TECHNOLOGY DEVELOPMENT FOR STRONG REDUCTION OF ENERGY CONSUMPTION AND CO_2 EMISSION IN LIME AND CEMENT MANUFACTURE

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Abstract

The cement and lime industries are responsible for 8% of global CO_2 emissions [1]. 35% of this CO_2 share comes from fuel combustion to heat and decompose limestone to produce lime or “clinker” in an open atmosphere while the remaining 65% comes from limestone rock itself.

Due to the new technology, high grades of both lime and CO_2 were obtained faster and at much lower than conventional temperatures and CO_2 was fully captured and utilized when using an HEVA reactor for limestone calcination. Clinker, a precursor of cement, was partly obtained at lower temperature when starting from HEVA lime and fine quartz after mechanochemical pretreatment.

Key words: CO_2 emission control, CO_2 utilization, lime and cement manufacturing, carbonic fertilization, CO_2 and microalgae growing, mechanochemical processing

1 INTRODUCTION

The mankind is quite acquainted with the problem of global warming caused by CO_2 emissions from industrial activity. Most research budgets are devoted to reduce or capture CO_2 emissions from power plants and transportation [2]; they have to deal with huge volumes of hot, dirty and low CO_2 concentrated gases that are expensive to concentrate, clean, storage or utilize [3].

On the other hand, the cement and lime global annual production is over 3,500 million tons that generates 8% of global CO_2 emissions [1]. The “state of art” of calcination is quite similar to the ancient practice since still uses fuel combustion to heat up furnaces.

As a result, 35% of total CO_2 come from fuel combustion, according to reaction (2), to heat and decompose limestone to produce lime or “clinker” in an open atmosphere, while the remaining 65% come from the limestone rock itself. Limestone[1], or calcium carbonate, decomposition is highly endothermic and occurs according to reaction (1):

$$CaCO_3\ (s) = CaO\ (s)\ +\ \mathbf{CO_2}\ (g) \qquad \Delta G^{o}_{r} = 177{,}100 - 158T\ (J/mol) \tag{1}$$

$$CH_4\ (g)\ +\ 2.O_2\ (g) = \mathbf{CO_2}\ (g) + 2.H_2O\ (g) \tag{2}$$

According to reaction (1), at normal pressure a temperature of 848°C is required to reach $\Delta G = 0$ and initiate the limestone decomposition. On the other hand, the partial pressure of CO_2 in air is about 0.04 KPa and Table 1.1 and Figure 1.1 show that above 550°C the equilibrium pressure of CO_2 exceeds its pressure in air and CO_2 evolves from limestone [4].

Nevertheless, the fuel combustion generates a CO_2 partial pressure of about 20 KPa inside the furnace that demands a temperature of at least 800°C to achieve this equilibrium pressure; such temperature differences for 0 and 15% CO_2 has also been reported by L. Tian [5] and I. Avila [6]. In actual industrial practice, limestone calcination is carried out at 1,200°C to achieve an acceptable decomposition speed and rate. Lime calcination and clinker formation demand a large amount of energy (3.6-4.5 GJ/ton [2]) which means a large amount of fuel. For complete combustion, it is necessary to employ a large excess of air that generates a very high flow of exit gases. As a result, exit gases report less than 14% CO_2 and coarse limestone (about 3 inches) has to be fed as a raw material to avoid an excess of dust in outgas. Limestone coarse particles decomposition requires longer reaction times and higher temperatures and dilute CO_2 gases demands higher cost for cleaning, concentration, storing and utilization [3].

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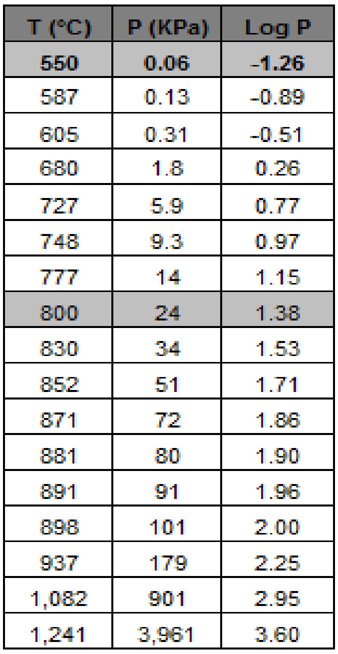
[1] The limestone used in the experimental work has 98.6% of $CaCO_3$.

Tab. 1: Equilibrium pressure of CO_2 over $CaCO_3$ vs temperature.



T (°C)	P (KPa)	Log P
550	0.06	-1.26
587	0.13	-0.89
605	0.31	-0.51
680	1.8	0.26
727	5.9	0.77
748	9.3	0.97
777	14	1.15
800	24	1.38
830	34	1.53
852	51	1.71
871	72	1.86
881	80	1.90
891	91	1.96
898	101	2.00
937	179	2.25
1,082	901	2.95
1,241	3,961	3.60

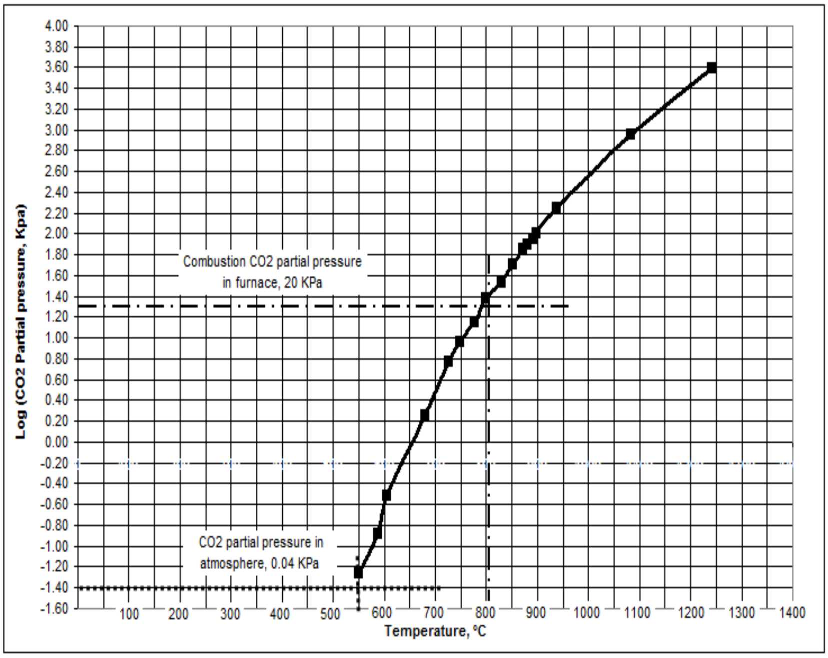


Fig. 1: Equilibrium pressure of CO_2 over $CaCO_3$ vs temperature; CO_2 pressure in air and within furnace during combustion is indicated.

In clinker production, the limestone decomposition to CaO (Reaction 1) occurs in the first section of a long rotary kiln, and the clinker formation, which is basically calcium silicates (Reactions 3 and 4), occurs in the remaining section of the furnace, with temperatures ranging from 800 to 1,450°C along the kiln. Limestone accounts for 80% of the raw material and silica most of the balance because alumina and iron oxides only accounts for 5%. Clinker contains about 80% CaO and 15% SiO_2 in a combined form. All clinker kilns in the world are heated by coal or natural gas combustion.

Calcium silicates formation reactions are [7]:

Belite (Larnite) formation: $2.CaO\ (s) + SiO_2\ (s) = Ca_2SiO_4\ (s)$ (3)

Alite formation: $CaO\ (s) + Ca_2SiO_4\ (s) = Ca_3SiO_5\ (s)$ (4)

Therefore, it would be possible to obtain clinker starting from lime (CaO) rather than limestone and use electrical energy instead the fuel combustion for heating up the furnace. If lime is previously obtained in a similar furnace that also captures the CO_2 outgas, the CO_2 emissions in the lime and cement industries could be avoided.

However, CO_2 emissions from the cement industry are significant. In Peru, the yearly consumption of lime and cement industries is about 1 and 10 million tons, respectively, and they both discharge 9.3 million tons of CO_2; the proposed system would capture 5.6 million tons/year and avoid the discharge of 3.7 million tons/year of CO_2. A large CO_2 consumption can be achieved through carbonic fertilization of microalgae, aquatic and land plants, according to the following equations [8]:

Microalgae growing: $6.CO_2\ (g) + 6.H_2O\ (l) + light = C_6H_{12}O_6 + 6.O_2$ (5)

Cellulose growing: $5.CO_2\ (g) + 5.H_2O\ (l) + light = C_5H_{10}O_5 + 5.O_2$ (6)

According to equations (5), (6) and (1), the full capture of this CO_2 could generate 0.68 or 0.54 ton of biomass (microalgae or cellulose) per ton of CO_2 or CaO obtained, respectively; in practice biomass productivity depends on several factors. In order to be economically feasible, captured CO_2 should be clean and highly concentrated.

2 EXPERIMENTAL PART

2.1 Limestone calcination with HEVA System

High quality limestone from the Peruvian Central Andes having 98.6% $CaCO_3$ was used for experimental studies. A sample was crushed and dry screened down to 74 microns and each particle size separated for individual calcination tests. The initial testwork was performed with limestone samples of 20 to 50 grams in a HEVA[2] reactor placed within an electrical furnace. The HEVA reactor has a vacuum and cooling system for CO_2 outgas which is also captured in a NaOH solution bath (see Photo 2.1). The CO_2 evolving and calcination rate were monitored through pH and the acid titration of NaOH solution.

The overall calcination efficiency measures $CaCO_3$ converted to CaO and was determined from the initial and final weights of sample. The lime CaO content was also calculated from the same data.

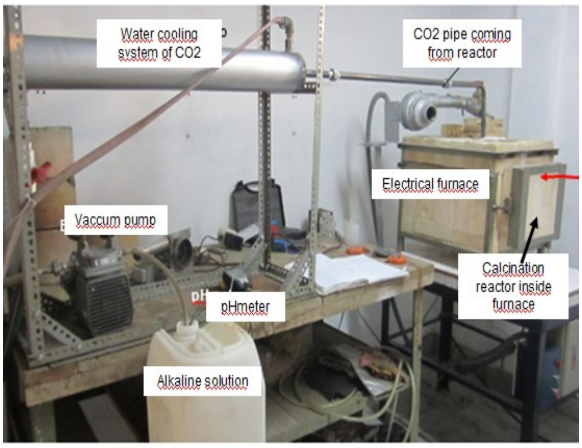


Photo 2.1: HEVA laboratory system; limestone was placed inside a stainless steel reactor under vacuum and heated using an electrical furnace.

Photo 2.2: Array of glass cylinders to grow microalga spirulina with injection of commercial and HEVA CO_2.

2.2 Clinker formation with HEVA Lime

Belite formation tests were performed heating a mixture of 2 parts of HEVA lime and 1 part of quartz sand, according to equation (3), in an electrical furnace at 900, 1,000 and 1,050 °C, during 90, 120, 180 and 240 minutes.

The dry mechanochemical pretreatment was carried out in a PE-075 Netzsch attritor with 1,440 rpm, 1,000 grams of 2 mm ZrO_2 balls, 20 grams of sample, during 10, 20 and 30 minutes; the temperature was kept at 52°C by means of a water cooling system. In a dry mode, grinding sticking problems arise as was reported before when dealing with cement [9]; we kept a high ball/sample ratio to overcome this.

Our test work was addressed to find out a quick response regarding the Belite or Alite formations; the extent of lime conversion to Belite was estimated measuring the conductivity of the product mixed with deionized water. The extent of conversion to Belite and other species was finally determined by X Ray Diffraction (XRD) of products which reported low conductivity. The laboratory of the San Marcos University used the Rietveld method to determine mineralogical species and their concentrations.

2.3 Reactivity of HEVA Lime

The reactivity of HEVA Lime was tested with a mine effluent from the Carolina Mine, Cajamarca, Peru, and compared with commercial lime. The sample was mixed with a lime solution in a laboratory agitator and monitored with a digital pH meter.

2.4 Carbonic fertilization with HEVA CO2

The suitability of HEVA CO_2 for the carbonic fertilization of land plants was tested in 15 m^3 greenhouses provided with temperature, moisture, light intensity, and CO_2 concentration controls; the results were determined by weights of plants, branches, leaves, roots, and fruits. HEVA CO_2 was prepared from 2.5Kg batches of limestone.

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[2] HEVA stand, in Spanish, for “Electrical Vacuum Furnace”

The growing of microalgae was tested in 2 arrays of 5 glass cylinders each fed by a mixture of regulated flow of CO_2 and air, provided with temperature and light intensity control (Photo 2.2). The biomass concentration increased and protein content of microalgae was determined for HEVA and commercial CO_2. Experts from IMARPE supervised this testwork [8].

3 RESULTS AND DISCUSSION

3.1 Limestone calcination with HEVA System

60 minutes electrical calcination under vacuum reaches over 95% limestone decomposition at 700°C as compared to only 38% obtained at atmospheric pressure (Figure 3.1). At 750°C, the HEVA system obtains the complete conversion to CaO and lime reports 97.5% CaO. Industrial practice, at 1,200°C and fuel combustion, only achieves 89% conversion and 82% CaO in lime after 2 hours. Thus, the HEVA calcination gets better results with less energy consumption.

The CO_2 average concentration in the HEVA product was 78.3 w/w% due to some leakage in the vacuum systems but is still well above 14% CO_2 concentration of industrial outgas. Table 3.1 shows the comparative balance for HEVA and conventional calcination processes to obtain 100 t/d of lime. The HEVA plant only discharges 91 /d of outgas compared to 555 t/d in conventional plant; also 81 and 6 L/s of water, respectively, is required to cool the gas in order to allow cleaning, compression and further utilization. The high concentration and lower temperature of HEVA CO_2 allow using it with little additional treatment.

Tab. 3.1: Material balance of HEVA and atmospheric calcination for 100 t/d of lime.

Input		**Convnt.**	**HEVA**
Limestone Weight	T/d	170	170
Oxygen Weight	T/d	64	4
Nitrogen Weight	T/d	412	16
Methane Weight	T/d	8	0
Output		**1,200°C**	**750°C**
Lime	T/d	100	100
Lime quality, CaO	T/d	82	98
CO2 Weight	T/d	93	71
Oxygen Weight	T/d	32	4
Nitrogen Weight	T/d	412	16
Water Weight	T/d	18	0
Total Outgas Weight	**T/d**	**555**	**91**
CO2 concentration	**%Wt**	**16.8**	**78.3**
Cooling water	**L/s**	**81**	**6**

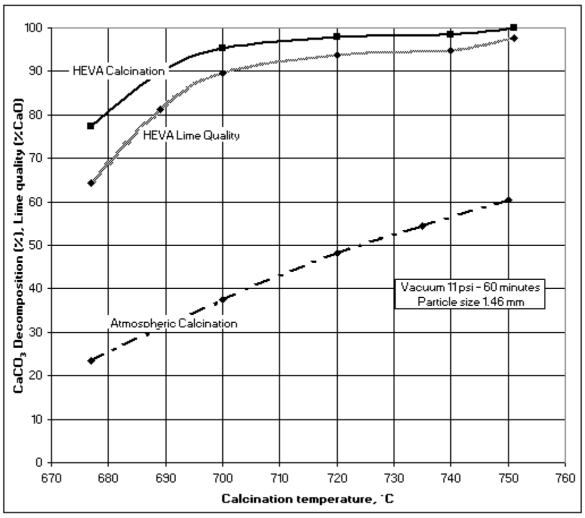

Fig. 3.1: Rate of limestone decomposition with HEVA and atmospheric calcination and temperature.

3.2 Clinker formation with HEVA Lime

Table 3.2 shows the parameters and results of 4 tests. The conversion to Larnite (Belite) is only 57.6% without mechanical activation even though the reaction time is larger (240 minutes). With the mechanical activation the Larnite conversion increases with the attrition time and reaches 87.4% in 20 minutes; the longer time does not improve the conversion. The temperature required (1,050 °C) is quite below industrial practice and the goal is now to shorten the reaction time.

Figure 3.2 and Table 3.3 show that without the mechanical activation about 20% of CaO is converted to Portlandite, $Ca(OH)_2$, instead of Belite, while 15% of Quartz and 6.7% CaO also remain unreacted at this temperature. Such amounts of $Ca(OH)_2$ and CaO should also generate a pulp with high conductivity, but it only reports 0.44 instead 10.0 mS or more; this suggests some kind of passivation that requires a higher temperature or mechanical activation to become more reactive.

Tab. 3.2: Parameters of clinkerization tests with HEVA lime and quartz sand.

Test No	Reactants							Mechanical activation					
	Sample weight, gr					Ratio CaO/SiO_2		Speed	Time	Balls		Filling	Temp.
	Lime	Sand	Total	CaO	SiO_2	Actual	Eq (3)	Rpm	minutes	Ø, mm	Grs	ratio	°C
M-004	13.33	6.67	20.00	12.87	6.57	1.96	1.80	- . -	- . -	- . -	- . -	- . -	25
M-007	13.33	6.67	20.00	12.87	6.57	1.96	1.80	1,440	10	2.0	1,000	0.58	52
M-008	13.33	6.67	20.00	12.87	6.57	1.96	1.80	1,440	20	2.0	1,000	0.58	52
M-009	13.33	6.67	20.00	12.87	6.57	1.96	1.80	1,440	30	2.0	1,000	0.58	52

Test No	Pre treatment		Clinkerization				
	Speed	Time	Temp.	Time	Conductivity, mS		Larnite
	Rpm	minutes	°C	minutes	water	pulp	%
M-004	0	0	1,050	240	0.12	0.44	57.6
M-007	1,440	10	1,050	180	0.16	0.63	66.1
M-008	1,440	20	1,050	180	0.16	0.64	87.4
M-009	1,440	30	1,050	180	0.16	0.69	87.5

The mechanical activation has been applied to increase the chemical reactivity of several minerals [10] with good commercial success, especially for leaching complex sulfides [11]. In a recent paper, Mucsi [12] reports the mechanical activation of fly ash and cement [9] in order to improve their performance as hydraulic binders. On the other hand, Sekulica [13] found that cement treated mechanically reported a compression stress 58% higher than an inactivated sample of similar composition; also reported that endothermic and exothermic reactions proceed at lower temperatures as indication of increased reactivity of mechanically activated sample.

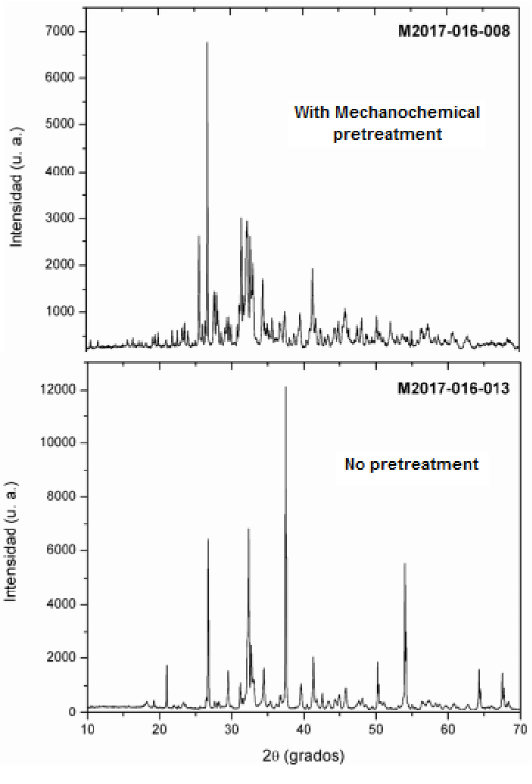

Fig. 3.2: XRD patterns of "clinker" after heating at 1,150 °C during 60 minutes, with and without mechanochemical pretreatment.

Tab. 3.3: Mineralogical composition of "clinker" after heating at 1,150 °C during 180 minutes.

Mechanochemical pretreatment	**Yes**	**No**
Test No. 2017-016-…	**M-008**	**M-004**
Larnite, Ca_2SiO_4	**87.4**	**57.6**
Portlandlite, $Ca(OH)_2$	0.0	19.4
Quartz, SiO_2	**1.6**	**14.6**
Calcium silicate sulfate, $Ca_5(SiO_4)_2.SO_4$	6.5	1.5
Anhydrite, $CaSO_4$	3.8	0.2
Calcium Oxide, CaO	**0.7**	**6.7**
Total	**100.0**	**100.0**

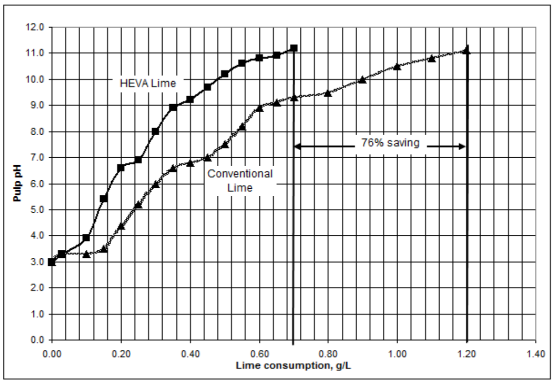

Fig. 3.3: Pulp pH versus lime consumption in acid effluent neutralization.

In the present case, the mechanical activation of clinker raw materials such as lime and quartz aims to reduce the temperature of clinker formation and replace heating by mechanical energy which can be supplied from a renewable energy source. Since the HEVA lime is obtained without any CO_2 emission, clinker and cement could also be obtained without CO_2 emissions.

3.3 Reactivity of HEVA Lime

Figure 3.3 shows that the HEVA Lime is much more reactive than the conventional lime, and 76% less consumption is required to neutralize acid mine effluents and remove dissolved heavy metals.

3.4 Carbonic fertilization with HEVA CO_2

Figure 3.4 shows that HEVA CO_2 can be utilized to increase the growing rate of radish plants in a green house. After 16 days, 38% increase in biomass production with respect to a normal atmosphere was obtained in a 1,200 ppm HEVA CO_2 atmosphere.

The growing rate of microalgae spirulina achieved with HEVA CO_2 was similar to that reported with commercial CO_2 that is used in the Peruvian Ocean Institute. The chemical analysis of HEVA microalgae performed at the La Molina University reported 47.2% of protein compared to 61.4% for commercial CO_2. This difference matches well with the lower concentration of HEVA CO_2 (78.3%) used as compared to 99.9% CO_2 in commercial gas.

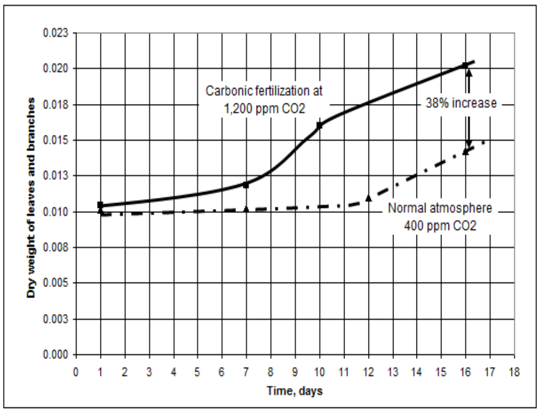

Fig. 3.4: Carbonic fertilization of radish (Raphanus sativum) with HEVA CO_2 compared with normal atmosphere.

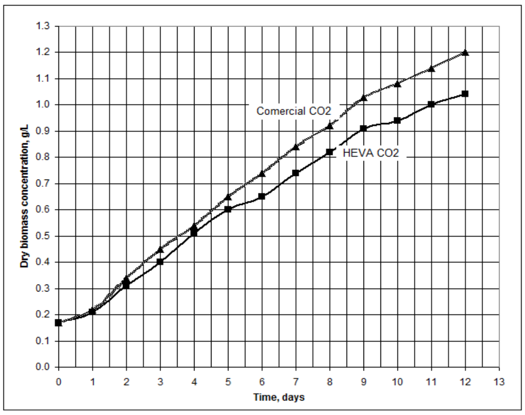

Fig. 3.5: Biomass generation rate in microalgae photo bioreactor fed with HEVA and commercial CO_2

4 CONCLUSIONS

The results of the HEVA process testwork show that high quality lime and biomass quality CO_2 can be obtained at much lower temperature than in conventional calcination process. Therefore, it would be feasible to obtain lime without CO_2 emission as far as the captured gas can be fully utilized for biomass generation.

On the other hand, cement could also be obtained without CO_2 emission if clinker is produced from HEVA lime and quartz sand (or clay), in an electrical furnace.

Preliminary results show that mechanochemical pretreatment improves the conversion rate of lime and quartz sand to Belite phase at lower than conventional temperature. This is an interesting area for future research.

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