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Valorization of Phosphogypsum in Crushing-Sand- Phosphogypsum -Cement-Lime Solid Bricks Grade SW

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Abstract

Phosphogypsum (calcium sulfate) is a naturally occurring part of the process of creating phosphoric acid (H3PO4), an essential component of many modern fertilizers. For every tonne of phosphoric acid made, from the reaction of phosphate rock with acid, commonly sulfuric acid, about 3 t of phosphogypsum are created. There are three options for managing phosphogypsum: (i) disposal or dumping, (ii) stacking, (iii) use-in, for example, agriculture, construction, or landfill.The need to reduce solid waste volume has caused scientists to invent new construction materials produced using waste materials. In this study, phosphogypsum (PG) from Tunisia, crushing sand (CS), natural hydraulic lime (NHL), cement (C) and water are used in solid bricks production. phosphogypsum, crushing sand, natural hydraulic lime and cement were mixed, humidified, compacted and cured for periods of 28, 56 and 90 days. The compressive strength, density, water absorption, saturation coefficient and leaching test of the bricks were measured.The obtained results showed that CS-NHL-C-PG bricks are found to be conforming to physical requirements of clay or shale building brick grade SW (severe weathering), bricks intended for use when high and uniform resistance to damage caused by cyclic freezing is desired and where the brick may be frozen when saturated with water. Therefore, CS-NHL-C-PG bricks can replace the clay or shale brick grade SW.

KEYWORDS: Phosphogypsum; Full brick grade SW; strength; water absorption, leaching test

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I. INTRODUCTION

Phosphogypsum is a by-product from the production of phosphoric acid by the wet process. In this process, the raw phosphate is treated by sulfuric acid and, besides the main Product which is phosphoric acid (H3PO4), gypsum and a small quantity of hydrofluoric acid are obtained. For every tonne of phosphoric acid made, about three tonnes of phosphogypsum are yielded. It is estimated that more than 22 million tonnes of anhydrous P2O5 are produced annually worldwide, generating in excess of 110 million tonnes of gypsum by-product [1]. Residual phosphogypsum is highly acidic (pH 1). Commercial uses, in agriculture and in manufacturing gypsum board and Portland cement, consume less than a few percent of this by-product. The vast majority is disposed of on land in gypsum stacks or is discharged into water bodies.Worldwide, four methods are being used by the phosphate industry to dispose of surplus phosphogypsum, namely: (i) discharging to water bodies; (ii) backfilling in mine pits; (iii) dry stacking; and (iv) wet stacking. Phosphogypsum consists primarily of calcium sulfate dehydrate with small amounts of silica, usually as quartz, and unreacted phosphate rock. Radium and uranium, aswell as minor amounts of toxic metals, namely, arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver and phytotoxic fluoride and aluminum are also present in phosphogypsum and its pore water. The concentra-tions of heavymetals and radionuclides depend on the composition of the phosphate rock feed. Aside from piling up in significant quantities wherever phosphate is processed, phosphogypsum also effuses radon gas which is radioactive. This means that phosphogypsum is inherently radioactive at some level. Exposure to high enough quantities, such as working for many years in a dust filled environment or through drinking water, could introduce enough radiation into the body to have the same effects as uranium refining tailings [2], [3], [4]-[5]. There are several areas of utilization for phosphogypsum. The two main fields are conversion of phosphogypsum to plaster and plaster products and replacement of natural gypsum in cement production. Unfortunately, high energy consumption is needed to dry phosphogypsum and the utilization of phosphogypsum is therefore limited [1], [2], [3], [4], [5]-[6]. By far, the biggest issue facing Tunisia's phosphate industry today is pollution.

Sfax is one of the most polluted places in all of the Mediterranean Sea. This is a result of several factors including not treating the liquid effluent streams of the refineries, and the massive accumulation of phosphogypsum piles which are unprotected from the elements. It is estimated that 10 million tonnes of phosphogypsum are annually produced. In Tunisia, phosphogypsum is currently contained by dumping it in large warehouses. When it rains or when the wind blows, phosphogypsum gets spread around the general vicinity of

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these warehouses long hot and dry summers in Tunisia mean that there are many phosphogypsum particulates floating around in the atmosphere. To deal with the phosphogypsum, Tunisia has decided to burry it somewhere in the interior of the country where it will have minimal environmental impact [7].

Some ways of valorization have also been investigated. Concerning Tunisia, the natural gypsum of good quality exists in many regions. This gypsum is employed among others to manufacture plaster for which consumption at the national level is less than 0.1 million tonnes per year. The purification of phosphogypsum for use in the plaster industry is not competitive for Tunisia. Not purified phosphogypsum was used in embankment construction [8]. The characterization of the Sfax phosphogypsum has pointed out a low radioactivity level, compared to other phosphogypsum in the world, but a very bad behaviour towards immersion. Phosph- ogypsum was treated by limestone sand and cement, for road use [9]-[10].

This paper presents the research work undertaken to study the properties of this new composite material which contains the various levels of, phosphogypsum (PG) from Tunisia, crushing sand (CS), natural hydraulic lime (NHL), cement (C) and water.

II. EXPERIMENTAL PROGRAM

A. Characteristics of the studied PG

The real densities of the grains were determined by the pycnometer method, by using water saturated with gypsum. The studied PG presents a density of about 2300 kg/m3. The high value is explained by a strong presence of impurities.

The chemical composition of PG is presented in Table 1. The PG is primarily (about 77%) made up of calcium sulfate (CaSO4). The remaining components are present at low percentage. It should be noted that the pH of PG samples are around 2.9, indicating a high acidity of the PG. Table1

Table I. Chemical composition of phosphogypsum

Elements	(%)
CaO	32.8
SO_3	44.4
P_2O_5	1.69
F	0.55
SiO_2	1.37
Fe_2O_3	0.03
Al_2O_3	0.11
MgO	0.07
Ignition loss at 1000°C	22.3

B. Characteristics of the crushing sand

Fig. 1 presents the granulometric curve of the crushing sand. The granular distribution of crushing sand was obtained by dry sieving. Fig. 1 shows also a suitable uniform

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granulometry, consequently, it gives an optimum compactness which influences the strength, mainly in compression.

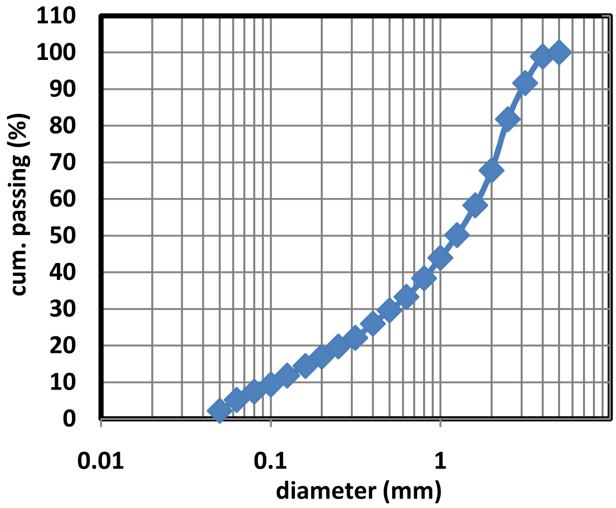

Fig. 1. Granulometric curve of the crushing sand.

The real densities of the grains were determined by the pycnometer method. The studied crushing sand presented a density of about 2740 kg/m3. This value is higher than the one of phosphogypsum.

C. Manufacturing of CS-NHL-C-PG solid bricks

1) Optimization of mixes:

The optimization of the mixes is based on the results of the evolution of pH of Phosphogypsum- crushing sand-lime mixtures. Figure 2 show that the crushing sand-mix increased slightly the pH without reaching neutralization. Therefore, a small adding lime (2%) is necessary.

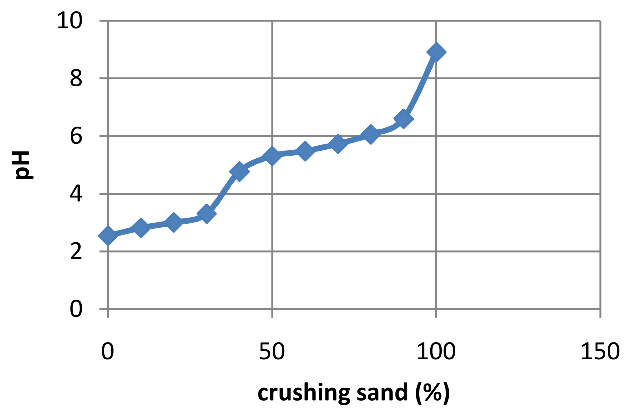

Fig. 2. pH phosphogypsum-sand mixtures versus crushing sand proportioning

Fig.3 shows the evolution of pH values with adding natural hydraulic lime. These results indicate that the adding of lime has allowed the neutralization of Phosphogypsum- crushing sand mixtures. All the formulations phosphogypsum-sand-lime presents white spots on the brick surface. To solve this problem, minor amounts of cement HRS 42.5 (3 to 10%) was introduced

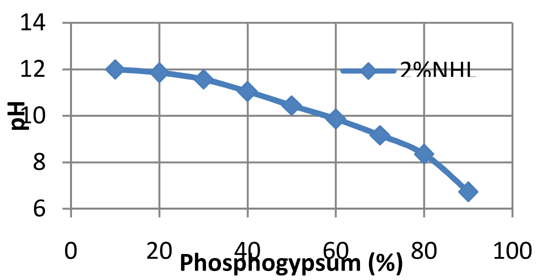

Fig.3. pH phosphogypsum-sand mixtures versus natural hydraulic lime (NHL) proportioning

The optimum composition of phosphogypsum-crushing sand-lime-cement mixes is based on the results of the evolution of pH. Figure 4 shows that the pH increases slightly with the addition of 3 and 4% cement. A significant rise in pH is remarkable from 5% cement. Besides, the pH shows a significant rise for mixtures which contain 2% CHN, 5 to 10% cement, 60 to 80% phosphogypsum and the rest is that of crushing sand. Mixtures containing 2% CHN, 5 to 10% cement, less than 60% of phosphogypsum and the rest crushing sand, shows a very slight increase of pH. Thus the percentages are set to 2% CHN, 5, 7.5 and 10 of cement, 60 to 80% phosphogypsum and the rest is that of crushing sand.

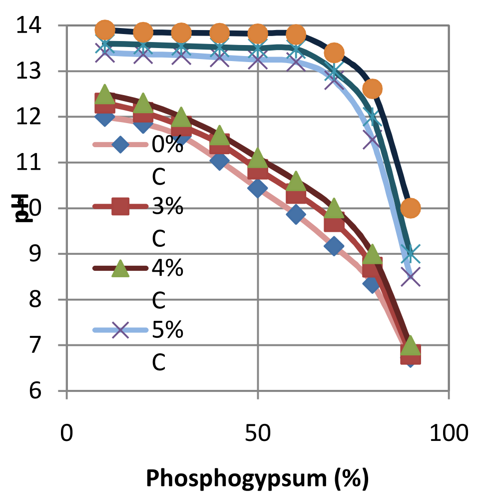

Fig.4. pH phosphogypsum-sand-lime-cement mixtures versus cement proportioning

The mix proportions of phosphogypsum, crushing sand (CS), lime and cement (cement HRS 42.5) for bricks are given in table 2. The mix proportions are given in terms of dry weights of the ingredients. The water contents of Phosphogypsum-crushing sand-lime mixtures were fixed to 5 %. Bricks produced with more than 5 % showed cracks after fabrication due to excessive water.

Table II.Mix proportions of CS-NHL-C-PG full bricks

Mix désignation	Constituant materials (Weight %)			
	Phosphogypsum	Sand (CS)	Cement	Lime
P-1	60	33	5	2
P-2	60	30.5	7.5	2
P-3	60	28	10	2
P-4	70	23	5	2
P-5	70	20.5	7.5	2
P-6	70	18	10	2
P-7	80	13	5	2
P-8	80	10.5	7.5	2
P-9	80	8	10	2

2) Mixing and fabrication of bricks: The dry phosphogypsum is sieved through 1 mm sieve. The weighed quantity of phosphogypsum, crushing sand, lime and cement are first thoroughly mixed in dry state for a period of 10 minutes to uniform blending. The required water is then gradually added and the mixing continued for another 5 min.

All full bricks were made on a bench model, semiautomatic press having a capacity of 25 tons, to produce bricks of 0.051×0.095×0.203 m in size under a static compaction of 27MPa. (Fig. 5).

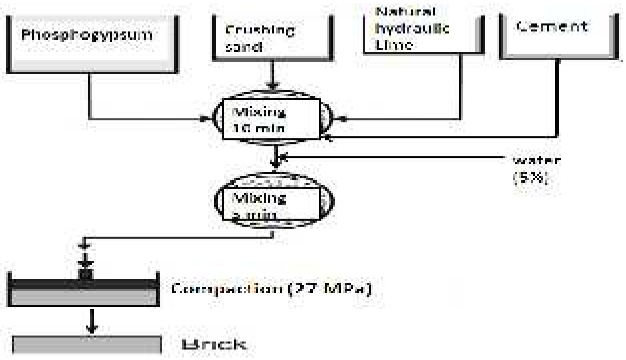

Figure. 5. Brick production.

D. Testing of Bricks

All bricks were dried to the free air for a period of 28, 56 and 90 days. The durability of phosphogypsum-based bricks was investigated by submersion in cold and boiling water.

Compressive strength, density, water absorption, saturation coefficient and leaching tests of bricks from different mixes of phosphogypsum, crushing sand, lime and cement with available mixing water content were determined.

1) Compressive strength: Compressive strength of the units was determined according to ASTM C67 [11]. ASTM C67 requires that the size of test specimen be full height and width, and approximately one-half of a brick in length, plus or minus 25.4 mm. Although ASTM C67 does not specifically state the method in which the samples are to be obtained.

The introduction of an eccentric load, if the specimen is not carefully centered, can result in a lower apparent compressive strength for the test specimen. Therefore, the specimens were carefully centered. Five specimens were tested.

2) Water absorption and saturation coefficient: Rate of absorption is an important property of brick because it affects mortar and grout bond. If the rate of absorption is too high, brick will absorb moisture from the mortar or grout at a rapid rate, thus impairing the strength and extend of bend.

Bricks contain pores; some may be “through” pores, others are “cul-de-sac” or even sealed and inaccessible. The “through” pores allow air to escape in the 24 hours absorption test and permit free passage of water. However, others in a simple immersion test or vacuum test do not allow the passage of water, hence the requirement for five hours boiling test. The absorption is the amount of water which is taken up to fill these pores in a brick by displacing the air. The saturation coefficient is the ratio of 24 hours cold absorption to maximum absorption in boiling.

Water absorption and saturation coefficient was determined according to ASTM C67 [11]. The test specimens were consisted of half bricks. Five specimens were tested.

3) Density: In order to determine the density of each brick, dry bricks were weighed accurately and their volumes were measured.

4) Leaching test: The leaching tests had been performed according to the French Norm NF EN 12457-3 [12] at an ambient temperature (20 ± 5°C). The specimens (three different samples for each mix-design) were crushed and an amount of 0.175 kg was taken to be analyzed. The distilled water was added to obtain a liquid/solid ratio of 10 l/kg.

The compressive strength of phosphogypsum-crushing sand-lime-cement full bricks was tested after 28, 56 and 90 days of treatment. Water absorption, saturation coefficient, density and leaching test were determined on bricks tested after 28 days of casting.

III. TEST RESULTS AND DISCUSSION

A. Dry density

The densities of CS-NHL-C-PG full bricks are shown in table 3. These densities range from 1621.5 to 1832 kg/m^3. Therefore the CS-NHL-C-PG full bricks have high density.

Table III. Dry densities (kg/m^3) of WS-NHL-C-PG full bricks

Mix désignation	Dry densities (kg/m^3)
P1	1621.5
P2	1636
P3	1662
P4	1630
P5	1660
P6	1690.5
P7	1759
P8	1796
P9	1832

B. Water absorption of studied bricks

Table 4 presents the results of the water absorption for the selected percentages of the bricks. The values obtained were favorable when compared with those of clay bricks (0 to 30%) [13].

The 24-h cold water absorption of each unit of a random sample of five CS-NHL-C-PG bricks exceeds 8%. So, the saturation coefficient requirement does apply [14].

The Water absorption after 24 hours in cold water+5hours in boiling water is shown in table 4. The fact that water absorption of bricks increased after 5hour boiling was noticed. This is due to that the 24 hours submergence alone will not fill all the pores spaces in a brick, so more will become filled during the boiling stage.

Besides, the results show that the water absorption by 5-h boiling of phosphogypsum-crushing sand-lime-cement bricks is less than the maximum limit for clay building brick grade SW (severe weathering) set by ASTM (17%) [14].

Table IV Physical characteristics of CS-NHL-C-PG full bricks

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Mix designation	Water absorption after 24 hr cold water (%)	Water absorption after 24 hr cold water +5hr boiling (%)	Saturation coefficient
P1	13.38	17.1	0.78
P2	11.32	15.1	0.75
P3	10.36	14.2	0.73
P4	12.1	16.13	0.77
P5	10	13.51	0.74
P6	9.2	12.77	0.72
P7	9.1	11.97	0.76
P8	8.7	11.75	0.74
P9	7.5	10.56	0.71

C. saturation coefficient

The saturation coefficient of those bricks is shown in table 4. The saturation coefficient of phosphogypsum-based bricks is less than the maximum limit for clay building brick grade SW set by ASTM (0.78)[14]. Therefore CS-NHL-C-PG bricks have severe resistance to damage by freezing when wet.

D. Compressive strength

The results, obtained as an average of measurements performed on three specimens, are shown in Figs. 6-8. For all the studied cases, the compressive strength of the 90 days cured full bricks was higher than 20.7 MPa, which is the minimum strength indicated by the standards [14].

These Figures also shows increase in the compressive strength with the phosphogypsum and cement additions. This result confirms the water absorption test outcome, where it has been indicated that the addition of phosphogypsum produces a decrease in the internal pore size. Thus, the brick becomes less porous causing an increase in the mechanical strength.

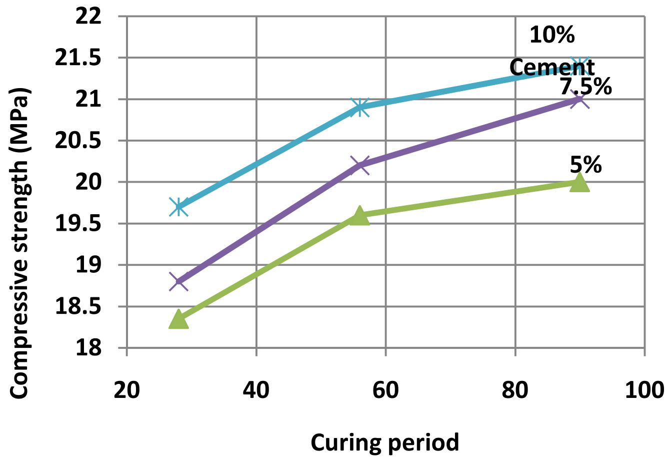

Figure.6 Compressive strength of CS-NHL-C-PG full bricks (phosphogypsum=60%)

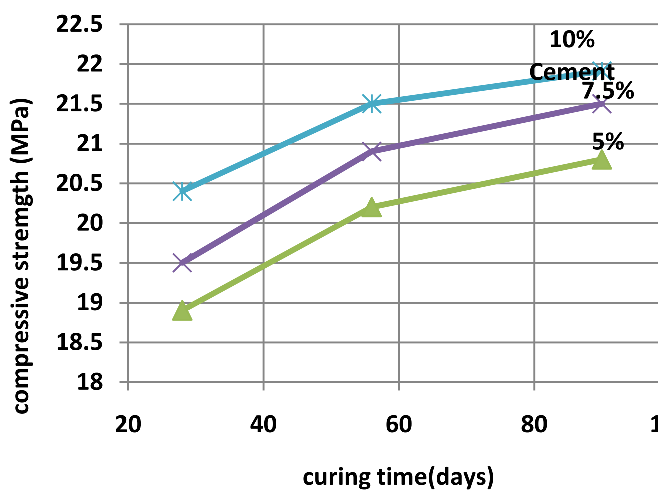

Figure.7 Compressive strength of CS-NHL-C-PG full bricks (phosphogypsum=70%)

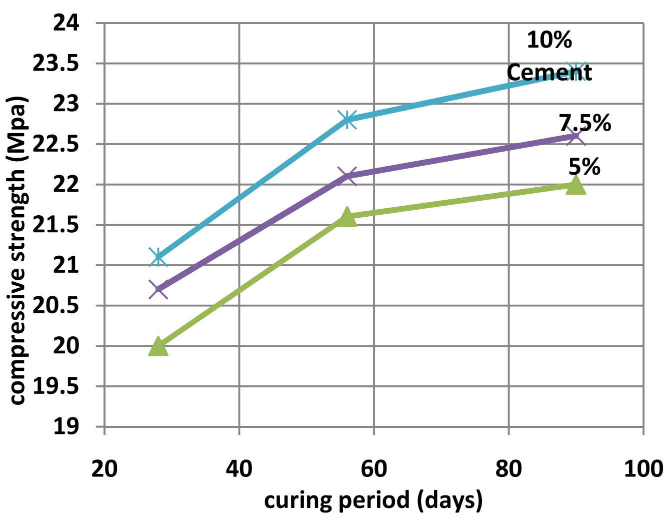

Figure.8Compressive strength of CS-NHL-C-PG full bricks (phosphogypsum=80%)

CS-NHL-C-PG bricks are found to be conforming to physical requirements of clay or shale building brick grade SW (severe weathering), bricks intended for use when high and uniform resistance to damage caused by cyclic freezing is desired and where the brick may be frozen when saturated with water [14](ASTM international: C62-08,2008). Therefore, CS-NHL-C-PG bricks can replace the clay or shale brick grade SW.

E. Leaching tests

The average values of the leaching test are presented in Table 5. The concentrations of the selected metal species, for all mix-design, were well below the regulatory limits. Thus, this result indicates that PG amended brick specimens can be considered as non hazardous materials.

Table V. Leaching test results, in mg/kg for L/S = 10 l/kg

Mix designation	Elements					
	Cr	Ni	Zn	Pb	Cu	Cd
P1	0.048	0.045	N	0.074	0.09	0.04
P2	0.045	0.04	N	0.065	0.055	0.02
P3	0.04	0.032	N	0.043	0.03	0.01
P4	0.038	0.035	N	0.064	0.08	0.025
P5	0.035	0.03	N	0.055	0.045	0.01
P6	0.027	N	N	0.036	0.02	N
P7	0.025	0.03	N	0.055	0.06	N
P8	N	N	N	0.037	0.035	N
P9	N	N	N	N	0.02	N
Limit values acceptable as inert	0.048	0.4	4	0.5	2	0.04
Limit values acceptable as non hazardous	50	10	50	10	50	1

IV CONCLUSION

Regarding the brick produced in this study, the following can be concluded:

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1) The physical and mechanical properties of brick samples with phosphogypsum, crushing sand, lime and cement are investigated. The test results show that the CS-NHL-C-PG combination provides results which are of potential to be used in the production of economical new solid brick grade SW material.

2) Phosphogypsum has more pronounced binding action than crushing sand.

3) CS-NHL-C-PG bricks with 80 % phosphogypsum, 7.5% cement, 2% lime and 11.5% crushing sand can be delivered after 28 days of manufacturing. This can reduce the cost of storing the bricks.

4) Notwithstanding the techno-economic virtues, CS-NHL-C-PG bricks grade SW comply with the criteria for environmentally friendly products manufactured with industrial by-product and the manufacturing process is totally energy conservative.

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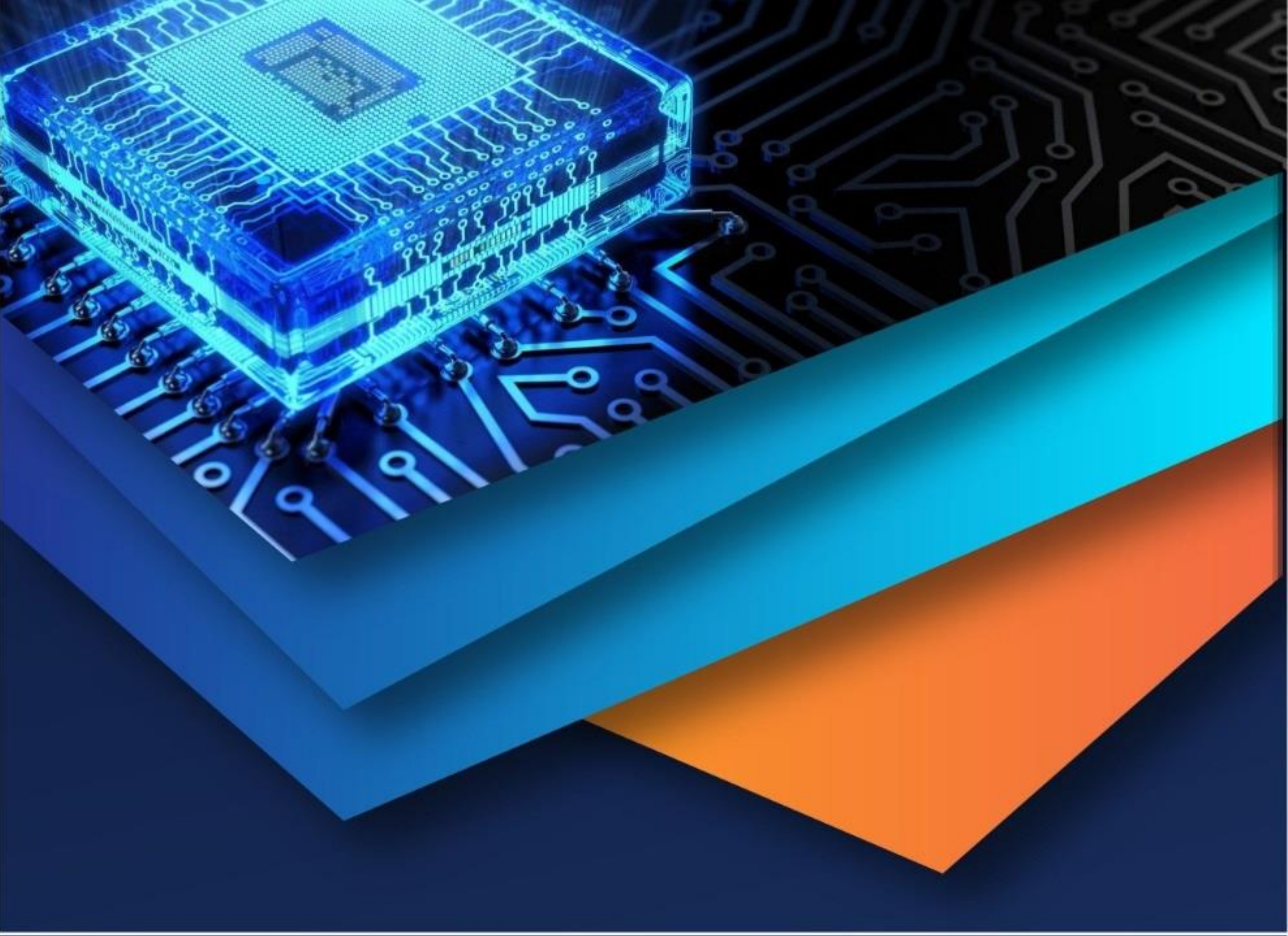

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