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GEE EMISSIONS IN CEMENT PLANT AND ITS CONTROL BY TECHNOLOGY, CO-PROCESSING AND THE USE OF ACTIVE ADDITIONS

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Abstract. *Cement plants due to intensive use of fossil in the production process, as well as by calcination of calcium carbonate for the production of clinker, have great generation of CO_2. This paper analyses the conventional process cement production in conventional rotary kilns with grate and satellite coolers. Then presents the technological advances regarding the use of precalciners with tertiary air for combustion, and the towers of cyclone preheaters up to six stages in order to improve fuel and thus reduce greenhouse gas emissions. Moreover, the co-processing of industrial waste allows to reduce the consumption of fossil fuels, while allowing the waste destruction. The use of waste from the steel industry also allows to reduce the clinker percentage in Portland cement, reducing the generation of CO_2 per ton of cement produced. Heat balances are presented, composition of materials used and the calculations of gains in reducing emissions. Fuels used in cement kilns were coal and petroleum coke national and imported, used tires and other co-processed industrial waste.*

Keywords: *Cement Plants, Rotary Kilns, Industrial Wastes, Fuels, CO_2*

1. INTRODUCTION

Cement is an essential construction material used as binder. The product is one of the world commodities. In 2012, Brazil was the 4th world's cement producer with 88 plants operating on their territory, belonging to 15 national and foreign industrial groups (SNIC, 2014).

The cement manufacturing process requires high energy consumption. According EPE (2013), more than 80% refers to the consumption of thermal energy during combustion of fuels to produce clinker, the main component of Portland cement. Therefore, the cement industry is responsible for major environmental impacts on the human environment, biotic and physical. These impacts are caused mainly by emissions of greenhouse gases from this burning. Among these gases, there is a large emission of CO_2, a major greenhouse gas. The cement industry is responsible for about 5% of anthropogenic source of CO_2 released into the atmosphere annually (WBCSD, 2009).

The emission of CO_2 is obtained from burning and decarbonation of the raw meal entering the cement kiln. The carbon part of the fuel after combustion is associated with oxygen releasing CO_2 as Eq. (1); and secondly, since the raw meal entering the clinkering process consists of $CaCO_3$ and $MgCO_3$, these elements, that the gain during the heat release process CaO, MgO and CO_2, as Eq. (2) and Eq. (3), which are components necessary for formation of clinker. Thus, the CO_2 released from raw materials represents a large portion of the total CO_2 emissions in cement plants (Benhelal et al, 2013).

$$C + O_2 \rightarrow CO_2 \quad (1)$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad (2)$$

$$MgCO_3 \rightarrow MgO + CO_2 \quad (3)$$

Some techniques have been used to reduce CO_2 emissions in the cement industry, one of which, the exchange of fuel and even partial substitution by alternative fuels; in addition to the partial substitution of clinker for cement production, for blast furnace slag, waste steel industry.

Due to the heating value of industrial waste, they are used as fuels, reducing consumption of fossil fuel during the clinker manufacturing process. These industrial wastes are called alternative or secondary fuels. The partial replacement of fuel used technique in rotary kiln clinker from cement industries is called co-processing.

Whereas the blast furnace slag consists of CaO, MgO, Fe_2O_3, Al_2O_3 and SiO_2, and knowing that these elements are the same constituents of the clinker obtained in a kiln of a cement plant, with formation changes, it is possible to replace part of clinker used in cement production by slag (Zhu et al, 2012). With this decreases the quantity of clinker required per ton of cement produced, that is, it reduces the amount of CO_2 emitted per ton of cement produced, because the lower consumption of clinker in cement production.

2. CO_2 EMISSION IN CEMENT PLANTS

2.1 Cement Plant Analyzed

To analyze the generation of CO_2 in the manufacture of cement, it was considered for calculating a route dried with cement plant preheater cyclones tower and precalciner, with a daily production capacity of 3,000 tons of clinker and a specific heat consumption of 3,150 kJ/kg clinker as Fig.1.

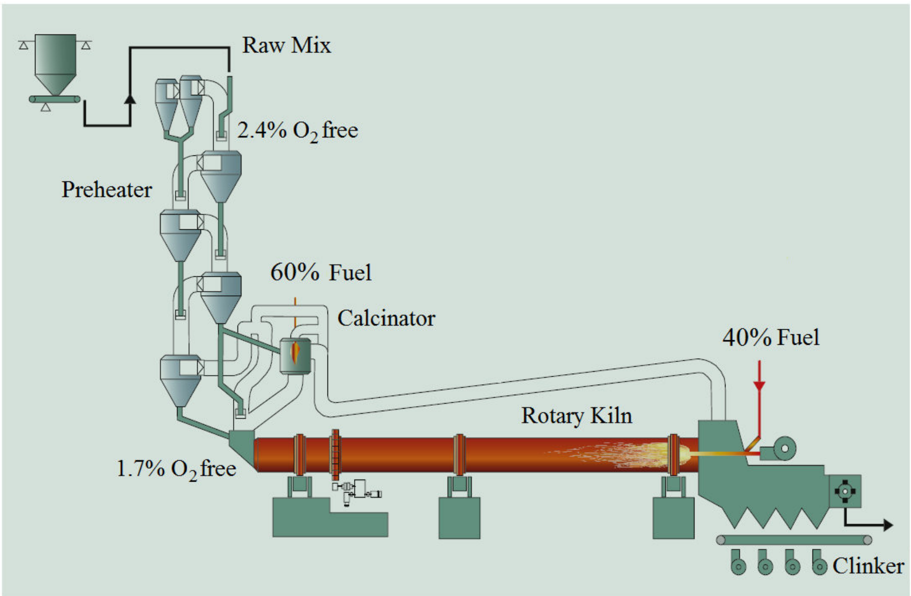

Figure 1 – Schematic diagram of a clinker kiln via-dry with preheater cyclone and calciner (GTZ, 2006) adapted.

2.2 Raw Materials Used

The portion of CO_2 emissions in cement plants corresponding to the raw material was calculated from two chemical compositions provided by companies in the central region of Minas Gerais, Brazil. Such compositions are shown in Tab. 1.

The Tab. 2 shows the flow of raw meal, at the entrance of cyclones, in kmol/s used in the calculations of CO_2 generation, for a clinker production of 34.72 kg/s, or 3,000 tons/day of clinker.

2.3 Quality of Clinker

To ensure the quality of clinker and consequently the cement, we must keep some parameters within certain values. These parameters are: the Lime Saturation Factor (LSF), the Silica Moduli (SM) and Alumina Moduli (AM) (Sorrentino, 2011).

Table 1 – Raw material composition fed in the kiln (wt%).

Composition	Composition 1 % weight	Composition 2 % weight
SiO_2	13.48	14.09
Al_2O_3	3.47	4.25
Fe_2O_3	2.19	1.88
SO_3	0.27	0.08
Na_2O	0.07	0.07
K_2O	0.61	0.60
CaO	43.07	42.63
MgO	1.01	0.49

Table 2 - Raw material composition fed in the cyclones (wt% and kmol/s) for the production of 3,000 tons/day of clinker.

Initial Composition	Composition 1		Composition 2	
	% weight	kmol/s	% weight	kmol/s
$CaCO_3$	76.92	0.416785	76.12	0.412451
SiO_2	13.48	0.121733	14.09	0.127254
Al_2O_3	3.47	0.018815	4.25	0.023005
Fe_2O_3	2.19	0.011854	1.88	0.010169
$MgCO_3$	2.13	0.011520	1.04	0.005615
SO_3	0.27	0.001438	0.08	0.000432
Na_2O	0.07	0.000405	0.07	0.000382
K_2O	0.61	0.003318	0.60	0.003235

The SM is a ratio between silica and the sum of the content of Al_2O_3 and Fe_2O_3 content. This module interferes with the firing of the raw meal in the glue forming the refractory kiln, the particle size of the clinker and in the liquid phase. According to Carpio (2005), the Silica Moduli must present the raw meal in a range of 2.3 to 2.7 so that production occurs in the best conditions, as Eq. 4. If the Silica Moduli has a high value, it causes an increase of C_3S (tricalcium silicate - $3CaO.SiO_2$) and C_2S (dicalcium silicate - $2CaO.SiO_2$), thereby decreasing the amount of C_3A (tricalcium aluminate - $3CaO.Al_2O_3$) and C_4AF (tetracalcium alumino ferrite - $4CaO.Al_2O_3.Fe_2O_3$) liquid phase. This condition implies a higher fuel consumption and increased production cost. However, if the value of the Silica Moduli has a low value, it favors the generation of the constituents in the liquid phase and also increase the collage of refractory kiln.

$$SM = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \tag{4}$$

The AM is a relationship between the amount of Fe_2O_3 and Al_2O_3 contained in the raw meal. Its value should be between 1.3 to 2.7 to obtain a suitable firing of the raw materials, as Eq. 5. The low value of the Alumina Moduli allows lower viscosity, which facilitates the occurrence of reactions. Its high value increases the viscosity, making it difficult reactions (Carpio, 2005).

$$AM = \frac{Al_2O_3}{Fe_2O_3} \tag{5}$$

The LSF represents the degree of calcium oxide can react with the other oxides and generate C_3S in the clinker. Its value must be between 90 and 100% by weight, as Eq. 6. The value of the Lime Saturation Factor outside the limits described above interfere in raw meal, as too in the clinker. When its value is high, then the meal is difficult to burn, demanding greater fuel consumption. Already with the lower value, the meal burn easily, but generates a very burnt clinker, which is not desirable (Carpio, 2005).

$$LSF = \frac{100\,CaO}{2.8\,SiO_2 + 1.1\,Al_2O_3 + 0.7\,Fe_2O_3} \tag{6}$$

The Tab. 3 shows the values obtained for the silica and alumina modules and with the lime saturation factor for the raw material compositions.

Table 3 – Silica Moduli, Alumina Moduli, and Lime Saturation Factor for the compositions of raw mix materials

SM		AM		LSF	
Composition 1	Composition 2	Composition 1	Composition 2	Composition 1	Composition 2
2.382	2.302	1.587	2.262	99.954	93.811

2.4 Specific Consumption of Heat for Cement Kiln

Table 4 shows the specific heat consumption for various cement plant settings (Ali et al, 2011).

Table 4 - Specific consumption of thermal energy in clinker production process.

Kiln process	Thermal energy consumption (GJ/ton clinquer)
Long dry process with internals	4.60
1-Stage cyclone preheater	4.18
2-Stage cyclone preheater	3.77
4-Stage cyclone preheater	3.55
4-Stage cyclone preheater + calciner	3.14
5-Stage preheater plus calciner + high efficiency cooler	3.01
6-Stage preheater plus calciner + high efficiency cooler	< 2.93

Fonte: Ali et al (2011)

2.5 Chemical Composition of Used Fuel

Table 5 shows the chemical composition in percentage by weight and individual heating value fuels used in the analysis.

Table 5. Elementary Chemical Composition (wt%) and Heating Value of the Individual Fuel.

Fuel Composition (%)	Pet Coke[(1)] Imported 1	Pet Coke [(1)] Imported 2	Pet Coke [(1)] National	Mineral Coal[(2)]	Scrape Tire[(2)]
C	88.4	89.45	90.76	70.12	72.15
H	3.70	3.50	3.16	4.51	6.74
O	0.00	0.00	0.00	1.13	9.67
N	1.56	2.43	1.46	2.25	0.36
S	6.16	2.47	0.73	1.28	1.23
Heating Value (kJ/kg)	34,350	34,859	35,069	26,928	32,580

Source: [(1)] Signoretti (2007), [(2)] Belato (2013)

2.6 Addition of Granulated Blast Furnace Slag in Cement

The granulated blast furnace slag is a by-product of the treatment of iron ore in blast furnaces, obtained in granular form, quenched, consisting mostly of silicates, aluminosilicates and calcium-alumina-silicates. Its composition must satisfy the relationship ABNT (1991b), presented in Eq. 7:

$$\frac{CaO + MgO + Al_2O_3}{SiO_2} > 1 \tag{7}$$

Table 6 shows the proportion of Portland cement components in accordance with the ABNT (1991a), ABNT (1991b) e ABNT (1991c).

2.7 Analyzed Cases

Considering the plant characteristics of Section 2.1, and the information presented in the previous sections, it was calculated the formations of CO_2 and SO_2 emissions for various fuel blends as shown in Tab. 7. The maximum use of scrap tires is around 15%, in the mixed fuel, is related to the emission of heavy metals and generation of CO in precalciner while maintaining control of combustion, dedusting system, and control of NO_x formation.

Table 6. Constituents of Portland Cement Composite.

Components (% in mass)					
Initials	Strength class	Clinker + calcium sulphates	Granulated Blast Furnace Slag	Carbonate Material	Standard
CP I	25 32 40	100	0	0	ABNT (1991c)
CP II-E	25 32 40	94 - 56	6 - 34	0 - 10	ABNT (1991a)
CP III	25 32 40	65 - 25	35 - 70	0 - 5	ABNT (1991b)

Table 7. Fuel blend by percentages

Blend	Coal (%)	Petcoke Imp. 1 (%)	Petcoke Imp. 2 (%)	Petcoke Nat.(%)	Scrap Tires (%)	Blend	Coal (%)	Petcoke Imp. 1 (%)	Petcoke Imp. 2 (%)	Petcoke Nat.(%)	Scrap Tires (%)
1	100	0	0	0	0	28	42.5	42.5	0	0	15
2	0	100	0	0	0	29	17.5	67.5	0	0	15
3	0	0	100	0	0	30	67.5	0	17.5	0	15
4	0	0	0	100	0	31	42.5	0	42.5	0	15
5	85	0	0	0	15	32	17.5	0	67.5	0	15
6	0	85	0	0	15	33	67.5	0	0	17.5	15
7	0	0	85	0	15	34	42.5	0	0	42.5	15
8	0	0	0	85	15	35	17.5	0	0	67.5	15
9	75	25	0	0	0	36	0	67.5	17.5	0	15
10	50	50	0	0	0	37	0	42.5	42.5	0	15
11	25	75	0	0	0	38	0	17.5	67.5	0	15
12	75	0	25	0	0	39	0	67.5	0	17.5	15
13	50	0	50	0	0	40	0	42.5	0	42.5	15
14	25	0	75	0	0	41	0	17.5	0	67.5	15
15	75	0	0	25	0	42	0	0	67.5	17.5	15
16	50	0	0	50	0	43	0	0	42.5	42.5	15
17	25	0	0	75	0	44	0	0	17.5	67.5	15
18	0	75	25	0	0	45	50	25	25	0	0
19	0	50	50	0	0	46	25	25	25	25	0
20	0	25	75	0	0	47	0	50	25	25	0
21	0	75	0	25	0	48	0	25	25	50	0
22	0	50	0	50	0	49	0	25	50	25	0
23	0	25	0	75	0	50	45	20	20	0	15
24	0	0	75	25	0	51	21.3	21.2	21.2	21.3	15
25	0	0	50	50	0	52	0	45	20	20	15
26	0	0	25	75	0	53	0	20	20	45	15
27	67.5	17.5	0	0	15	54	0	20	45	20	15

The Tab. 8 and Tab. 9 show the results for CO_2 emissions per ton of clinker and cement ton, plus the emission of SO_2.

3. DISCUSSION OF RESULTS

The SO_2 emission limit established by COPAM (2010), corrected to 11% O_2, in dry basis, for raw material compositions 1 and 2 is 400 mg/Nm^3 and 680 mg/Nm^3, respectively, considering the content SO_3 in the process input raw meal. Thus, only the fuel mixtures: case 2 (100% Petcoke Imp 1) case 6 (85% Petcoke Imp 1 and 15% Scrap Tires) case 11 (75% Petcoke Imp 1 Pet. and 25% Coal) and case 18 (75% Petcoke Imp. 1 and 25% Petcoke Imp. 2) violate the norm for raw meal composition 1. As for the raw meal composition 2, all mixing variants meet the same standard. As for the raw meal composition 1, considering only the different fuel blends was obtained for case 1 (100% Coal) the highest emission level equal to 845.4 kg of CO_2 per ton of cement clinker, and in case 7 (mixture of 85% Petcoke Imp. 2 and 15% Scrap Tires), the lowest emission level equal to 834.6 kg of CO_2 per ton of clinker, i.e. a reduction of emissions from a production 1,095,000 tons of clinker per year, approximately 11,825 tons of CO_2 per year. The burning of tires reduces the CO_2 emissions due to higher content of hydrogen (H) in tires composition, in relation to the composition of imported petroleum coke. Also, considering the partial substitution of clinker by blast furnace slag, reductions are obtained approximately 39,240 tons of CO_2 per year for an approximate production of 1,128,860 tons of cement per year (type CP I); reductions of approximately 359,100 tons of CO_2 per year for an approximate production of 1,128,860 tons of cement per year (type CP II-E); and reductions of approximately 519,030 tons of CO_2 per year for an approximate production of 1,128,860 tons of cement per year (type CP III).

Table 8. CO_2 emissions per ton of clinker and per ton of cement produced, and the SO_2 emissions.

Case	kg/ton clinker	mg/Nm^3	kg CO_2/ton cement			Case	kg/ton clinker	mg/Nm^3	kg CO_2/ton cement		
	CO_2	SO_2 (11%)	CP I (0%)	CP II-E (30%)	CP III (50%)		CO_2	SO_2 (11%)	CP I (0%)	CP II-E (30%)	CP III (50%)
1	845.4	127.2	820.0	524.1	376.2	28	836.9	280.7	811.8	518.9	372.4
2	841.9	494.0	816.6	522.0	374.6	29	836.0	374.1	810.9	518.3	372.0
3	841.1	198.4	815.9	521.5	374.3	30	837.8	137.2	812.7	519.4	372.8
4	843.6	58.6	818.3	523.0	375.4	31	836.9	154.9	811.8	518.9	372.4
5	838.4	125.1	813.2	519.8	373.1	32	836.0	173.1	810.9	518.3	372.0
6	835.4	440.3	810.3	517.9	371.8	33	838.0	113.4	812.9	519.6	372.9
7	834.6	186.0	809.6	517.5	371.4	34	837.6	96.3	812.5	519.3	372.7
8	836.8	66.2	811.7	518.8	372.4	35	837.1	78.8	812.0	519.0	372.5
9	844.6	216.9	819.3	523.7	375.8	36	835.2	388.5	810.1	517.8	371.7
10	843.7	307.9	818.4	523.1	375.4	37	835.0	314.0	810.0	517.7	371.6
11	842.8	400.3	817.5	522.5	375.0	38	834.8	238.9	809.8	517.6	371.5
12	844.3	144.4	819.0	523.5	375.7	39	835.7	364.4	810.6	518.1	371.9
13	843.2	162.0	817.9	522.8	375.2	40	836.1	255.0	811.0	518.4	372.1
14	842.1	180.0	816.8	522.1	374.7	41	836.5	144.4	811.4	518.6	372.2
15	845.0	110.7	819.7	523.9	376.0	42	835.1	161.5	810.0	517.8	371.6
16	844.5	93.8	819.2	523.6	375.8	43	835.7	126.3	810.6	518.1	371.9
17	844.1	76.5	818.8	523.3	375.6	44	836.4	91.0	811.3	518.6	372.2
18	841.7	421.0	816.4	521.9	374.6	45	843.5	235.3	818.2	523.0	375.4
19	841.5	347.4	816.3	521.7	374.5	46	843.0	219.9	817.7	522.7	375.1
20	841.3	273.2	816.1	521.6	374.4	47	842.1	313.1	816.8	522.1	374.7
21	842.3	387.0	817.0	522.2	374.8	48	842.5	204.1	817.2	522.4	374.9
22	842.8	278.8	817.5	522.5	375.0	49	841.9	238.7	816.6	522.0	374.6
23	843.2	169.3	817.9	522.8	375.2	50	836.8	212.5	811.7	518.8	372.4
24	841.7	163.6	816.4	521.9	374.6	51	836.3	204.4	811.2	518.5	372.2
25	842.3	128.7	817.0	522.2	374.8	52	835.5	293.8	810.4	518.0	371.8
26	843.0	93.7	817.7	522.7	375.1	53	836.0	183.6	810.9	518.3	372.0
27	837.8	188.7	812.7	519.4	372.8	54	835.3	218.6	810.2	517.9	371.7

4. CONCLUSIONS

Analyzing Tab. 8 and Tab. 9, it is found that the insertion of the industrial waste, scrap tires, contributes to the reduction of CO_2 emission to the atmosphere. The burning of used tires in cement kiln makes possible the removal of the environment of a waste of difficult discard. This waste deposited improperly can serve as a site for the breeding of disease vectors. From the results it can be seen that variations of the fuels used in cement plants coupled with the fact that the use of mineral admixtures such as Granulated Blast Furnace Slag in Portland cement manufacture can result in significant reductions in CO_2 atmosphere. Only in Brazil were manufactured in 2013, 263,000 tons of cement type CP I, 41.249 million tons of cement type CP II-E and 9.405 million tons of cement type CP III (SNIC, 2014). This reality is an effective reduction of the generation of CO_2 in cement manufacturing process Portland, per ton produced. The production of Portland cement CP-II represents a reduction of over 35% in the generation of CO_2 per ton of Portland cement type CP-I.

Table 9. CO_2 emissions per ton of clinker and per ton of cement produced, and the SO_2 emissions.

Case	kg/ton clinker	mg/Nm^3	kg CO_2/ton cement			Case	kg/ton clinker	mg/Nm^3	kg CO_2/ton cement		
	CO_2	SO_2 (11%)	CP I (0%)	CP II-E (30%)	CP III (50%)		CO_2	SO_2 (11%)	CP I (0%)	CP II-E (30%)	CP III (50%)
1	831.8	128.0	806.8	515.7	370.2	28	823.2	282.5	798.5	510.4	366.3
2	828.3	497.1	803.5	513.5	368.6	29	822.4	376.5	797.7	509.9	366.0
3	827.4	199.7	802.6	513.0	368.2	30	824.0	138.1	799.3	510.9	366.7
4	830.0	59.0	805.1	514.6	369.4	31	822.9	155.9	798.2	510.2	366.2
5	824.7	125.8	800.0	511.3	367.0	32	821.8	174.2	797.1	509.5	365.7
6	821.7	443.1	797.0	509.5	365.7	33	824.4	114.1	799.7	511.1	366.9
7	821.0	187.2	796.4	509.0	365.3	34	823.9	96.9	799.2	510.8	366.6
8	823.2	66.6	798.5	510.4	366.3	35	823.5	79.3	798.8	510.6	366.5
9	830.9	218.3	806.0	515.2	369.8	36	821.6	391.0	797.0	509.4	365.6
10	830.0	309.9	805.1	514.6	369.4	37	821.4	316.1	796.8	509.3	365.5
11	829.2	402.8	804.3	514.1	369.0	38	821.2	240.5	796.6	509.1	365.4
12	830.7	145.3	805.8	515.0	369.7	39	822.0	366.8	797.3	509.6	365.8
13	829.6	163.0	804.7	514.4	369.2	40	822.5	256.7	797.8	510.0	366.0
14	828.5	181.2	803.6	513.7	368.7	41	822.9	145.4	798.2	510.2	366.2
15	831.3	111.4	806.4	515.4	369.9	42	821.5	162.5	796.9	509.3	365.6
16	830.9	94.4	806.0	515.2	369.8	43	822.1	127.1	797.4	509.7	365.8
17	830.4	77.0	805.5	514.8	369.5	44	822.7	91.6	798.0	510.1	366.1
18	828.1	423.7	803.3	513.4	368.5	45	829.8	236.8	804.9	514.5	369.3
19	827.8	349.6	803.0	513.2	368.4	46	829.4	221.3	804.5	514.2	369.1
20	827.6	275.0	802.8	513.1	368.3	47	828.5	315.2	803.6	513.7	368.7
21	828.7	389.5	803.8	513.8	368.8	48	828.9	205.4	804.0	513.9	368.9
22	829.1	280.6	804.2	514.0	368.9	49	828.3	240.2	803.5	513.5	368.6
23	829.5	170.4	804.6	514.3	369.1	50	823.2	213.9	798.5	510.4	366.3
24	828.0	164.7	803.2	513.4	368.5	51	822.7	205.7	798.0	510.1	366.1
25	828.7	129.6	803.8	513.8	368.8	52	821.9	295.7	797.2	509.6	365.7
26	829.3	94.4	804.4	514.2	369.0	53	822.3	184.8	797.6	509.8	365.9
27	824.1	189.9	799.4	511.0	366.7	54	821.7	220.0	797.0	509.5	365.7

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