Flue gas decarbonization

1. Introduction

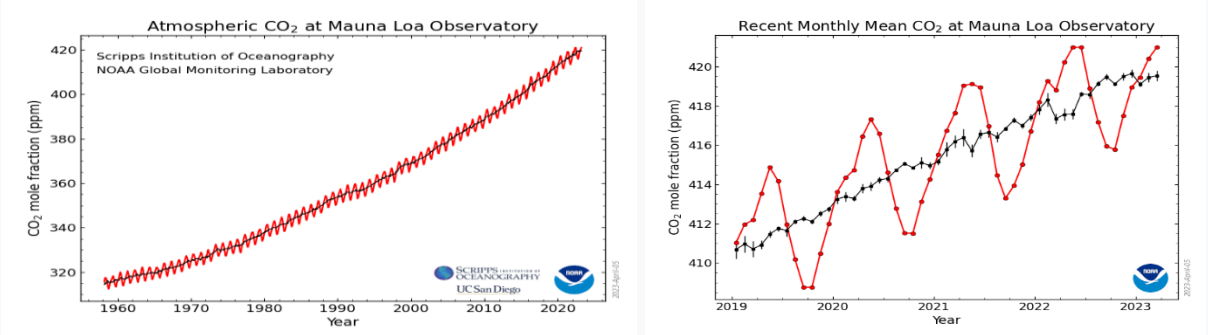
The generation of energy by combustion, that is, the oxidation of fossil fuels in mechanical arrangements such as engines, turbines, boilers, and furnaces, generates gaseous emissions containing high fractions of carbonic acid that impact the planet's troposphere, preventing the return of solar rays and contributing to the so-called greenhouse effect. The imbalance of the carbon balance in urban centers and air basins in industrial zones makes it a priority to control the concentration of particulate matter $PM_{2.5}$, $PM_{1.0}$, nitrogen oxides, and carbon dioxide in external air intake. prima, being naturally composed of 78% nitrogen, 21% oxygen, 0.04% carbon dioxide, and 0.96% noble gases, however other components such as dust, soot, smoke, combustion gases, water vapor, salt spray, and microorganisms make the air a contaminated and unsuitable raw material; The removal of elements foreign to the natural composition requires dynamic technologies capable of processing large volumes and removing substances in different physical states such as solids and gases.

Two new concepts are closely linked, which are environmental inertia and resilience, this is the ability to resist environmental pressures. These terms are somewhat related and are probably best exemplified by climax communities, that is, an ecological community in the final phase of succession, in which the species composition remains relatively stable until a disturbance such as pollution occurs. These environments are able to withstand changes in environmental pressures (resilience), but at the same time, are slow to change in response to changes (inertia). Both properties are a function of biodiversity in a climax community. The greater the diversity, the more stable the communities, for example, temperate forests are generally more diverse than grasslands, so their resilience and inertia would be greater.

Currently, the decarbonization of our planet's atmosphere is humanity's challenge, as the repercussions are global, as demonstrated on climate websites where the air quality is bad or harmful, even in remote locations; As for the gaseous impact, the issue is more democratic, as carbon dioxide is a gas and as such expands continuously, as measured in isolated locations such as Manua Loa in Hawaii, which show the change in tangent, alerted in 2000, configured as shown in Graph 1, where we have the evolution in the form of a mountain range of CO_2 rates in the global atmosphere with values such as 421 ppm of CO_2 in April 2023. Texts from the last decade indicate urban values between 400 and 600 ppm and indoor values of up to 3,500 ppm in religious temples. These values, on an ongoing basis, according to Canadian research, cause the demineralization of bones due to the action of carbon dioxide, which is an acid.

The Intergovernmental Panel on Climate Change (IPCC) stated in 2018 that the world needs to reach net zero emissions by around 2050 if it is to meet the Paris Agreement target of limiting global warming to 1.5°C. The 2050 deadline was later included in the Glasgow Climate Pact agreed at COP26 in 2021 (Serin E., 2023).

Graph 1- Evolution of carbonic acid concentration in the atmosphere



Source: https://gml.noaa.gov/ccgg/trends/mlo.html, 2023.

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Mitigating this effect has different fronts, however, it is clear that this migration takes at least two decades to become a significant reality. In this sense, applying technologies to convert this gaseous contaminant into another substance makes sense, as it enables a rapid inversion of the tangent of the carbon dioxide concentration growth curve in the atmosphere. Here we will present empirical results achieved in a power generation facility, based on diesel oil, with the application of multiventuri liquid centrifugation technology, which achieved extremely satisfactory results both in the hydraulic dragging of particulate matter and in the conversion of carbonic acid into a soluble salt, that is, gas turns into a soluble solid, eliminating carbon dioxide from the atmosphere and generating a by-product of economic value.

2. Chemical and technological basis

We will contextualize the scenario for the insertion of decarbonization, current global goals, mitigation trends, chemical formation and neutralization reactions, and carbon dioxide transformation technologies.

Our approach aims to establish a counterpoint in the currents of global mitigation actions, with this study being restricted to those that act on combustion gases, the initiatives of CCS- Carbon Capture & Storage, CCUS- Carbon Capture, Utilization & Storage, gain a new proposition under our argument is CCT - Carbon Capture & Transform. They all have the challenge that in the combustion gas streams, the CO_2 concentration varies according to the fuel, for example, 12% for heavy oil, 14% LPG, and 21% biomass, in addition to the combustion conditions. Therefore, the capture and separation of carbon dioxide from the gas stream requires a segregating effort to separate it from the remaining 86% as nitrogen oxides that will not be stored or processed.

According to the Massachusetts Institute of Technology (MIT) Environmental Solutions Initiative, some of the captured carbon dioxide is pumped into oil wells as a way to "dispose of hard-to-extract oil." Additionally, it is used in some greenhouses to help grow plants. Other potential uses include "turning CO2 into plastics, building materials like cement and concrete, fuels, futuristic materials like carbon fibers and graphene, and even household products like baking soda, bleach, antifreeze, and paints." None of them are in large-scale production yet.

> In the US, the Infrastructure Investment and Jobs Act passed in 2021, allocated more than US$12 billion for CCUS projects, with two projects approved in 2023 of US$1.2 billion for two direct carbon dioxide capture projects in Texas and Louisiana, both on a commercial scale. (Greg Daugherty, 2023).

Well, among the pros and cons, we have difficulty justifying a palliative and temporary solution such as underground storage for centuries and at the same time offering society a solution for immediate implementation that can influence the drop in CO_2 concentration in the atmosphere. We defend CCT-Carbon Capture & Transform, which transforms the gaseous fraction into a salable solid, as an economical and viable way of mitigating the greenhouse effect.

As the main chemical reaction characteristic of energy generation operations we have the oxidation of fossil fuels, the so-called combustion process, with oxygen promoting the breakdown of organic molecules, and generating a rate of 3.66 t CO_2 / t Carbon burned, According to Equation 1, where we have a quarter of the sum of carbon and hydrogen atoms as the number of molecules required for stoichiometric burning.

$$C_xH_y + \frac{x+y}{4} O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O + \text{Particulate matter("fly ash")} + \text{Energy} \quad (1)$$

The products of the combustion reaction include other gaseous oxides, such as nitrogen, a critical pollutant currently that will not be addressed in this study, but which will be subject to the

same reaction medium and will be converted into nitrate and nitrite salts. The classic chemical reaction of double exchange has been detected in urban centers and oceans, the largest carbon dioxide sink on the planet, we have carbonic acid generated in the combustion of motor vehicles and thermoelectric plants reacting with the limestone in the marble of European monuments or Australian marine corals forming calcium carbonates.

2.1. Chemical Route

Carbon dioxide emissions are being compared using technologies to separate the other components contained in the combustion gas streams, given the large proportion of nitrogen oxides and excess oxygen, in addition to solid contaminants such as particulate matter. Among these, we have absorption and desorption by amines, adsorption on active carbon, and the typical reactions acid + alkaline base >>> salt + water, through gas scrubbers that represent a more rational solution for transforming carbon dioxide into a solid for everyday use. and with added economic value, such as calcium carbonates and sodium bicarbonate where the mass balance shows the mass incorporation in the products resulting from the reactions, in which one of the reactants is in the air as a contaminant. Here we will restrict ourselves to the analysis of the wet route of gas scrubbers, more specifically that of hydrodynamic precipitators due to their compact dimensions, performance stability, and mainly carbon dioxide conversion efficiency.

According to Equations 2 and 3, we have a stoichiometry with gains of 37% and 55% in mass of the products resulting from spontaneous chemical reactions, with calcium hydroxide in Equation 2, and a chemical neutralization reaction caused by sodium hydroxide in Equation 2. Equation 3, in both reactions, carbon dioxide transforms into a soluble solid.

$$CO_2 + 2CaOH > Ca_2CO_3 + H_2O.$$

$$44 + 118 > 140 + 18 \quad (2)$$

$$CO_2 + 2NaOH > Na_2CO_3 + H_2O.$$

$$44 + 80 > 106 + 18 \quad (3)$$

Therefore, again, nature shows us the way, such as rainfall events that are capable of purifying the air in large urban centers with the precipitation of suspended particles, mainly PM_{10}, $PM_{2.5}$, and anthropogenic $PM_{1.0}$; We now have coral carbonation showing how to mitigate carbon dioxide from the atmosphere, unfortunately at the expense of marine life, but which has become a natural marker of environmental degradation.

The OPEX analysis of this technological route shows a financial tie between the cost of the raw material and the cost of the product, a fact that explains the procrastination in implementing large CCT units in urban centers or industrial complexes. These CCT units are more efficient when processing large flows of concentrated gas streams typical of industrial processes and energy plants, as the cost of the process must be guaranteed by the 55% mass difference that should make the operation viable. This is the need for a public determination imposing on large carbon-emitting enterprises at risk of paralyzing activities, otherwise the “status quo” will remain and perhaps worsen. Air pollution has already brought circulation restrictions, blocking of industrial activities, and fines, that is, coercive actions are necessary because once environmental resilience is broken, there will be significant inertia of the system in returning to a previous level even if drastic actions are taken.

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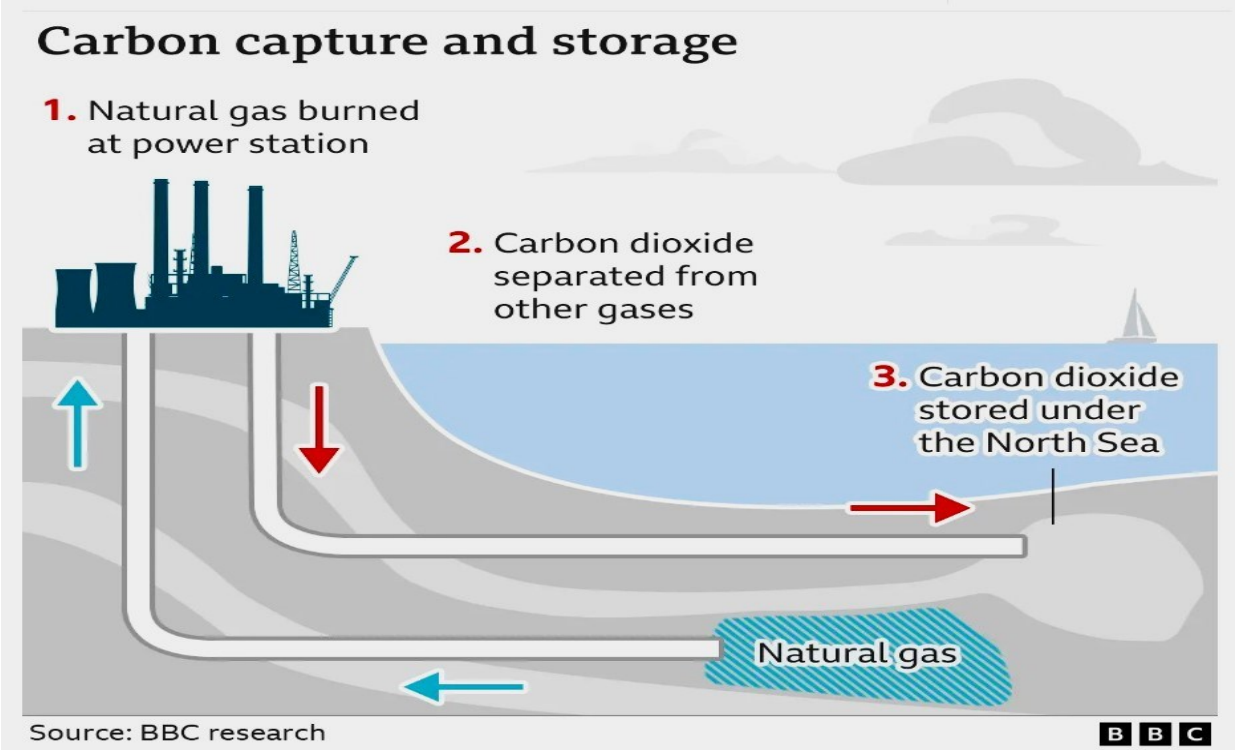
2.2. Technological Route

Criticism regarding the inefficiency, cost, or inadequacy of the solutions presented and promoted, including in international challenges, such as XPRIZE Carbon Removal, and COP28 in Dubai in December 2023, where an agreement was drawn up that marks the "beginning of the end" of the era of fossil fuels, setting the stage for a rapid, fair and equitable transition, underpinned by deep emissions cuts and increased financing. The agreement recognizes the science and establishes that global greenhouse gas emissions need to be reduced by 43% by 2030, compared to 2019 levels, to limit global warming to 1.5°C, as per the protocol. from Paris. The agreement establishes the Global Goal on Adaptation (GGA) which identifies targets that the world needs to reach to be resilient to the impacts of a changing climate, on adaptations and the need for financial, technological, and capacity-building support to reach them.

In an overview of the list of CCS technological routes for CO_2 sequestration, as illustrated in Figure 2, the techniques range from capturing carbonic acid before being released into the atmosphere in power plants and storing it underground, to the use of trees for fixing or equipment capable of removing it directly from the ambient air.

Figure 2 – CCS concept of carbon dioxide capture and storage in underground caves



Source: https://www.bbc.com/

Air and Flue gas washing with amines, is currently the reference technique for CO_2 sequestration, however, the energy consumption is around 0.2 – 0.5 MWh/t CO_2 segregated, which represents 20-30% of the production capacity. thermoelectric generation. The R&D status of carbon capture technologies is challenging and complex and includes absorption, adsorption, membrane, biological capture, and cryogenic separation (Xiaoxing Wang, 2020). Special attention should be paid to biological capture by microalgae, which has proven to be more efficient, in addition to the fact that algae do not have lignin, being a photosynthetically fixed carbon that is easily converted in the food chain, or for extracting oil to generate energy.

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This synthetic exposition shows the incipience of the technologies in use, a fact that makes the use of BADCT technologies (“Best Available Demonstrated Control Technology”) mandatory, that is, the best control technologies proven to exist. The multiventuri liquid centrifugation technology was developed and patented in Brazil, and its underlying concept is based on the convergence of molecular vibration amplitude, in which we cool the gaseous stream and increase kinetic energy in the refrigerated alkaline liquid to excite the liquid and reduce the enthalpy of the gas, and thus, through a multiventuri mechanical apparatus, promote the synergistic interaction between fluids in a turbulent environment of mass and energy transfer.

Hydrodynamic precipitators differ completely from the traditional countercurrent absorption towers currently adopted, as they promote a high contact factor, behaving as a compact and very effective dynamic reactor in converting two-phase reactions such as capture, solubilization, and conversion of carbon dioxide. carbon into a marketable product.

Figure 3 Urban CCT arrangement with direct air capture and transformation of CO2 and supply of purified air in the corporate building's air conditioning system

Source: Veltha despoluição atmosférica www.veltha.com.br

Characterized by a “limit load” type rotor capable of promoting the aspiration of the gaseous stream and its centrifugation with cooled alkaline liquid, in order to inoculate the carbon dioxide in the liquid medium that is a reaction and converts the gas into a soluble solid in one step single; This direct concept is the CCT, as illustrated in Figure 3, which transforms CO_2 into a commercial product directly, without gaseous storage for future use or simply keeping it stored for no purpose and with maintenance and management costs for monitoring these underground gaseous wells.

Drawing 4– Hydrodynamic precipitator technology with multiventuri centrifuge rotor, a dynamic reactor with a high conversion rate.

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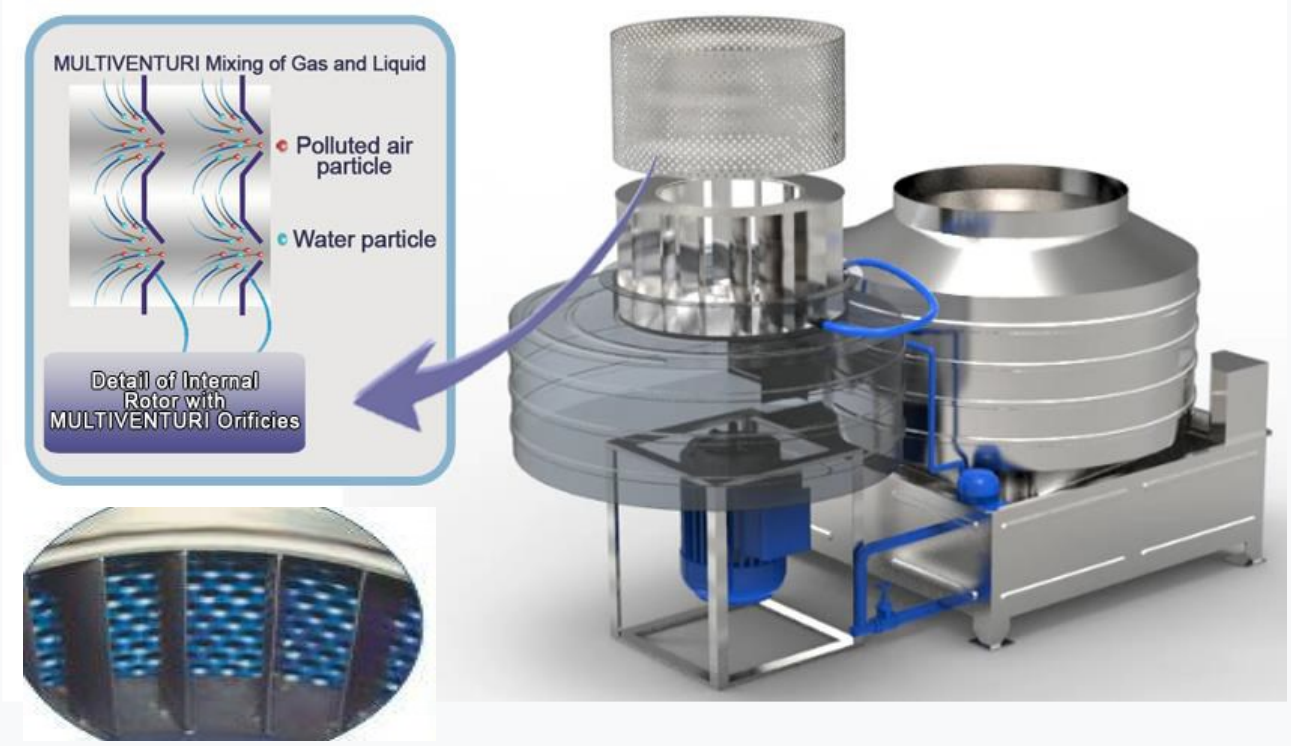
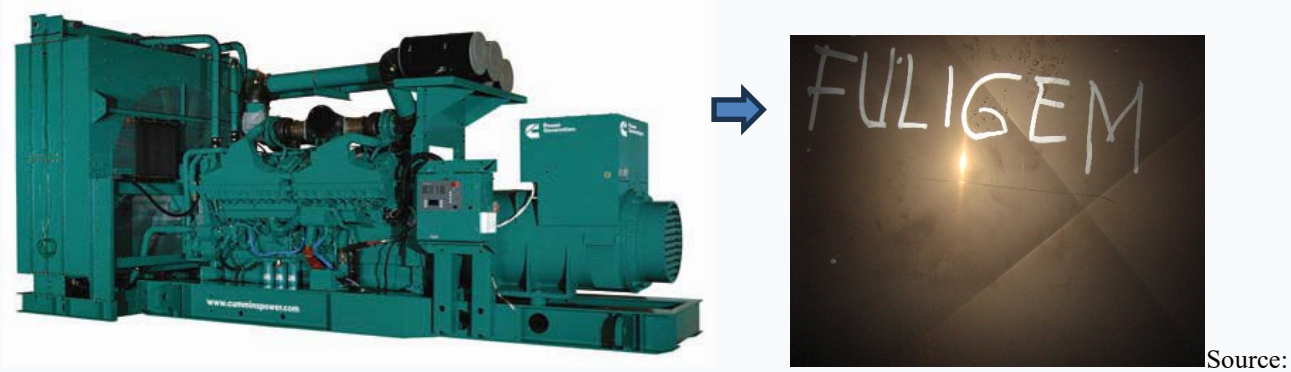


Source: Veltha Despoluição Atmosférica www.veltha.com.br

2.3 Effective empirical CCT trial

Based on a neighborhood impact demand for combustion gases, we had the opportunity to develop an application study in a plant of five generating sets that total 12.5 MW of energy generated from diesel oil, and which are part of a critical mission. large call center. Multiventuri liquid centrifugation technology has been developed and applied with the scope of controlling pollutants such as particulate matter, acid neutralization, vapor condensation, and odor control, and in this application study, we come across the prospect of carbon fixation as a way to score the project positively in a LEED classification analysis and generation of carbon credits. Thus, from the conception and implementation of the multiveturi alkaline liquid centrifugation technology of hydrodynamic precipitators applied to the treatment of combustion gases in a 12.5 MW plant of 2500 kVA generator sets, with Cummins engines model DQKC, 16-cylinder turbo diesel oil. As shown in Figure 5, they are state-of-the-art micro-processed TIE3 engines, and in practice, they emit pollutants with a smaller amount of particulate matter, but are more harmful, as $PM_{2.5}$ and $PM_{1.0}$ prevail, and with higher rates of CO_2, as the combustion is perfect.

Figure 5 – 2500 kVA TIE3 microprocessor turbocharger engine and fine particulate emissions



Source: Cummins data sheet and author- SP

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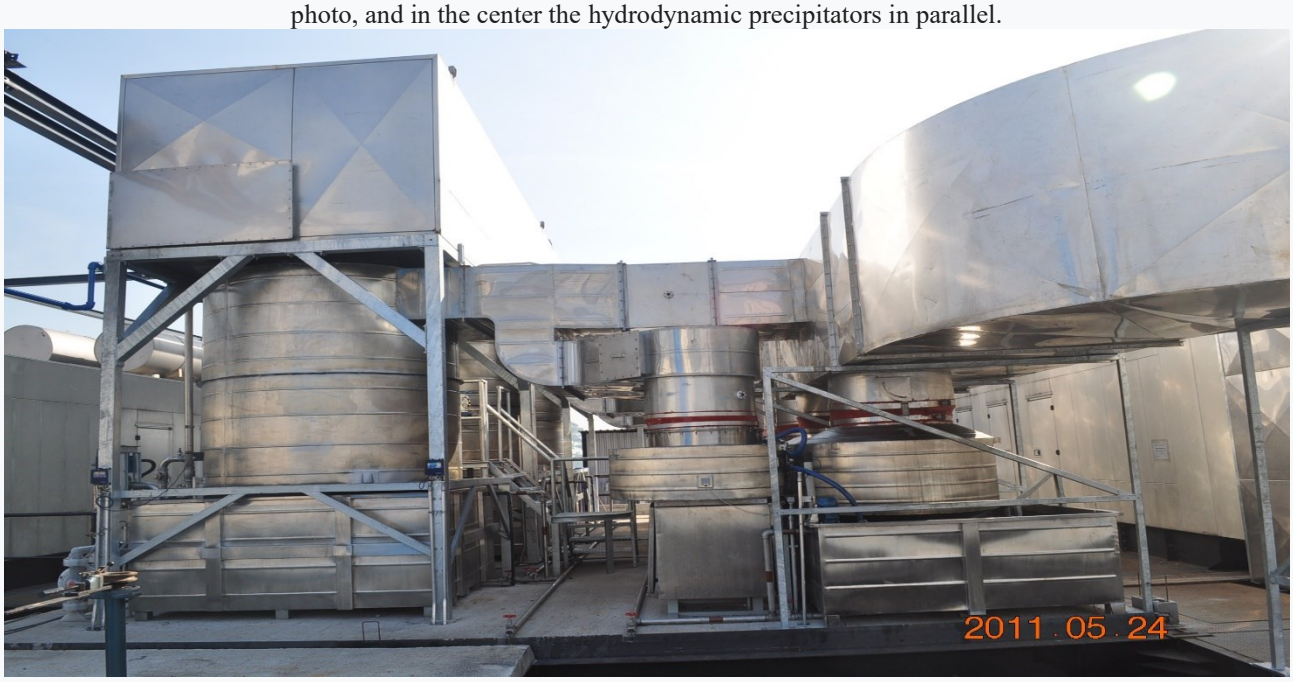
The combustion gas treatment system operates as a complete integrated solution, and the reports demonstrate the feasibility of decarbonizing gases by alkaline neutralization of carbonic acid in a stable, water-soluble salt, which has economic value and favorable stoichiometry as it incorporates mass from a component that is in the air. The installation consists of an expansion plenum that receives the discharge of hot gases (450°C) from the five generators at a speed of 30 m/s and reduces it to 4 m/s, with the gas stream being admitted to the primary quencher. , when the gases have their temperature reduced to 120°C and the moisture content raised to a saturated level. These pre-treated combustion gases are admitted, due to the depression generated by the hydrodynamic precipitators, into the centrifuge rotor when they are subjected to synergistic mixing with the injected alkaline liquid, forming a reaction mixture in which carbonic acid, CO_2, is converted into bicarbonate. sodium, a soluble solid with market value. The treated gases are discharged into the atmosphere and the circulating liquid is filtered, forming a cake of particulate matter, with the clarified liquid circulating until saturation when precipitation of sodium salts occurs.

Figure 6- 12.5 MW cogeneration plant, expansion plenum, and primary combustion gas quencher on the left of the photo, and in the center the hydrodynamic precipitators in parallel.



Source: author in the field- SP

The system has pH control and automatic correction of the stipulated value at pH= 8.5 through pumps dosing a 25% sodium hydroxide solution that is consumed according to the load of oxides present in the combustion gas stream, i.e. the system is always able to absorb process fluctuations that result in variations in the concentrations of carbon dioxide emitted.

Figure 7 Summary of the combustion gas analysis report after the ECP (pollution control equipment)

PRAMEQ

OS: **00000815** Contract: 000403

Sampling No.: 2

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Collection Date: 21/5/2011 Collection Location: **Generator 1 duct after Pollution control equipment**- 21.05.11-outlet duct

ORSAT ANALYSIS			
GASES	**MOLECULAR MASS (MM)**	**VOLUME %**	**MM x X**
CO2	44	0,00	0,00
O2	32	20,40	6,53
CO	28	0,00	0,00
N2	28	79,60	22,29
		100	**Mms: 28,82**

Client: ITAU UNIBANCO S.A

Report Issue Date: 29/7/2011

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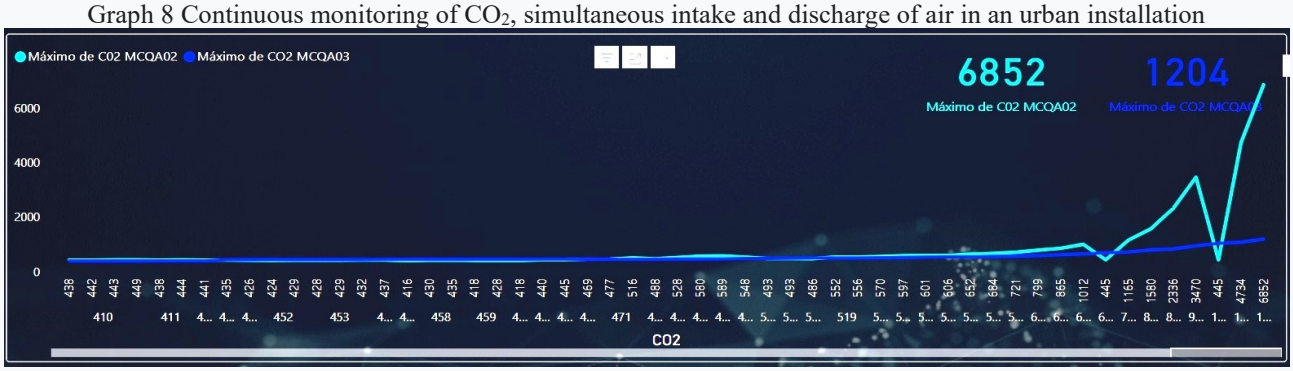
Source: Relatório Prameq - SP

This is a technological difference between the CCT to the CCS, as the physical-mechanical separation processes that always process the entire stream, after managing to sequester the carbon dioxide, begin the reverse process of separation and recycling of the amines, being a fraction lost to the atmosphere as a secondary pollutant. The performance certification of the installation in question established the monitoring of the system's final emissions for the parameters of particulate matter, sulfur oxides, and carbon dioxide. The report issued with field measurements results in the total absence of CO and CO_2 in the gas stream exhausted to the atmosphere, as shown in Figure 7; That said, we began to investigate the presence of sodium bicarbonate in the liquid solution circulating in the system, confirmed by analysis by the Mauá Institute of Technology.

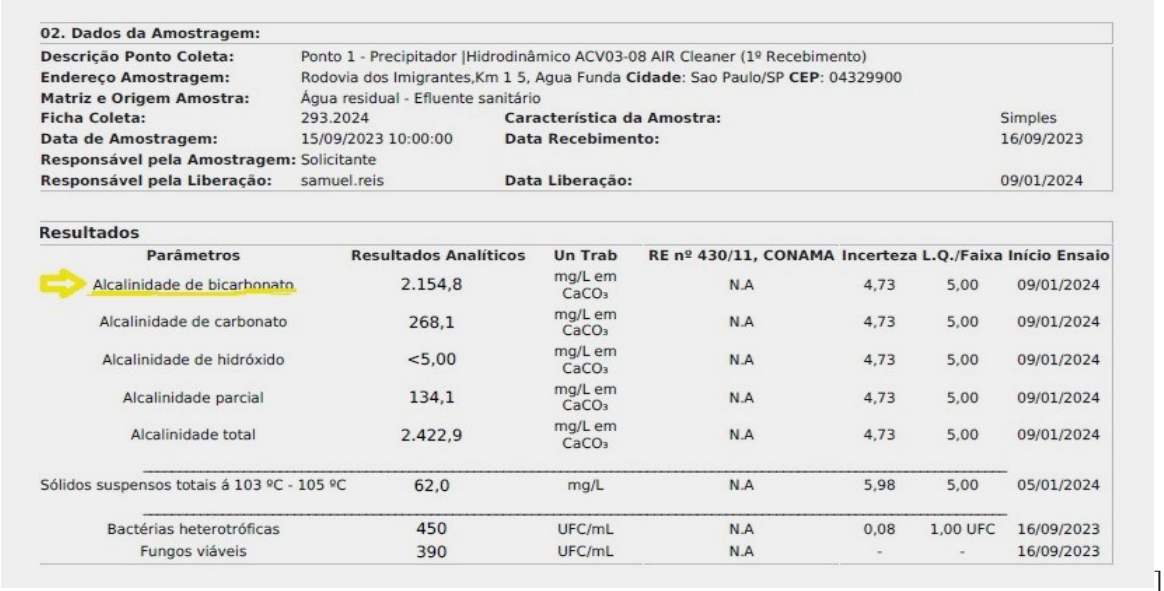
Graph 8 Continuous monitoring of CO_2, simultaneous intake and discharge of air in an urban installation



Source Monitor Continuo 3R Brasil- RJ

We recently operated another test in an air intake installation in a shopping center and at an event in a large exhibition center, whose objective was saline removal, and we also continuously and remotely monitored parameters such as PM_{10}, $PM_{2.5}$, $PM_{1.0}$, CO_2 for six consecutive days and in the end we simulated an extreme carbon dioxide scenario, and the results showed an efficiency of 82.4% in reducing this gas even at a concentration of more than 6000 ppm. Graph 8 of continuous monitoring before and after refrigerated alkaline centrifugation demonstrates this performance and the circulating liquid report Figure 9 proves the transformation of CO_2 into sodium bicarbonate.

Figure 9 GHS Analysis Report No.: 3946.2024- V.0 of circulating liquid



02. Dados da Amostragem:

Descrição Ponto Coleta:	Ponto 1 - Precipitador |Hidrodinâmico ACV03-08 AIR Cleaner (1º Recebimento)		
Endereço Amostragem:	Rodovia dos Imigrantes,Km 1 5, Agua Funda **Cidade**: Sao Paulo/SP **CEP**: 04329900		
Matriz e Origem Amostra:	Água residual - Efluente sanitário		
Ficha Coleta:	293.2024	**Característica da Amostra:**	Simples
Data de Amostragem:	15/09/2023 10:00:00	**Data Recebimento:**	16/09/2023
Responsável pela Amostragem:	Solicitante		
Responsável pela Liberação:	samuel.reis	**Data Liberação:**	09/01/2024

Resultados

Parâmetros	Resultados Analíticos	Un Trab	RE nº 430/11, CONAMA	Incerteza	L.Q./Faixa	Início Ensaio
Alcalinidade de bicarbonato	2.154,8	mg/L em $CaCO_3$	N.A	4,73	5,00	09/01/2024
Alcalinidade de carbonato	268,1	mg/L em $CaCO_3$	N.A	4,73	5,00	09/01/2024
Alcalinidade de hidróxido	<5,00	mg/L em $CaCO_3$	N.A	4,73	5,00	09/01/2024
Alcalinidade parcial	134,1	mg/L em $CaCO_3$	N.A	4,73	5,00	09/01/2024
Alcalinidade total	2.422,9	mg/L em $CaCO_3$	N.A	4,73	5,00	09/01/2024
Sólidos suspensos totais á 103 ºC - 105 ºC	62,0	mg/L	N.A	5,98	5,00	05/01/2024
Bactérias heterotróficas	450	UFC/mL	N.A	0,08	1,00 UFC	16/09/2023
Fungos viáveis	390	UFC/mL	N.A	-	-	16/09/2023

]

Source Report GHS – SP/RJ

Another aspect under initial study for the technology will be to operate via a biological route for fixing solubilized CO2 for fixation in cyanophyte algae cultivation, generating a protein extract or source of oils.

Conclusion

The results achieved allow us to affirm that the concept of CCT – Carbon Capture Transform is one of the immediate solutions to changing trends in carbonic acid concentrations in the atmosphere and that multiventuri centrifugation technology is the most efficient to capture, solubilize and transform gaseous CO2 in solid and commercial salt, or in a multiplier nutrient for professional cultivation of cyanophyte algae capable of being transformed into protein raw material, biomass or oil extraction. Operation with a refrigerated cycle in applications for direct CO2 capture purposes is suitable for air conditioning systems, as the air will also be purified from the presence of fine particulate matter.

We are sure that the lines of research will continue towards providing complete units integrated into the concept of circular economy, transforming a substance that impacts the planet's climatic conditions into a product for society to use.

Acknowledgments

A long way since 1968 when the first experiments on treating combustion gases from urban incinerators in Copacabana- RJ, gave us the nickname “smoke bottlers”, Giuseppe Capulli, a visionary Italian always ahead of his time, we thank him for his legacy of knowledge, but more than that, the example of persevering, intuiting, testing and reprocessing until achieving the imagined results of society with quality of life and enjoying the comforts provided by human creativity.