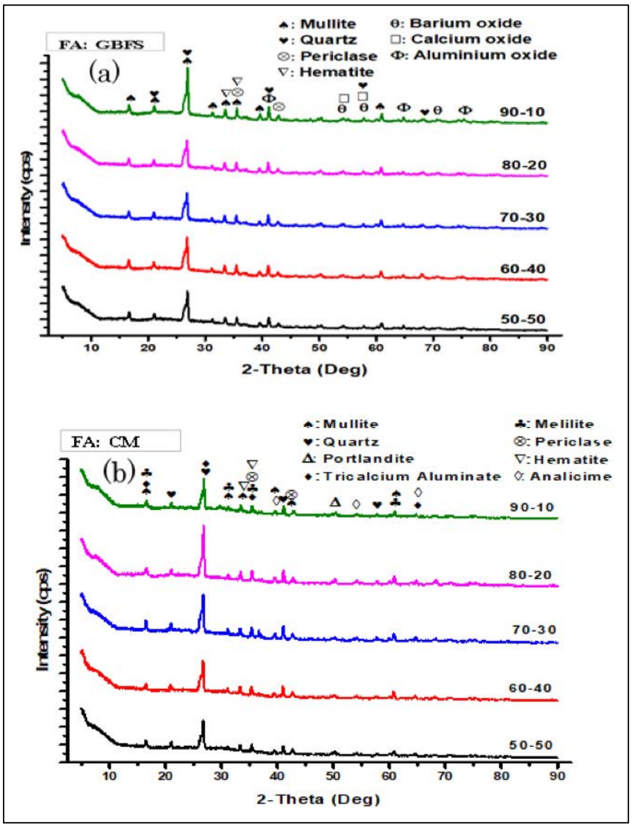

Figure 4. XRD of **(a)** GBFS stabilised FA, **(b)** CM stabilised FA.

EFFECT OF CURING TIME ON THE UCS OF CM STABILISED FA

The CM stabilised FA composites were further studied, to investigate the effect of curing period on the UCS of the composites. Curing periods of 3, 4, 14, 28, 56 and 90 days, at ambient temperature were investigated. The results obtained are presented in Figure 5.

There development of UCS was evident for longer period of curing for up to 90 days. The strength obtained reached 16.03 MPa. According to ASTM C62-10, minimum UCS of 10.3 MPa is required for building bricks (under negligible weather conditions) [26]. Bricks vary in compressive strength ranging from a minimum of 2.4 MPa for different application as shown in Table 6, following ASTM C 270 property specifications [27]. The CM:FA brick cured for 7 days to 90 days can be used for different application with a minimum strength requirement of 2.4–10.34 MPa, Table 7.

MICROGRAPHY OF FA, GBFS, CM, GBFS STABILIZED FA AND CM STABILISED FA

Figure 6 shows the SEM of raw materials (FA, GBFS and CM), GBFS stabilised FA and CM stabilised.

The FA consisting of fine solid spherical particles (microspheres), crystalline phase was also observed in the microstructure of fly ash (Figure 6a). The GBFS comprises of irregular and angular particles (Figure 6b). CM had granular particles, with a rough surface (Figure 6c). In the GBFS stabilised FA there was agglomeration between smaller and bigger particles (Figure 6d). CM stabilised FA composites had more uniform smaller particles (Figure 6e). The developed composited were solid, intact, did not exhibit any cracks and could be handled without any breakage or crumbling indicating good workability of the material.

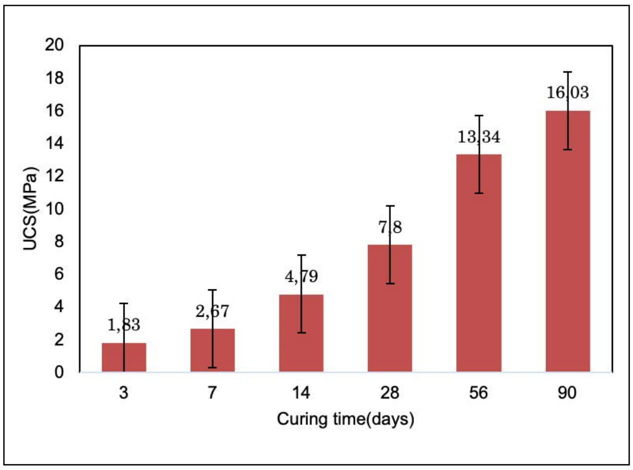

Figure 5. UCS development of CM stabilised FA.

Table 7. ASTM C 270 property specifications: mortar for unit masonry [26]

	Type S mortar	Type N mortar	Type O mortar
Average UCS at 28 days	10.34 MPa	5.17 MPa	2.4 MPa
Uses	Underground, foundations, retaining walls, manholes, sewer walls, brick patios, pavements, and walkways	Above ground, general purpose, interior, exterior, mild load-bearing, chimneys, soft-stone or low-fired brick masonry	Above ground, non-load-bearing, interior.

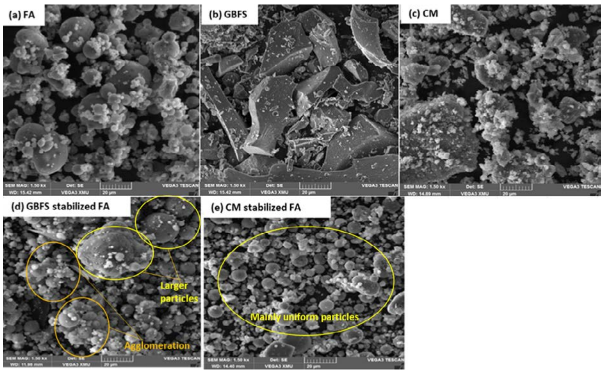

Figure 6. SEM of **(a)** FA, **(b)** GBFS, **(c)** CM, **(d)** GBFS stabilised FA, **(e)** CM stabilised FA.

CONCLUSIONS

This study investigated the use of geopolymerised cementitious material and granulated blast furnace slag as additives to stabilise readily available fly ash. GBFS had limitation in improving the properties of FA. CM synthesised from a geopolymerisaton process proved to have binding properties, that are close to that of cement. This was shown by evaluating the elemental analysis. Long term unconfined compressive strength development of 16.03 MPa when the composites were cured for 90 days was obtained. This study also proved that voluminous quantities of FA can be used to produce building materials, this was proven by optimum strength obtained from a mix design containing 50% FA and 50% CM. Comparing the strength to normal commercial mortar bricks, which stipulates a minimum UCS of 3.5 MPa for loadbearing material for burnt masonry clay according to The South African standard (SANS 227, 2007) [22], it was evident that building bricks can be produced successfully from CM and FA. In a country where access to housing is a societal challenge, the developed solution can be explored. This will not only address the societal challenges in South Africa but it will provide a solution to environmental challenges as a result of landfilled FA.

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Conflict of Interest:

The authors declare that they have no conflict of interest.

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