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Assessment of Solar Energy Resource in Niger Delta: Case Study Port Harcourt and Yenagoa

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Abstract: This paper presents an assessment of solar energy resources in Niger Delta case study of Port Harcourt and Yenagoa. The use of alternative sources of electricity is gaining popularity in different parts of the world especially with lots of interest being focused on harnessing solar energy. This work point out the irradiance viability and characteristic of solar sunshine per hour in Port Harcourt and Yenagoa City in the Niger Delta region of Nigeria. Several literatures were reviewed. Data were collected from the Nigerian Meteorological Agency (NiMET) and were analyzed. Matlab/Simulink was employed in the analyses and the output results were discussed. The result shows that Yenagoa City has more solar energy viability than Port Harcourt.

Keywords: Renewable energy, solar energy, viability, Niger Delta, MATLAB

1.0 INTRODUCTION

The use of alternative sources of electricity is gaining popularity in different parts of the world especially with lots of interest being focused on harnessing solar energy. To make use of this energy effectively, a proper knowledge of its behavior and characteristic has to be understood. Solar energy is available at any part of the world, but the potential of energy available varies with respect to geographical locations, times and seasons. The amount of solar irradiance falling on any location determines the solar energy available at that particular geographical. The solar radiation intensity falling on a surface defines solar irradiance and it is measured in N/m^2 or KW/m^2. Some researchers and authors refer to it as isolation value. The average radiation intensity falling on an imaginary object or surface, perpendicular to the sun's ray and at the edge of the earth's atmosphere is called the solar constant (Isc).

Solar constant is sometimes misleading because of the earth's elliptical orbit the intensity of the solar radiation falling on the earth changes by about 7% between January 1st, when the earth is nearest the sun and July 3rd, when the earth is furthest from the sun. When an average yearly value is taken the solar constant will be equals $1367W/m^2/s$. This value is still not accurate because the output of the sun changes by about 0.25% due to sunspot cycles [1]. According to [2] only about 13 percent of this radiation reaching the earth may be absorbed by the atmosphere and 12 percent scattered. This implies that the direct radiation available at the surface of the earth near the tropics in the middle of a cloudless day is about 75 percent of the level of the radiations at the surface of the atmosphere, which gives us about $1KJ/m^2/s$.

This is believed to be true if the earth is assumed to be an immovable body. Also it is known from our basic knowledge of physics that we can receive up to $1,367W/m^2/s$ for a part of each day since the earth rotates. The solar radiation reaching the surface of the earth changes for different geographical locations at a given season and time. This is the reason why meteorological information of any geographical location is of utmost importance before modeling a solar system for that location. [1] revealed that geographical factors like isolation value are required for a proper design of a solar power system. The Nation Nigeria is located at the western region of Africa at latitude between 4˚N and 13˚N and longitude between 3˚E and 15˚W. The country is made up of 36 states and a Federal capital territory. It is important to note that one can attach an average value for every geographic data when considering a location as reference, but the fact remains that there are still differences in the amount of energy reaching different locations within her.

Studies on how a particular geographical location encounters changes in solar energy distribution have shown that the various 36 states that make up Nigeria possess different meteorological data which accounts for the variation in solar energy distribution/radiation.

It is known generally that the Northern region of Nigeria is always hotter than every other region while plateau and its environs are always cold. The eastern, western and southern regions have slightly moderate weather condition. All these are as a result of variation in solar irradiance brought about by variation in their position on the earth surface.

The southern part of Nigeria is known for oil rich natural resources, and its aquatic source of avenue for its economic

growth. Solar renewable energies have not been harnessed. Electricity challenges in Nigeria particularly in the Niger Delta Region is high. There are various renewable energies in this region that is left untouched that would have help solve the growing demand of energy challenge.

This paper point out theoretically the irradiance viability and characteristic of sunshine per hour in Port Harcourt and Yenagoa City in the Niger Delta region of Nigeria. The study also help us to make decision in harnessing solar energy from the Niger Delta region particularly Port Harcourt and Yenagoa city.

The scope of this study is the assessment of solar energy resource in Niger Delta: case study of Port Harcourt and Yenegoa. Sunshine hours were used to determine the available power.

THEORETICAL REVIEW

2.1 SOLAR ENERGY

Solar energy is radiant light and heat from the Sun that is converted into used using a range of techniques such as solar heating, solar architecture, photovoltaic, solar thermal energy, molten salt power plants and artificial photosynthesis [3]. It is an essential source of renewable energy and its techniques are broadly characterized as either passive solar or active solar depending on how they trap and distribute solar energy or convert it into solar power. Active solar technologies include the use of photovoltaic systems, concentrated solar power and solar water heating to harness the energy. Passive solar technologies include orienting a building to the Sun, selecting materials with favorable thermal mass or light dispersing properties and designing spaces that naturally spread air.

The huge amount of solar energy available makes it a highly appealing or attractive source of electricity. The 2,000 World Energy Assessment programme of the United Nation Development reveals that the annual potential of solar energy was about 1,575 – 49,837 exajoules(EJ). This is at different times larger than the total world energy consumption, which was 559.8 EJ in 2012 [4].

In 2011, the International Energy Agency also reveals that the development of inexhaustible, affordable and clean solar energy techniques will have large long term benefits. Energy security in various countries will be increase through reliance on an indigenous, affordable and mostly import independent resource, reduce pollution, enhance sustainability, lower the costs of mitigating global warming, and keep fossil fuel prices lower. These benefits are global. Though its early deployment is costly but these costs should be considered learning investments, considering the long term benefits [3].The utilization of solar energy depends on the appropriate technology and its availability [5]. For centuries, the idea of using the sun's power as a source of solar energy has held scientist to grips [6]. Also, for most of its evolution, mankind has relied on the sun as a source of energy since it is constantly replenished. When fire was discovered as a source for the provision of heat and for the processing of food, the demand for energy increases, these demands were met by constantly renewed sources.

Later other sources of renewable energy such as water and wind powers were harnessed to the service of mankind. Throughout the early phase of human development one of the key constraint of mankind was the availability of the readily renewable sources of energy, this has affected the size and distribution of population [7]. The sun radiates huge amount of energy per year. It radiates energy in one year than people have used since the beginning of times.

It takes about millions of years for the energy in the sun's core to find its way to the surface, and then about another eight (8) minutes to travel to the earth. Solar energy travels to the earth at the speed of light, which is about 3.0×10^8m/s [8]. Small amount of the energy radiated by the sun strikes the earth surface, one part in two million. Yet, this amount of energy is large. Huge amount of solar energy strikes the earth to supply its energy needs. It was discovered in 1831 that the sun's energy could produce a photovoltaic effect [8]. In 1878, the first solar energy to mechanical energy conversion system was demonstrated, when sunlight was concentrated by focusing a collector on a steam boiler that ran a small printing press [9].

In 1980s, selenium photovoltaic cells were developed, that were able to convert sunlight into electricity but how the conversion was done was not thoroughly understood, they had 1- 2% efficiency. Solar power therefore has been a curiosity over the years. In 1901, larger focusing collector in truncated cone form generate steam for a 4.5hp engine. But between 1907 and 1911, solar steam engine of different horse power that were used for pumping water was built. [10] has it that by mid 1950s the efficiency was improved by 45% and later 11% increased was achieved with silicon photovoltaic cells. As a result, interest in solar power intensified. During the late 1950s and 1960s, the space program took active role in the development of photovoltaic. The cells were perfect sources of electric power for satellite, they were lightweight, rugged, and could meet the power requirements reliably. Unfortunately, the cells were not practical on earth due to the high cost of making them efficient and lightweight [11]. Consequently, further research was needed.

Climate is the average weather condition of a place over a given period of time. It is known primarily by distance from the coast and secondarily by elevation. [6]. Nigeria is entirely between the equators, Nigeria's electrical energy consumption in the year 2001 is 15×106 kWh and the tropic of cancer [12]. Its climate changes from tropical to subtropical. There are two main seasons in Nigeria; the dry season which last from October to March and the rainy season which last from April to October. It is hot and dry in the northern part. Rainy season extends between April and September. It is hot and wet in the south. Rainy season extends between March and

December. From December to March there is a long dry season. Temperatures at the coast rarely rise above 32 °C. The north is drier with temperature ranging between 32 °C and 42 °C, humidity of about 95% , [12]. The sun has enough hydrogen to burn for about 10 million years, it has been shining for about 4.5 billion years. All energy on earth results from the sun's energy directly or indirectly. Green plants absorbed the sun's ultraviolet rays to make their food. The dead, buried, decayed plants and trees over centuries turned into coal, oil and gas. Waterpower also comes from the sun; water is evaporated from the earth by the sun and this produces rainfall that fills the seas, lakes, rivers, oceans and reservoir.

Wind power also comes from the sun, the difference in heating of the earth globally results in kinetic energy [13]. The availability of solar energy in a particular region at present and at some other time in the future is the first concern to the designer of solar energy system. The availability of solar energy on earth is determined by the geographical location and time scale. The sunshine hours and consequently the radiations in different zones differ. The sun's power reaching the earth is typically about 1000W/m^2 [14].

2.2 SOLAR THERMAL

Solar thermal is the direct application of solar energy to produce heat. Solar thermal application has been dated back to ages, where the sun were used for drying and so on, common in the equatorial region where people have programmed themselves to sun drying of personal effects such as drying of agricultural commodities, clothing and so on resulting to various researches in solar thermal equipment like water heaters, Oven, cabinet dryers, hatchery, among others. In Nigeria, solar thermal have been developed for various purposes; some of these are chick brooding devices, solar cookers, solar pulverizes, [15]. Regarding the drying of Agricultural produce, there are four (4) major drying technologies, these are namely: open air drying, fire wood/fuel drying, electrical drying and solar drying [16].

2.3 SOLAR PV

Here, solar cells are used to convert solar radiation in electricity. These include Water Pumping for Irrigation in the rural areas, lightings and other purposes. The United Nation Commission on Sustainable Development has called for much wider access to sustainable energy as a prerequisite for reducing poverty to about 50% by the year 2015 and all world leader reaffirmed in the year 2005 world summit in New York. By sustainable energy, it means energy produced and used in a way that supports human development over the long term in all its social, economic and environmental development [17]. There can be immediate and widespread deployment and application of solar energy which can easily cover large area of Nigeria especially rural and river-rine areas because of many advantages of solar energy application over the present energy supply sources; especially when decentralized application is involved. Decentralization of Solar Energy installation means individual acquisition, utilization and application of the system. In this system, no high or low tension transformer will be required, high or low tension wiring, equipment and logistic will not be involved in the distribution of the energy, which means the solar PV (panels) can easily be carried, deployed and installed on individual establishment and premises in any part of the country at low cost within a very short period.

2.4 REVIEW OF PREVIOUS WORKS

[18] developed a model for prediction of solar energy in Nigeria using an artificial neural network model. Meteorological data from the National Aeronautics and space administration (NASA) for a period of 10 years from 1983 to 1993 of 195 cities in Nigeria were used. Geo-satellite data base were used for training and testing the network. He used meteorological data such as monthly sunshine duration, relative humidity, mean temperature, latitude and longitude were used as inputs to the network while the solar radiation intensity was used as the output of the network. He reported in his work that the monthly mean solar radiation potential in the North ranges from 7.01 - 5.62 kWh/m^2 while in the South it ranges from 5.43 – 3.54 kWh/m^2 [17] proposed an empirical model for estimating global solar radiation on horizontal surfaces for seven cities in Nigeria; Benin, Nsukka, Lagos, Kastina, Yola, and Abuja. He reported that, these cities from March through August (rainy season) experienced a decrease in the horizontal global solar radiation. Benin City was seen to have the lowest monthly mean daily horizontal global solar radiation of about 3.46 kWh/m^2/day in July. They also reported that the variation of daily horizontal global solar radiation with month of the year in Kastina varies from other cities because Kastina is located at longitude 7.6˚E, and latitude 13.0˚N. [18] developed a number of multi-linear regression equation based on Angstrom equation to predict the connection between global solar radiations with one or more combinations of some weather parameters for Iseyin Nigeria for five years. He reported that the expression with the highest value of correlation coefficient (r), least value of root mean square error (RMSE), mean bias error (MBE), and mean percentage error (MPE) was adopted for the estimation of different geographical location in Nigeria.

The motivating factor behind this work was the quest for meteorological models and data to model solar power systems. Meteorological data from four (4) different states were studied, evaluated to establish solar isolation potential, models and comparison.

This work adopts statistical method with the help of MATLAB in achieving the aim of this study.

3.1 METHODOLOGY

The assessment of solar energy resource in Niger delta using Port Harcourt and Yenagoa as case study. The data of sunshine hours for the year 2015, 2016 and 2017 were used in correlating the data's used in running the simulation in MATLAB.

The simulation was run in MATLAB to show the month in the year that the sunshine was at its maximum (peak) and minimum (low), this aid in the feasibility of harnessing the solar energy in Port Harcourt and in Yenagoa.

Table 3.1: Sunshine Per hour for Yenagoa

Months	2015 (hr.)	2016 (hr.)	2017 (hr.)
Jan	3.9	6.3	4.9
Feb	6.1	3.6	4.9
Mar	4.5	5	5.6
Apr	6	3.8	4.4
May	5	4.6	5
Jun	4.1	3.8	1.9
Jul	3	2.9	1.3
Aug	3.2	2.1	1.4
Sep	2.7	3.2	1.9
Oct	4	4	4
Nov	6.3	6.3	5.7
Dec	5.5	6	5.3

Source: Nigerian Meteorological Agency (NiMET) [19]

Table 3.2: Power Available, using PV module size of 200W in Yenagoa.

Month	2015 (hr)	2016 (hr)	2017 (hr)	AVERAGE (hr)	PV=200W, POWER GENERATED IN A DAY (Whr)	PV=200W, POWER GENERATED IN A MONTH (Whr)	USING PV=200W, POWER LOSSES (Whr)	USING PV=200W, AVAILABLE POWER (Whr)	LOAD OF 200W, HOUR POWER (hr)
JAN	3.9	6.3	4.9	5.0	1000.0	31000	9300	21700	108.5
FEB	6.1	3.6	4.9	4.9	980.0	28420	8526	19894	99.5
MA	4.5	5	5.6	5.0	1000.	31000	9300	21700	108.5
R					0				
APR	6	3.8	5.6	5.1	1020.0	30600	9180	21420	107.1
MAY	5	4.6	5	4.9	980.0	30380	9114	21266	106.3
JUN	4.1	3.8	4.4	4.1	820.0	24600	7380	17220	86.1
JUL	3	2.9	1.3	2.4	420.0	13020	3906	9114	45.6
AUG	3.2	2.1	1.4	2.2	440.0	13640	4092	9508	47.5
SEP	2.7	3.2	1.9	2.6	520.0	15600	4680	10920	54.6
OCT	4	4	4	4.0	800.0	24800	7440	17360	86.8
NOV	6.3	6.3	5.7	6.1	1220.0	36600	10980	25620	128.1
DEC	5.5	6	5.3	5.6	1120.0	34720	10416	24304	121.5

Table 3.3: Sunshine Per hour for Port Harcourt

MONTHS	2015 (hr.)	2016 (hr.)	2017 (hr.)
Jan	4.4	5.8	5.2
Feb	4	5.0	6.2
Mar	3.9	4.1	4.2
Apr	4.8	5.4	5.3
May	5.5	4.9	5.1
Jun	4.2	4.0	3.0
Jul	2.7	2.5	3.1
Aug	2	2.9	1.3
Sep	2.8	3.1	2.0
Oct	3.6	4.3	2.8
Nov	4.6	5.6	5.8
Dec	4.1	5.7	5.7

Source: Nigerian Meteorological Agency (NIMET)

Table 3.4: Power Available, using PV Module size of 200W in Port Harcourt.

Month	2015 (hr)	2016 (hr)	2017 (hr)	AVERAGE (hr)	PV=200W, POWER GENERATED IN A DAY (Whr)	PV=200W, POWER GENERATED IN A MONTH (Whr)	USING PV=200W, POWER LOSSES (Whr)	USING PV=200W, AVAILABLE POWER (Whr)	LOAD OF 200W, HOUR POWER (hr)
JAN	4.4	5.8	5.2	5.1	1020	31620	9486	22134	110.7
FEB	4	5.0	6.2	5.1	1020	28560	8568	19992	100
MAR	3.9	4.1	4.2	4.1	820	25420	7626	17794	89
APR	4.8	5.4	5.3	5.2	1040	31200	9360	21840	109.2
MAY	5.5	4.9	4.1	4.8	960	29760	8928	20832	104.1
JUN	4.2	4.0	3.0	3.7	740	22200	6660	15540	77.7
JUL	2.7	2.5	3.1	2.8	560	17360	5208	12152	60.8
AUG	2	2.9	1.3	2.1	420	13020	3906	9114	45.6
SEP	2.8	3.1	2.0	2.6	520	15600	4680	10920	54.6
OCT	3.6	4.3	2.8	3.6	720	22320	6696	15624	78.1
NOV	4.6	5.6	5.8	5.3	1060	31800	9540	22260	111.3
DEC	4.1	5.7	5.7	5.2	1040	32240	2862	29378	146.9

The table 3.1 and table 3.3 are used to illustrate a graphical representation of the data, in MATLAB simulation.

MATLAB (short for Matrix Laboratory) is a high level language and interactive environment that enhance computationally intensive tasks faster than with traditional programming languages such as FORTRAN, C and C++. It is used for numerical computation, visualization and programming in an easy to use atmosphere where problems and solutions are expressed in a simple mathematical notation. MATLAB today is a standard tools for scientist and engineers for computations, programming and research.. An additional package, Simulink, adds graphical multi-domain simulation and model-based design for dynamic and embedded system.

3.2 EQUATIONS

$A_V = X + Y + Z$ (Hours) 1

Where,

Av = Monthly Average Hours of Sunshine (hours)

X=Year 2015

Y= Year 2016

Z= Year 2017

$H = A_v \times 200w$(Whr) 2

Where,

H= Power generated in a day using PV of 200watt (Whr)

$E = H \times No\ of\ days\ in\ the\ month$ 3

Where,

E= Power generated in a Month using PV of 2OOwatt (Whr)

$P_L = 30\% \times E$ 4

Where,

$P_L = Power\ lossess$ on Power generated in Months using PV of 2OOwatt (Whr)

$A_E = E - P_L$ 5

Where,

$A_E = Available\ Power$ in a Month (Whr)

$A_P = \frac{A_E}{L_d}$ 6

Where,

A_P =Available Hours of Power in a Month

$L_d = Load$

3.3 CALCULATIONS

Calculating for the first month of the year January for Yenagoa Sunshine per hour

From equation 1

Monthly Average Hours of Sunshine (hours)

$A_V = X + Y + Z$

$A_V = \frac{3.9+6.3+4.9}{3} = 5.0\text{hr}$

From equation 3.2

Power generated in a day using PV of 2OOwatt (Whr)

$H = A_v \times 200w$

$H = 5.0 \times 200 = 1000\text{(Whr)}$

From equation 3.3

Power generated in a month using PV of 2OOwatt (Whr)

$E = H \times No\ of\ days\ in\ the\ month$

$E = 1000 \times 31 = 31000\ \text{(Whr)}$

From equation 3.4

$Power\ losses$ On Power generated in a month using PV of 2OOwatt (Whr)

$P_L = 30\% \times 31000 = 9300\text{(Whr)}$

From equation 3.5

Available Power in a Month ((Whr)

$A_E = E - P_L$

$A_E = 31000 - 9300 = 21700\text{(Whr)}$

From equation 3.6

Available Hours of power in a Month

$A_P = \frac{A_E}{L_d}$

Assuming a load of 200W

$A_P = \frac{21700}{200} = 108.5\ hours/month$

RESULTS AND DISCUSSION

4.1 TEST

The testing was done by simulating the data gotten from the Nigerian meteorological agency (NiMET) using table 3.1 and table 3.3

The data shows the graphical representation of the sunshine in YENEGOA and PORT HARCOURT. The MATLAB code used in the study is shown in figure 4.1.

```
>> x = [3.9, 6.1, 4.5, 6, 5, 4.1, 3, 3.2, 2.7, 4, 6.3, 5.5];

>> y = [6.3, 3.6, 5, 3.8, 4.6, 3.8, 2.9, 2.1, 3.2, 4, 6.3, 6];

>> z= [4.9, 4.9, 5.6, 4.4, 5, 1.9, 1.3, 1.4, 1.9, 4, 5.7, 5.3];

>>> t = [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12];

>> figure

>> hold on

>> plot (t, x, 'blue', t, y, 'red', t, z, 'green')
```

And for Rivers State the code is

```
>> x = [4.4, 4, 3.9, 4.8, 5.5, 4.2, 2.7, 2, 2.8, 3.6, 4.6, 4.1];

>> y = [5.8, 5.0, 4.1, 5.4, 4.9, 4.0, 2.5, 2.9, 3.1, 4.3, 5.6, 5.7];

>> z= [5.2, 6.2, 4.2, 5.3, 5.1, 3.0, 3.1, 1.3, 2.0, 2.8, 5.8, 5.7];

>> figure

>> hold on

>> plot(t, x, 'blue', t, y, 'red', t, z, 'green')
```

4.2 RESULT

The result is shown in figure 4.1 for Yenegoa.

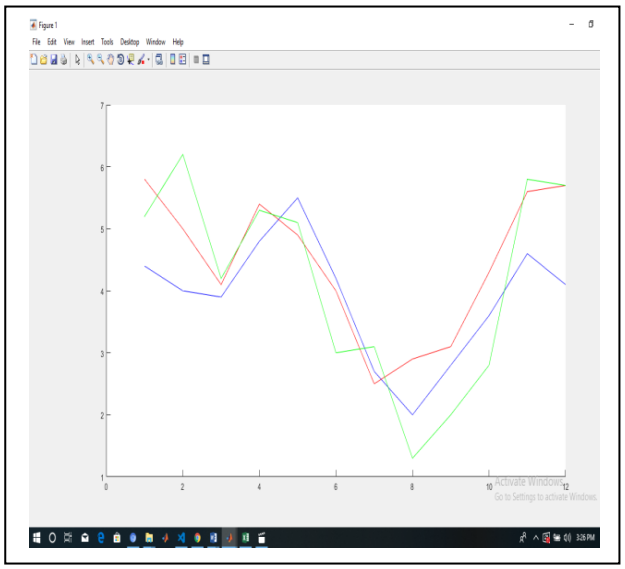

Figure 4.1: Graphical Result of the Data from Yenagoa.

Figure 4.1, shows the graph of sunshine hours in Yenagoa. From the graph the peak period of the year is from January to May and from October to December

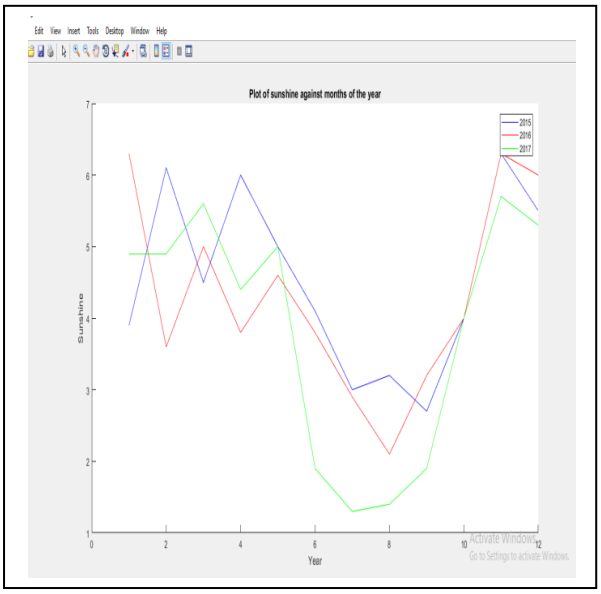

Figure 4.2: Graphical Result of the Data from Port Harcourt

Figure 4.2, shows the graph of sunshine hours in Port Harcourt. From the graph the peak period of the year is from January to May and from October to December. The lowest sunshine period is from July to August.

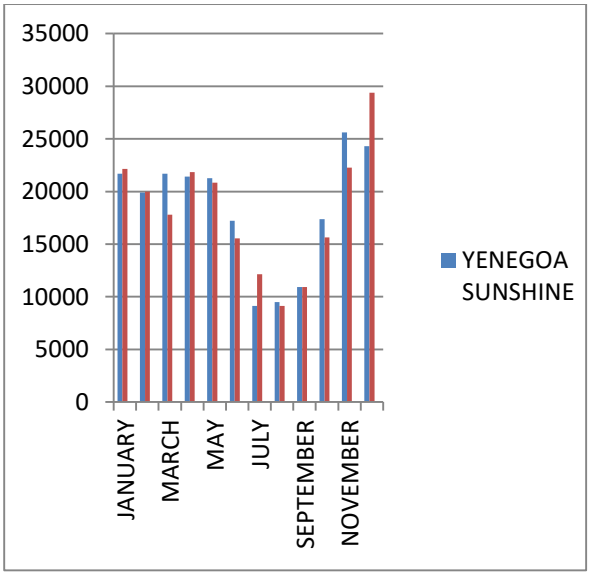

Fig 4.3: Available Power in a Month between Yenagoa and Port Harcourt.

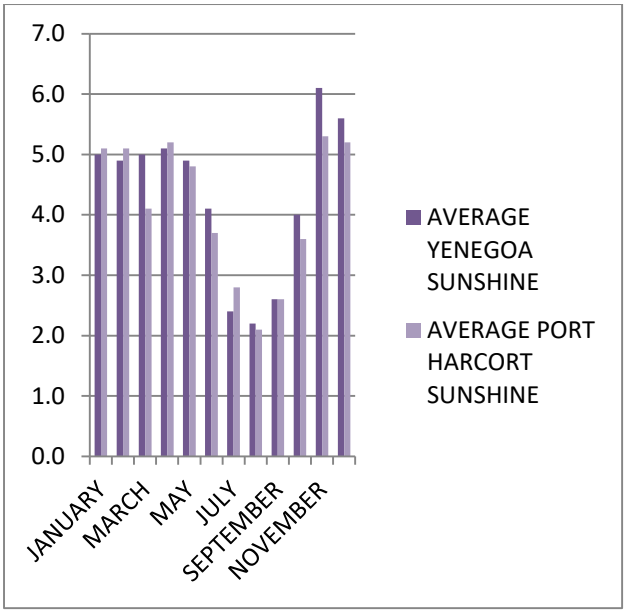

Fig 4.4: Monthly Average Sunshine Between Yenagoa and Port Harcourt for Year: 2015-2017

CONCLUSION

This study on assessment of solar energy resource in Niger delta (case study Port Harcourt and Yenagoa) was carried out using the sunshine per hour in Port Harcourt and Yenagoa. The data of the sunshine was gotten from the Nigerian meteorological agency (NiMET). The data gotten is used to run a simulation on MATLAB to show the high and low peak of the sunshine in Port Harcourt and Yenagoa.

The solar sunshine shows that solar energy can be harness to provide power to the residents of Port Harcourt and Yenagoa.

The research shows that Yenagoa city has more solar energy viability than Port Harcourt city. Yenagoa city has six months (March, May, June, August, October and November) of available power more than Port Harcourt while Port Harcourt has five months(January, February, April, July, and December) of available power than Yenagoa, while the month of September the available power was the same.

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Effect of Alkaline Activator on the Strength of Titanium-Gypsum Based Cementitious Materials

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Abstract: In order to determine the type of alkaline activator for gypsum-based slag cementitious materials, the fixed mass ratio of titanium slag and gypsum to 9: 1, and Na_2SiO_3, triethanolamine, Na_2SiO_3 mixed with triethanolamine were used to three activators. Then, nine groups of gypsum-based slag cementitious material test pieces were made with the dosage of alkaline activator 0.6%, 1%, and 1.2%, and the unconfined compressive strength was performed for 7 days. The experimental results showed that triethanolamine should not be used alone as an activator, the effect of compound Na_2SiO_3 and triethanolamine is better than that of Na_2SiO_3 used alone, and the 7-day unconfined compressive strength of the cementing material is higher than 1.5Mpa.

Keywords: Cementitious materials, Titanium-gypsum, Alkali excitation, Compressive strength

1. INTRODUCTION

Titanium gypsum is an industrial by-product produced during the production of titanium dioxide by the sulfuric acid method. It is mainly produced by adding lime to neutralize acidic wastewater generated in the production process, and produces solid waste mainly composed of dihydrate gypsum. When it just came out of the treatment workshop, it was gray-brown, and Fe^{2+} in the air was gradually oxidized to Fe^{3+} and turned red, so it was also called red gypsum. In China, the general production of 1t sulphuric acid titanium dioxide will produce 6 ~ 10t of titanium gypsum. At present, the annual production of titanium-gypsum is about 10 million in China, but its utilization rate is very low, most of which adopt the way of open dumping [1].

In the preparation of cementitious materials by industrial waste gypsum, some experts and scholars have done a lot of research, which is of referential significance to the preparation of titanium-gypsum based slag cementitious materials. Hyeoneun Park[2] added 10% gypsum to lime activated slag (slag: lime: gypsum = 85:5:10) can have the best mechanical properties, and the compressive strength can reach 30Mpa and 40Mpa in 7 and 28 days. M.S. Morsy [3] through the fixed ratio of metakaolin-fly ash-lime (40:30:30), with different content of anhydrite (0%, 2.5%, 5%, 7.5%, 10%) test, found that the compressive strength is not the same age period is along with the increase with the increase of the content of anhydrite, its compressive strength is within 7 days of growth is slower, but in the later as the growth of the curing age. Sun jiaying [4] added titanium-gypsum with an admixture of less than 4% into the lime-fly ash stabilized material, and found that the early strength of the mixture was improved, with no negative effect on the later strength. Jiangwei Li [5] found that the 7-day unconfined compressive strength of clinker-fly ash-gypsum(45:45:10) stabilized gravel pavement base material was higher than that of P.S 32.5 cement, and the strength was nearly 10% higher than that of P.S32.5 cement. Zhao deqiang [6] prepared pavement base cementite by using 40% clinker, 35% fly ash, 15% phosphogypsum and 10% steel slag as the optimal mix ratio, and its strength was 20% ~ 50% higher than that of the compacted material stabilized by two-ash broken gravel.

Based on the above research status, the use of alkaline activators for gypsum based cementing materials is mostly based on cement clinker or lime, which will not only aggravate the exploitation of natural resources such as limestone, but also cause environmental damage. So, If can reduce economic cost, reduce the use of lime and other natural resources for the principle, in order to improve the utilization rate of titanium gypsum for the purpose, if the titanium-gypsum and slag materials are combined together through the appropriate alkaline activator, the strength of the cementitious materials can be effectively improved, and a low-cost and high-quality alkaline activator of gypsum based cementitious materials can be realized, which is of great significance for the preparation of titanium-gypsum based cementitious materials. In this paper, the effect of alkaline activator on the strength and properties of titanium-gypsum based slag cementitious materials was studied, and the optimal form of alkaline activator was determined.

2. MATERIALS and METHODS

2.1 Raw Materials

1) Titanium-gypsum: It was taken from the industrial waste generated by a chemical enterprise in Zibo, Shandong. The

main component is $CaSO_4 \cdot 2H_2O$, and the content is generally 60% ~ 80%. The other main chemical components are shown in Table1. The crystalline water and adsorbed water in titanium-gypsum exist at the same time. The titanium-gypsum was dried at 60℃ to a constant weight and then turned pale yellow. After cooling, it was passed through a 2.43mm square-hole sieve.

2) Slag: Obtained from a building materials enterprise in Hebei province, this is a light gray powdery solid with a density of 2.9g/cm^3, a specific surface area of 418m^2/kg, and a 28-day activity index of 97%. Its main chemical composition are shown in Table 1.

Table 1. The chemical composition of titanium-gypsum and slag (mass fraction %)

Composition	Titanium gypsum	Slag
AI_2O_3	1.82	13.5
CaO	30.21	39.4
MgO	1.92	7.5
SO_3	37.06	2.28
SiO_2	2.83	26.4
TiO_2	3.84	1.31
Na_2O	-	0.423
K_2O	-	0.305
MnO	-	0.384
Fe_2O_3	7.83	0.406

3) Na_2SiO_3: Produced by Wuxi Yatai united chemical co., LTD., AR analysis pure, the molecular formula is $Na_2SiO_3 \cdot 9H_2O$, the molecular weight is 284.22, white or gray white block or powder, easy to weathering, soluble in water, Na_2O content is 19.3~ 22.8%, Na_2O and SiO_2 mass ratio is 1:1.

4) Triethanolamine (TEA): Produced by Tianjin Dingsheng Xin chemical industry co., LTD., AR analysis pure, molecular formula is $C_6H_{15}NO_3$, molecular weight is 149.1882, colorless to light yellow viscous liquid, easy to absorb moisture, easy to dissolve in water.

2.2 Experimental Methods

In this experiment, first, the fixed mixing ratio of titanium gypsum and slag to 9: 1, followed by the addition of different contents of Na_2SiO_3, triethanolamine, compound Na_2SiO_3 and triethanolamine as three kinds of activator, made 9 sets of cementitious material test pieces, the mixing ratio is shown in Table2. The activators used in this paper were dissolved in water and mixed into titanium-gypsum. According to the optimal water content of titanium-gypsum, the water consumption of less than two percentage points was taken as the optimal water content of all the proportions, and then experiment after mixing and sealing for 12 hours. The specific experiment methods is as follows:

1) Proctor compaction test: According to JTG E40-2007[7], this experiment adopts light compaction test I-1, the determination of the maximum dry density and optimum water content of titanium gypsum. The moisture content of 20%, 22%, 24%, 26%, 28%, 30% and 32% were selected for proctor compaction test, and the results are shown in figure 1. It can be seen from the test results that the optimal water content of titanium-gypsum is around 26%, and its maximum dry density is 1.394 g/cm^3. When the water content is within the range of 24~ 28%, the density changes little, both within the maximum dry density ± 0.02 g/cm^3.

2) 7-day unconfined compressive strength test: According to JTG E51-2009[8], the standard φ50mm×H50mm specimen was prepared by static pressing with universal press, and the specimen was put into the standard curing box (20℃ ± 2℃, relative humidity ≥95%) for curing to the required age. On the last day of the curing period, the specimen was taken out and placed in 20℃ ± 2℃ water. The water surface was about 2.5cm on the top of the specimen. After soaking for 24h, the water on the surface of the specimen was absorbed with a soft cloth. No less than 6 parallel samples were set for each group of experiments, and their representative values were taken for analysis.

Table 2. The mix proportions of specimen(mass fraction %)

Group	titanium gypsum	slag	Na_2SiO_3	triethanolamine
1	88	10.8	0.6	0.6
2	90	9.4	0.4	0.2
3	90	9.4	0.2	0.4
4	88	10.8	1. 2	-
5	90	9	1	-
6	90	9.4	0.6	-
7	88	10.8	-	1.2
8	90	9	-	1
9	90	9.4	-	0.6

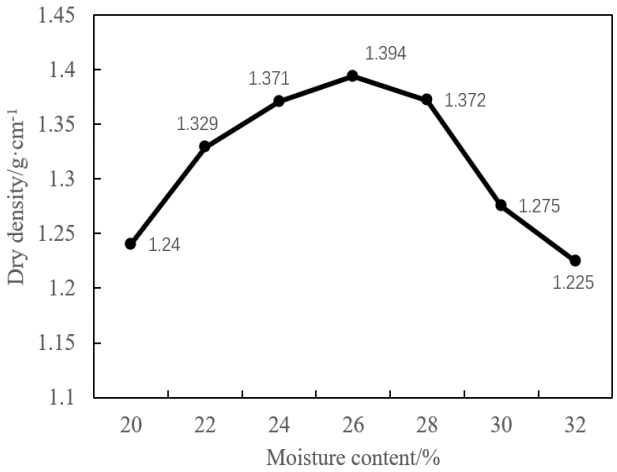

Figure 1. Dry density - moisture content curve of titanium-gypsum

3. RESULTS AND DISCUSSION

3.1 Effects of Na_2SiO_3 single activator on compressive strength of cementitious materials

The effects of Na_2SiO_3 single activator on the compressive strength of cementitious materials are shown in Figure 2. It is to see that the strength of Na_2SiO_3 only as an alkaline activator can reach above 1.5Mpa, in which the compressive strength reaches the maximum when the content of Na_2SiO_3 is 0.6%, and the compressive strength is 2.2Mpa. By comparing other mix ratios, it is found that when the Na_2SiO_3 content is 1.2%, the compressive strength is only higher than 0.2Mpa with 1% content, with no significant difference between the two. This shows that the compressive strength are the best when the content of Na_2SiO_3 is 0.6%, and the compressive strength in the early stage is obviously better than that of ordinary lime fly ash cementing materials.

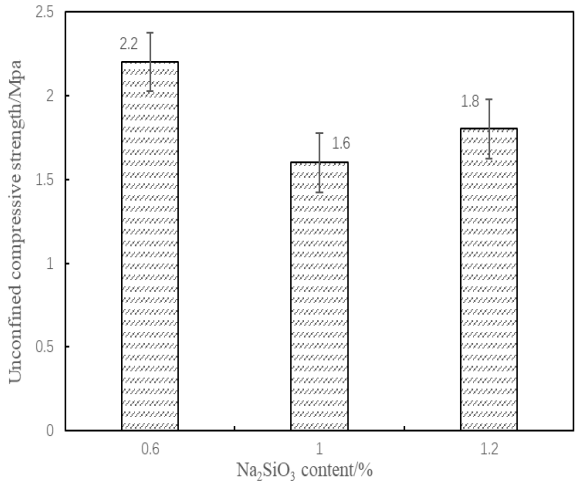

Figure 2. Effects of Na_2SiO_3 single activator on the compressive strength

This early strength was mainly due to the pozzolanic reaction between gypsum and slag[9]. Because there are a large number of SO_3 and CaO compounds in titanium-gypsum, as well as a small amount of SiO_2, AI_2O_3 and other active substances, this provides the basis for the early hydration reaction of the mixture. On the one hand, Na_2SiO_3 has a certain bond, which is because Na_2SiO_3 can exchange with CO_2 and water to form a part of silica gel, which can realize the close connection of particles between the mixture and improve the strength of the mixture [10]. In addition, Na_2SiO_3 can also react with $CaSO_4 \cdot 2H_2O$ to produce silica gel and sodium sulfate crystals, which can bond gypsum particles and make the structure more compact, which is conducive to improving the strength of stabilized titanium-gypsum mixture[11]. Na_2SiO_3, meanwhile, is able to provide hydration reaction of alkaline environment, can make the Si-O keys inside the slag and AI-O keys vitreous body is broken by immediately, and quickly involved in the hydration reaction, can effectively generate hydrated calcium silicate (C-S-H), hydrated calcium aluminate (C-A-S-H) gel material, improve the compactness of mixture between, improve the strength, but in standard curing 7 days, the formation of these substances is weak [12]. On the other hand, the generation of early ettringite also provides the basis for the early strength, because $CaSO_4 \cdot 2H_2O$, SO_3, CaO and AI_2O_3 can produce calcium sulphoaluminate hydrate (AFm), which is not yet fully developed to produce ettringite, and calcium sulphoaluminate hydrate (AFt), which has initially developed into aciculus. In addition, the formation rate of ettringite is also related to the concentration and diffusion rate of OH^-, SO_4^{2-} and Ca^{2+} in the hydration environment. The diffusion of these ions to the solid-liquid interface formed by ettringite can lead to the continuous formation of ettringite [13]. These generated AFm and AFt crystals can fill the interstitial space in the mixture, making the mixture more compact, thus improving the early strength.

3.2 Effects of triethanolamine single activator on compressive strength of cementitious materials

When single triethanolamine (TEA) was used as an alkaline activator, the specimen was intact for 6 days before standard curing, and rapid disintegration occurred when it was soaked in water on the last day, in figure 3. In the three mixing ratios of group 6, 7 and 8, disintegration occurred, which was quickly completed within half an hour after soaking in water. The most important part was gradual erosion from the root of the specimen, in figure 3a). After soaking for one day, some specimens completely disintegrated, in figure 3b). After complete disintegration, the specimen has a large particle size, sandy texture, and some viscous shape, in figure 3c).

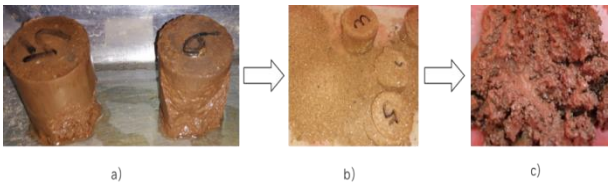

Figure 3. Disintegration of specimen only with triethanolamine
a) Water immersion 0.5h; b) Water immersion for 24h; c) specimens after disintegration

Triethanolamine, as an organic matter, is also a good activator for slag. This is because the unshared electron pair on the N atom in its molecule is easy to form covalent bonds with Ca^{2+} in the liquid phase of the mixture, resulting in the complexation reaction to form the TEA-Ca^{2+} complex. However, the complex formed at this time is more soluble in water, and will form soluble zone points on the surface of the cementitious mineral particles, thus promoting the hydration reaction. Complex formed in the liquid phase, would result in higher hydration environmental PH value, promote the gelation of slag minerals (C_2S/C_3S, $Ca(OH)_2$, etc.) in the secondary hydration generated hydrated Tetracalcium aluminate (C_4AH_{13}), inhibit the hydration tricalcium aluminate (C_3AH_6) formation, can prevent the mixture in loose the production of crystal structure, improve the density and mechanical properties of hardened cement paste [14].

The rapid disintegration is mainly caused by the high content of triethanolamine and the short curing time, because

triethanolamine has a strong alkalinity at a PH of 10.5 in an aqueous solution of 0.1mol/L, and the content of triethanolamine in this experiment was 0.17~0.4mol/L. In curing age, as a result of triethanolamine on the early hydration process of C_3S and C_2S has certain inhibition, and early generated TEA-Ca^{2+} complex soluble in water[14], and because of the early C-S-H gelling material such as the generation of a weak [12], the internal structure of the mixture was loose, and led to the complete disruption in the final 1d of soak, so need to extend the curing age considering its hydration products late effect or to reduce the content of triethanolamine.

3.3 Effects of Na_2SiO_3 mixed with triethanolamine activator on compressive strength of cementitious materials

The effects of Na_2SiO_3 mixed with triethanolamine activator on the compressive strength of cementitious materials are shown in Figure 4. In the form of Na_2SiO_3 mixed with triethanolamine, when the mass ratio of Na_2SiO_3 to triethanolamine was 1:1, the compressive strength reaches the maximum, which is 3.1Mpa. In by comparing with the dosage of Na_2SiO_3 and triethanolamine quality ratio of 2:1 and 1:2, Na_2SiO_3 content is higher than that of triethanolamine, the compressive strength is 2.4Mpa, compressive strength is greater than the group 3, this means that when the dosage of Na_2SiO_3 content higher than that of triethanolamine, the role of excitation of the mixed agent in the mixture has a positive effect. Therefore, properly controlling the mass ratio of titanium gypsum to triethanolamine is beneficial to improve the strength of titanium gypsum-based slag cementitious material.

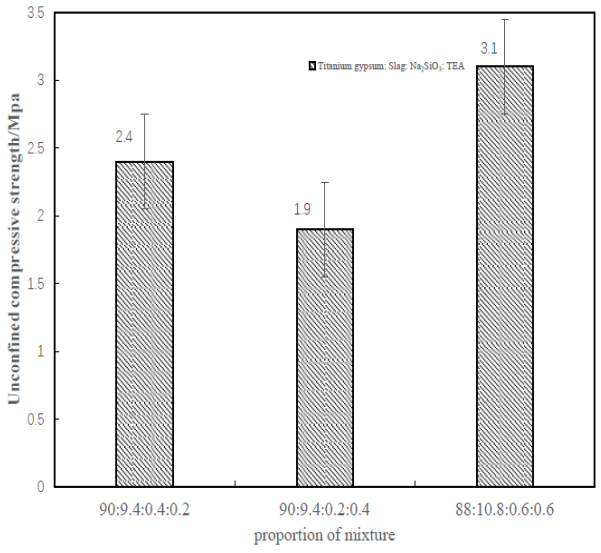

Figure 4. Effects of Na_2SiO_3 mixed with triethanolamine on compressive strength

Based on the comparison of Na_2SiO_3 single admixture and complex admixture forms, it can be seen from figure 5 that with the same amount of stimulant, the admixture strength of triethanolamine and Na_2SiO_3 is significantly higher than that of Na_2SiO_3 single admixture. When the mixture content of activator is 1.2%, it is obviously better than the mix ratio of Na_2SiO_3 mixed form, and its compressive strength reaches 3.1Mpa, which is 1.5 times higher than that of Na_2SiO_3 mixed alone. When the co-admixture of activator was 0.6%, the compressive strength of group 2 in the compound admixture was higher than 0.2Mpa for Na_2SiO_3. When the content of Na_2SiO_3 is 0.6%, which is group 1 and group 6, it can be found that the compressive strength of the compound mixture is higher than that of the single mixture. It can be concluded from the above, using compound Na_2SiO_3 and triethanolamine as the activator of cementitious materials in the early compressive strength is superior to the Na_2SiO_3 single activator.

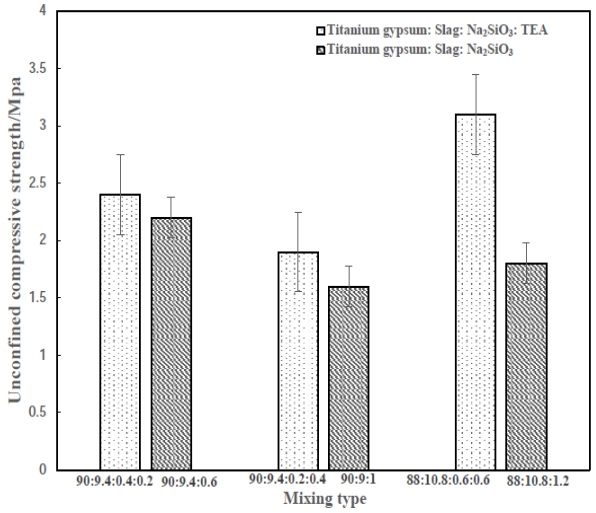

Figure 5. Comparison of compressive strength between compound admixture and single admixture

In terms of strength formation mechanism, this is mainly due to the fact that triethanolamine and Na_2SiO_3 can provide an alkaline environment for the hydration reaction in the mixture, then improve the PH value and promote the generation of hydration products. In addition, with the incorporation of triethanolamine(TEA), part of triethanolamine can also promote the solid for the TEA-Ca^{2+} complex formation Ca^{2+} from the dissolution of hydration products, accelerate the hydration reaction rate, and thus promote the sulfate, Na_2SiO_3 and $Ca(OH)_2$ in hydration reaction, accelerate the gelling material (C-S-H) formation, but also can expand the gelling material (C-S-H) layer spacing, is advantageous to the induction of random aggregation C-S-H ordered arrangement and spongy structure formation, and TEA-Ca^{2+} complex formed many soluble in aqueous solution, The diffusion rate of hydration products is increased, secondary hydration of sulfate and C_3A is realized, and the generation of ettringite is accelerated, which is generated in large quantities in the early stage, so as to improve the compactness and compressive strength of the mixture[15]. At the same time, part of the hydrogen in the hydroxyl group of triethanolamine and Na_2SiO_3 form a composite crystal of silica gel ($mSiO_2 \cdot nH_2O$) and triethanolamine sodium salt ($N(C_2H_4ONa)_3$) composite crystal ($N(C_2H_4ONa)_3 \cdot mSiO_2 \cdot nH_2O$) [16]. The formation of

these crystals can fill internal voids and improve their mechanical properties.

4. CONCLUSION

(1) When single Na_2SiO_3 was used as alkaline activator, the 7-day compressive strength of titanium-gypsum based slag cementation materials is higher than 1.5Mpa when the dosage is 0.6%, 1% and 1.2%. When the dosage is 0.6%, the compressive strength is the highest among the three component ratios, reaching 2.2Mpa.

(2) When single triethanolamine was used as alkaline activator, rapid disintegration occurs after 0.6%, 1% and 1.2% are added to titanium-gypsum slag cementitious materials. So triethanolamine should not be used as the activator alone.

(3) When Na_2SiO_3 mixed with triethanolamine were used as alkaline activator, the 7-day compressive strength of Na_2SiO_3 mixed with triethanolamine is generally higher than that of Na_2SiO_3 alone, especially when the activator content is 1.2%, when the 7-day compressive strength is the highest.

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