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Utilization of Fly Ash - A Waste Byproduct of Coal for Shielding Application

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Absrtract

A matrix having conducting, magnetic and dielectric filler, due to their unique attenuation and electrical properties have shown their potential application in electromagnetic interference (EMI) shielding. However, the difficulties of reflection of microwave are yet to be overcome. Recently, exfoliated graphite along with iron oxide and fly ash found to a better alternate to the conventional shielding materials. Conductivity of composites lies in the range 0.013"14.57 S/cm. The microwave absorption properties of the composites have been studied in the 8.2-12.4 GHz (X"Band) frequency range which shows a shielding effectiveness up-to 59.83 dB, which strongly depends on dielectric loss and weight fraction of fly ash and γ-Fe_2O_3 in EG matrix.

Keywords : *Composite materials, Magnetically ordered materials, X-ray diffraction (XRD), Scanning electron microscopy (SEM)*

1. INTRODUCTION

In the modern electronic era, all commercial, military equipment, scientific electronic devices, communication instruments and radiation sources require electromagnetic shielding because of the massive use of electronics and radio frequency radiation sources. Electromagnetic interference (EMI) is undesired byproduct of electronic devices which can interfere with other electrical or electronic equipment whereas EMI shielding refers the restriction of electromagnetic fields into a space by reflecting or absorbing them with a barrier, which thereby acts as a shield against the penetration of the field through the shield. Electrically conducting composites have gained popularity recently, compared to conventional metal-based composites, because of their light weight, resistance to corrosion, flexibility, and processing advantages.[1] It is observed that at a given frequency, the high conductivity, magnetic permeability, thickness and dielectric constant of the materials are important for better electromagnetic interference (EMI) shielding[2]. Therefore, metals are good reflectors and commonly used for EMI shielding. On the other hand absorption based shield can be made using carbon-based materials[3, 4], such as carbon black[5], graphite[6], graphene oxide (GO) [7], carbon fibers[8, 9] and conducting polymers[10, 11], along with some magnetic and dielectric filler. At the same time, the ability to make stronger bond with materials along with the high conductivity, saturation velocity, flexibility and mechanical strength of exfoliated graphite (EG) make it an excellent choice for high-performance EMI shielding. [6, 7]. Flyash (FA) have so far drawn great concerns from both academia and industries, Since FA lacks the ability to shield electromagnetic pollution, hence coating of EG along with magnetic filler play a major role in achieving high value of SE and used to customized electromagnetic properties of FA based material. The shielding in the frequency range of 8.2-12.4 GHz (X band) is

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The EMI SE of a composite material depends mainly on the filler's intrinsic conductivity[13], dielectric constant, and wt% ratio. Beside high electrical conductivity, it's very high surface area of graphene[14] which makes it a unique candidate to having moderate EMI shielding[15] in polymer composites with light weight. However, graphene lacks in magnetic properties and hence participated less in absorption of EM waves. In order to overcome this limitation we have incorporated different wt% ratios of iron oxide???-Fe_2O_3)[16-19] in EG matrix which absorbs more electromagnetic interference because of its magnetic permeability.

Here, we report, the waste material of coal power plant - fly ash which can be used as dielectric filler in EG matrix containing magnetic nanoparticles to customize the properties of fly ash for EMI SE applications.[20, 21] The obtained results of composite are focused on the conductivity, shielding measurements and surface morphology of EG/γ-Fe_2O_3/fly ash three phase systems. Octadecylamine (ODA) has been used as a capping agent in composites. The composites having thickness 2.5±0.1 mm have shown high value of shielding effectiveness ranging from 32.16 to 59.83 dB (~99.99%) in the microwave range (X-band).

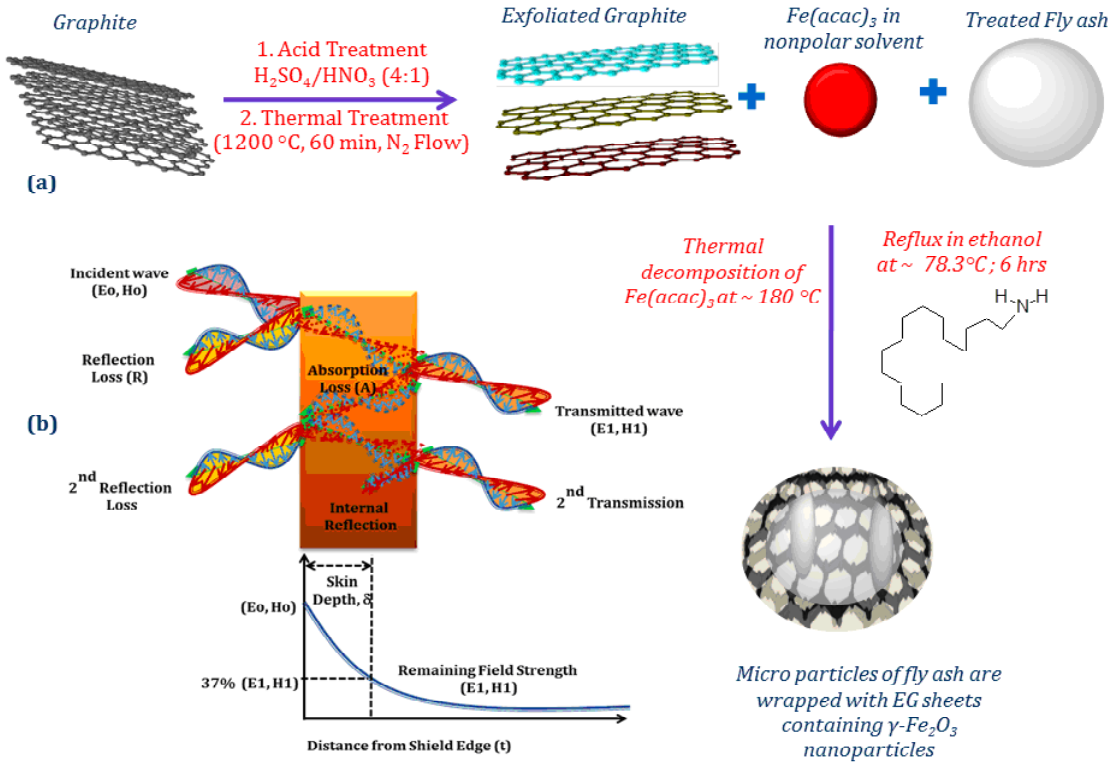
2 EXPERIMENTAL SECTION

2.1 Materials

Expandable graphite (Grade extra pure, particle size 60 mesh) has been procured from Loba Chemie, India,. Ethanol and Iron acetylacetonate has been procured from Merck, India. Double distilled water (specific resistivity of 10^6 &!-cm) used for have been preparing aqueous solutions and for filtration purpose. ODA has been procured from Across Organics, USA. H_2SO_4 and HNO_3 were purchased from Sigma-Aldrich, India. The other chemicals were of reagent grade and were used as received. Fly ash is used after removing unburned carbon and other oxides and named as treated fly ash.

2.2 Insitu synthesis of r-Fe_2O_3 nanoparticles in fly ash, EG matrix: EGIOFA composite

The synthesis of EGIOFA composite was carried out by the in situ generation of ?-Fe_2O_3 nanoparticles in a EG matrix containing flyash particles by chemical reflux method. Prior to EGIOFA synthesis, In a typical process, to obtain graphite intercalated compound (GIC), the natural graphite powder (5 g) was dispersed in a 4:1 mixture of concentrated H_2SO_4/HNO_3 (160:40 mL) at room temperature and the mixture was put in an ace bath for 1 hour. The addition of a large amount of deionized water (2000 ml) to the above mixture caused violent effervescence and temperature was increased to 50°C, The mixture was then stirred at 65 °C for 24 hours by to form the GIC. The GIC suspension was centrifuged (10000rpm, 30min) and the supernatant was decanted away. The remaining solid material was then washed two times in succession with 200 mL of water, 200 mL of ethanol. For each wash, the mixture was centrifuged (10000 rpm for 30 min) and the supernatant decanted away. The paste collected was dried at 100±5 °C in a vacuum oven, which is then rapidly exfoliated at temperatures between 800 and 900°C to form EG[22, 23]. But, it is observed that EG is not transformed in single or double layer graphene sheet because of insufficient oxidation of natural graphite while doing acid treatment or inadequate pressure that builds-up during thermal and chemical exfoliation. Next, The EG, iron acetylacetonate, fly ash and ODA were mixed in ethanol and refluxed for 5 hours at 80°C. The subsequent mixture is further heated to 230°C and checked simultaneously with external magnet until the magnetic property appear in the sample. The composites of EG, ?-Fe_2O_3 and fly ash have been formed by fixing 1 wt% of EG, 1 wt% of iron oxide and by varying fly ash ratio from 1, 2, 3, 4 wt% and are abbreviated as EGIOFA1, EGIOFA2, EGIOFA3, EGIOFA4 respectively.



Scheme 1. (a) Schematic representation of preparation of different composites of EG/?-Fe_2O_3/fly ash by fixing 1 wt% of EG, 1 wt% of iron oxide and with varying ratios of fly ash using ODA as a capping agent in the organic medium (b) illustrates the interaction of electromagnetic wave with the shield.

more important for radar and radio communications applications[12].

2.3 Materials Characterization

The surface morphology of EG, fly ash and EGIOFA1 have been examined using scanning electron microscope (SEM, Zeiss EVO MA"10) at an acceleration voltage 10.0 kV. The dc electrical conductivity of EG composites has been measured by a standard four-probe technique on pressed rectangular pallets of dimension 13.0×7.0×1.00± 0.1 mm^3 at room temperature in order to eliminate contact resistance effects, using Keithley programmable current source (model 6221) and nano voltmeter (model 2182A). Electromagnetic shielding [24-26] have been carried out using

Agilent E8362B Vector Network Analyzer in the 8.2"12.4 GHz (X"band) microwave range. The composite has compacted in a piston cylinder assembly at 60MPa for 5 min into a 2.0 ± 0.2 mm thick rectangle pellet with a dimension to fit the waveguide dimensions. Schematic representation of incorporation of ?-Fe_2O_3 and fly ash into EG matrix is shown in Scheme 1.

3. RESULTS AND DISCUSSION

3.1 Scanning electron microscope analysis

SEM examination was carried out to

determine the distribution of EG, ?-Fe_2O_3 and fly ash in the composites. The fly ash particle size is seen up to few micrometers as seen in Figure 1 (a). Figure 1 (b) shows the sheets of EG having area of 2-10 cm^2. Determination of thickness of EG platelets is considered difficult by SEM. It is well known that the back scattered electrons (BSE) image provides information on the composition of the sample[27]. Figure 1(c) demonstrates that EG sheets containing magnetic nanoparticles are incorporated on fly ash surface and there is some spacing between them.

3.2 Conductivity Measurements

The maximum value of conductivity of the order of 14.57 S/cm is observed for EGIOFA1 and minimum value of 0.013 S/cm is observed for EGIOFA4. It is acceptable because the higher wt% of insulating ?-Fe_2O_3 and fly ash particles hinders the free flow of electrons in the composite. According to percolation theory, the electrical conductivity of a material is determined by the ability to form a conducting network. EGIOFA1 shows high conductivity because of high wt% loading of EG which forms conducting network. Although electrical conductivity of EG and EGIOFA1 is high, but it is much smaller than that of graphene reported theoretically. This is because the inter transport of charge carriers in EG and EGIOFA1 is a complex phenomenon of electron tunneling and hopping and is different from single layer of graphene. Due to loading of ?-Fe_2O_3 and fly ash, the electrical conductivity and EMI shielding properties have been adversely affected for composites due to insulating character of fly ash. Table1 shows the variation of electrical conductivity of EG/?-Fe_2O_3/fly ash composites having different weight fraction ratio of flyash 1, 2, 3, 4 wt%. It is observed that electrical conductivity falls sharply on higher loading of fly ash. This is contributed to two reasons. Firstly, the fly ash particles are insulating in nature. Secondly, as we kept the % of ?-Fe_2O_3, EG fixed and on increasing the loading of fly ash results in reduction in conductivity of EG composites.

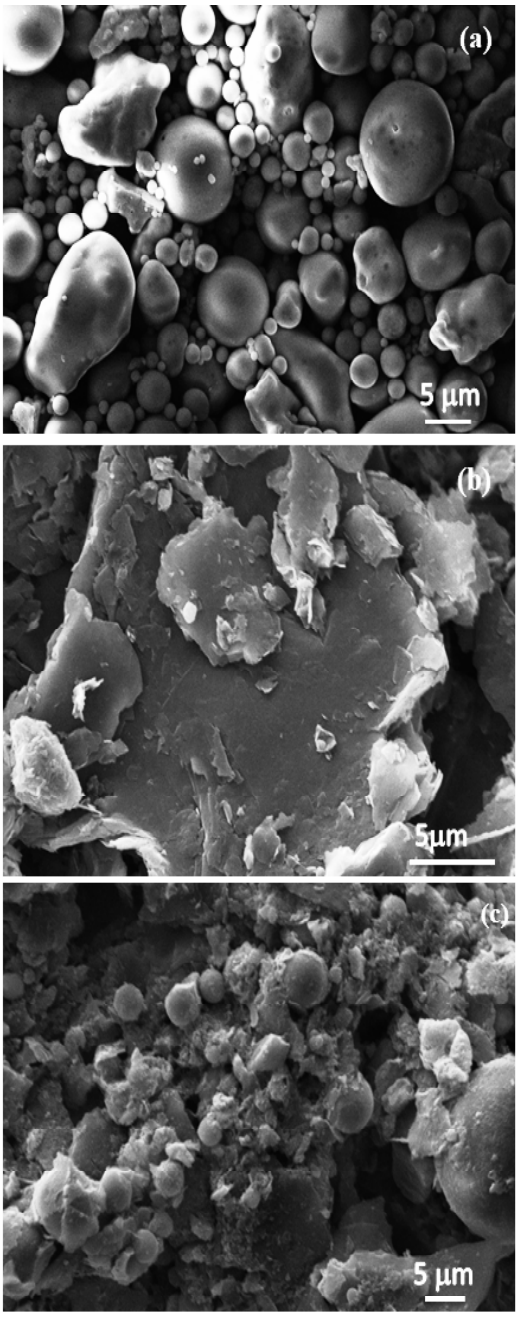


Fig. 1. (a) SEM images of fly ash micro-particles, (b) EG sheets, (c) EGIOFA1 having EG, $Fe(acac)_3$ and fly ash are taken in 1:1:1 wt.% ratio by using ODA as a capping agent in the ethanol medium

3.3 X-ray diffraction analysis

Fig .2 shows the XRD spectra of EGIOFA1, fly ash, exfoliated graphite and iron oxide. The main peaks for iron oxide are observed at 2θ=30.263° (d=2.9530 Å), 2θ=35.659° (d=2.5177 Å), 2θ=49.779° (d=1.83027 Å), 2θ=57.321° (d=1.6073 Å) and 2θ=62.981° (d=1.4758 Å) corresponding to the (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) reflections which matches with the standard XRD pattern of γ-Fe_2O_3 (Powder Diffraction File, JCPDS No. 39–1346). The main peaks of exfoliated graphite are observed at 2θ=26.524° (d=3.347 Å) and 2θ=54.821° (d=1.673 Å). The main peaks of fly ash are fixed at 2θ=26.660° (d = 3.3409 Å), 33.240° (d = 2.6931 Å), 35.260° (d = 2.5433 Å), 40.880° (d = 2.2057 Å), 42.620° (d = 2.1196 Å), 54.040° (d = 1.6955 Å), 60.680° (d = 1.5249 Å) and 64.500° (d = 1.4435 Å). The peaks present in γ-Fe_2O_3 and fly ash were also observed in EGIOFA1 which indicate the presence of ferrite particles and fly ash in the EG matrix. While the presence of EG is confirm by the broad peaks at 2θ=26.441° (d=3.368), 2θ=54.599° (d=1.679 Å) in the composite.

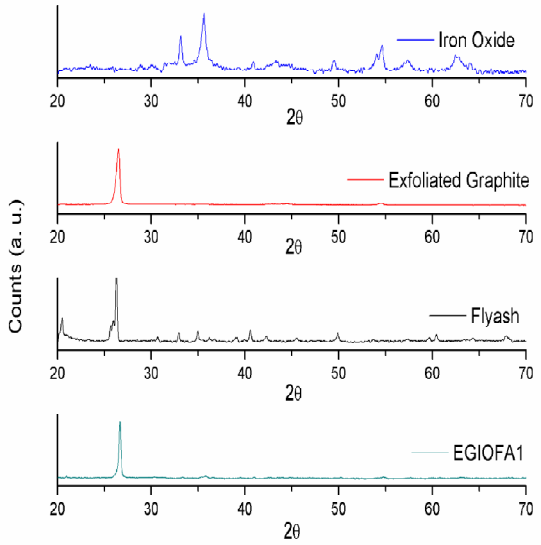


Fig. 2: X"ray diffraction patterns of EGIOFA1, fly ash, exfoliated graphite and iron oxide.

Table 1: Variation of electrical conductivity and shielding effectiveness of EG/?-Fe_2O_3/fly ash composites

Sample Name	Thickness mm	σ (S/cm)	Shielding Effectiveness (dB)
EG	1.0 ± 0.07	1531.57	--
Fly ash	1.0 ± 0.08	1.27×10^{-9}	8.36 ± 0.78
EGIOFA1	2.5 ± 0.12	14.57	59.83 ± 0.41
EGIOFA2	2.5 ± 0.16	6.18	47.62 ± 0.72
EGIOFA3	2.5 ± 0.13	0.47	36.83 ± 0.54
EGIOFA4	2.5 ± 0.08	0.013	32.16 ± 0.78

The crystalline size of γ-Fe_2O_3 particle can be calculated by using Debye Scherer's formula

$$D = k\lambda / \beta Cos\theta$$

Where D is crystalline size for individual peak, λ is the X-ray wavelength, K the shape factor, θ is the half angle in degrees, and β is the line broadening measured by half-height in radians. The value of k is often assigned a value of 0.89, which depends on several factors, including the Miller index of the reflecting plane and the shape of the crystal. The average size of iron oxide particles was calculated using above equation and estimated as 20.78 nm for pure iron oxide

3.4 Electromagnetic shielding

The EMI shielding effectiveness (SE) of a material is expressed in terms of ratio of incident and transmitted energy and can be mathematically expressed in logarithmic scale as

$$SE(dB) = 10\log(P_T / P_I) = \mathrm{SE_R} + \mathrm{SE_A} + \mathrm{SE_M} \quad (2)$$

where P_I and P_T are the power of incident and transmitted EM waves respectively, whereas SE_R, SE_A and SE_M represent the contributions in total shielding effectiveness due to reflection,

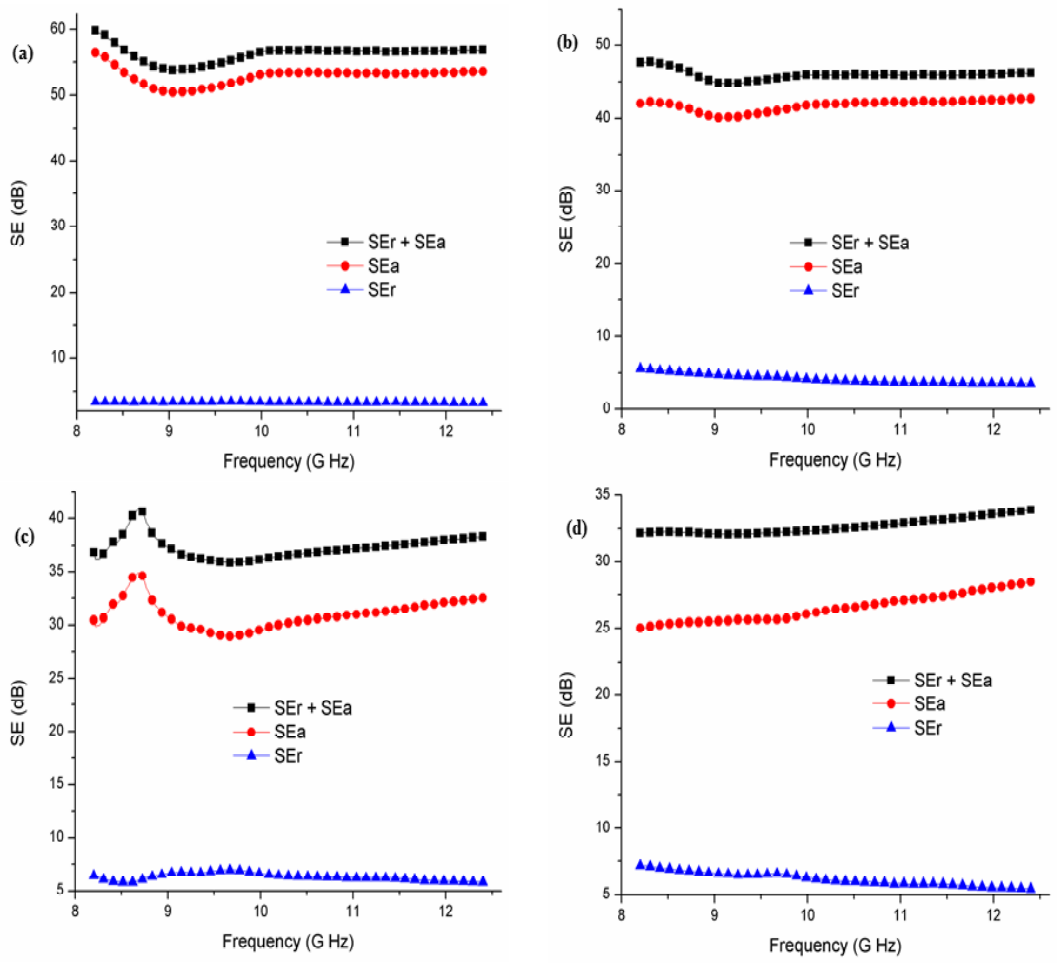


Fig 3. Variation in EMI shielding effectiveness SE_A, SE_R and total SE of (a) EGIOFA1, (b) EGIOFA2, (c) EGIOFA3 and (d) EGIOF4 as a function of frequency

absorption, and multiple reflections respectively and can be defined as

$$SE_R = -10\log(1-R) \quad (3)$$

$$SE_A = -10\log(1-A_{eff}) = -10\log(T/1-R) \quad (4)$$

$$SE_M = -20\log(1-e^{-2t/\delta}) = -20\log(1-10^{-SE_A/10}) \quad (5)$$

whereas SE_M is multiple reflection between both faces of shield and can be neglected when SE_A >10 dB.[28-30] Therefore, the effective absorbance (A_{eff}) can be expressed as

$$A_{eff} = (1-R-T)/(1-R)$$

with respect to the power of the effectively incident EM wave inside the shielding material Fig. 3 shows the dependence absorption, reflection and total EMI SE with frequency in the 8.2-12.4 GHz range. From the experimental measurement, the shielding effectiveness for the composite EGIOFA due to absorption (SE_A) has been found to vary from 56.45"25.01 dB in the composite while the SE_R varies from 3.38 to 7.15 dB for the composites.

Thus, the total SE achieved for the fly ash composite is 59.83 dB (EGIOFA1) which is much higher than the pristine fly ash. It has been observed that for conducting EG/?-Fe_2O_3/fly ash composite, shielding effectiveness (SE) is mainly dominated by absorption while the shielding effectiveness due to reflection (SE_R) is constant and contributes comparatively little.

4. CONCLUSIONS

EG and its composite with iron oxide and fly ash (EGIOFA1) have been successfully prepared by using chemical reflux method. The fly ash particles are wrapped with EG layers containing iron oxide nano particles embedded in between the layers enhances the interfacial polarization and the effective anisotropy energy of composite, which contributes to high shielding effectiveness (SE_A~56.4 dB) as compared to conventional fly ash. Addition of nano particles of iron oxide (magnetic filler) and fly ash in the conducting EG matrix gave a new kind of composite materials having better microwave absorption properties (SE_T~59.83 dB) which strongly depends on weight fraction of iron oxide and fly ash in EG matrix. As a result, fly ash composite with dielectric core are also promising as new types of microwave absorption materials with usability in radio frequency range maintaining strong absorption. The presence of conducting matrix, magnetic filler and dielectric are helpful for proper impedance matching, which is necessary for enhancing the absorption of the electromagnetic wave. These exceptional properties of new composite using waste fly ash which is byproduct of coal based thermal power stations, assure that it could be an ultimate choice for future building block of EMI SE applications.

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