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Theoretical study of the issues related to corrosion phenomena in oil equipment

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Abstract

Corrosion is a complex, pervasive, and critical phenomenon in the oil and gas industry. Having closely observed its effects on facilities, particularly pipelines and storage tanks, we have realized how it can compromise the safety, profitability, and sustainability of infrastructure. From an economic perspective, corrosion is of paramount importance. It is estimated that each year, a quarter of steel production is destroyed by corrosion, which corresponds to approximately 150 million tons per year or 5 tons per second. These losses could have been higher without corrosion protection. Electrochemical corrosion is one of the main causes of deterioration of oil and gas equipment, resulting in economic losses, environmental risks, and threats to industrial safety. This article provides an in-depth study of corrosion mechanisms affecting hydrocarbon pipelines and storage tanks, integrating a theoretical approach, an analysis of aggravating factors (CO_2, H_2S, chlorides, naphthenic acids) and an evaluation of protection methods (coatings, inhibitors, cathodic/anodic protection). A case study conducted in the Bongor Basin (Chad) illustrates the application of these methods in real conditions, with results showing a significant reduction in corrosion rates. This work highlights the importance of proactive and multidisciplinary corrosion management to ensure the sustainability of oil infrastructure.

Keywords: Electrochemical corrosion; Hydrocarbon storage tanks; Oil industry; Chad

1. Introduction

Many corrosion problems are encountered in the oil industry, whether during drilling and well operation, transportation or refining of crude oil [1-3]. Electrochemical corrosion is responsible for 97% of industrial corrosion cases. It occurs when there is heterogeneity either in the metal or in the surrounding environment (or both). This heterogeneity will produce a potential difference between different points of the metal and if this material is in an electrolyzable environment, there will be the formation of batteries which will discharge into the metal mass because they are short-circuited. The anodic zones corrode and disappear [4]. Corrosion results in the formation of rust. This product composed of more or less hydrated oxides only forms in the presence of oxygen and water at ordinary temperature. This corrosion is called aqueous and is the most widespread form in metal construction. Other forms of corrosion can occur under specific conditions. Corrosion is an electrochemical phenomenon, meaning that cells are created on the surface of the steel, in which one of the electrodes, the anode, is consumed to the benefit of the other, the cathode, which is intact. The electrolyte is made up of water, which is more or less conductive and oxygenated [5]. There are three types of corrosion: chemical corrosion, electrochemical corrosion and bacterial corrosion. We will only describe electrochemical corrosion, also called wet corrosion, which occurs predominantly in the field of oil refining. [6-9]. Steel, due to its physical, chemical, and mechanical properties, occupies an important place in the ferrous metals industry, hence its use in various fields, such as the pipeline transportation and storage of crude oil and petroleum

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products. It is used in the manufacture of pipelines (gas and oil pipelines) to transport large quantities of hydrocarbons over long distances from their deposits to consumption and processing areas. To be efficient, these pipelines must meet profitability and safety requirements.

Pipelines buried in the ground are subject to significant stresses and a corrosive environment [10-12]. Due to the products they may contain or the environment in which they operate, many pieces of equipment are exposed to corrosion risks. Corrosion is one of the main modes of deterioration for steel storage tanks and accessories. It is generally electrochemical in nature and can affect all components of a storage tank, both internally and externally. Furthermore, it can be either localized or generalized. It brings together multiple phenomena linked to the environment in which it is found. These phenomena depend on a large number of factors which intervene not individually, but in more or less complex relationships with each other (nature and structure of the material, the environment and its chemical characteristics, nature of the stored products, temperature, etc.) **[13].** We will present a literature review of the main mechanisms, forms, and methods for combating electrochemical corrosion, drawing on concrete examples and the technological context of the bibliography. We will conduct a scientific analysis of technical journals that present the state of the art in electrochemical methods for studying and monitoring corrosion. These bibliographic results highlight the fundamental principles, practical applications, and limitations of these techniques.

Several authors in the bibliography recall the intrinsic historical link between electrochemistry and corrosion, dating back to Volta's pile. Corrosion is presented as an electrochemical process in which a galvanic couple forms between an anodic zone (which dissolves) and a cathodic zone. The spatial distribution of these zones determines the type of corrosion (generalized or localized).

The fundamental principle governing the interpretation of the measurements is the mixed potential (or corrosion potential, Ecorr), illustrated by the Evans diagram. The position of Ecorr relative to the anodic and cathodic curves determines the state of the material immunity, active corrosion or passivity, a concept also supported by the Pourbaix diagrams

2. Materials and Method

2.1. Presentation of the Bongor Basin study area

The Bongor Basin is located southeast of Lake Chad in Africa, 300 km southeast of Chad's capital, N'Djamena. It is part of Block H of the exploration and development program undertaken by CNPC in Chad, which has become the 100% shareholder and operator of Block H. 14

The oil field is 180 km from the starting point of the Komé pipeline and is located at the intersection of the Central and Western African Fault Valley.

The Bongor Basin has a tropical rainforest climate with scorching temperatures and heat throughout the year. Its highest temperature is 44°C and its lowest is 14°C.

The Baobab field's exploitation methods consist of natural energy in the early stages and the injection of suitable water in the later stages. Vertical wells are suitable in the Bongor field, and horizontal wells will be carried out depending on reservoir conditions.[15]

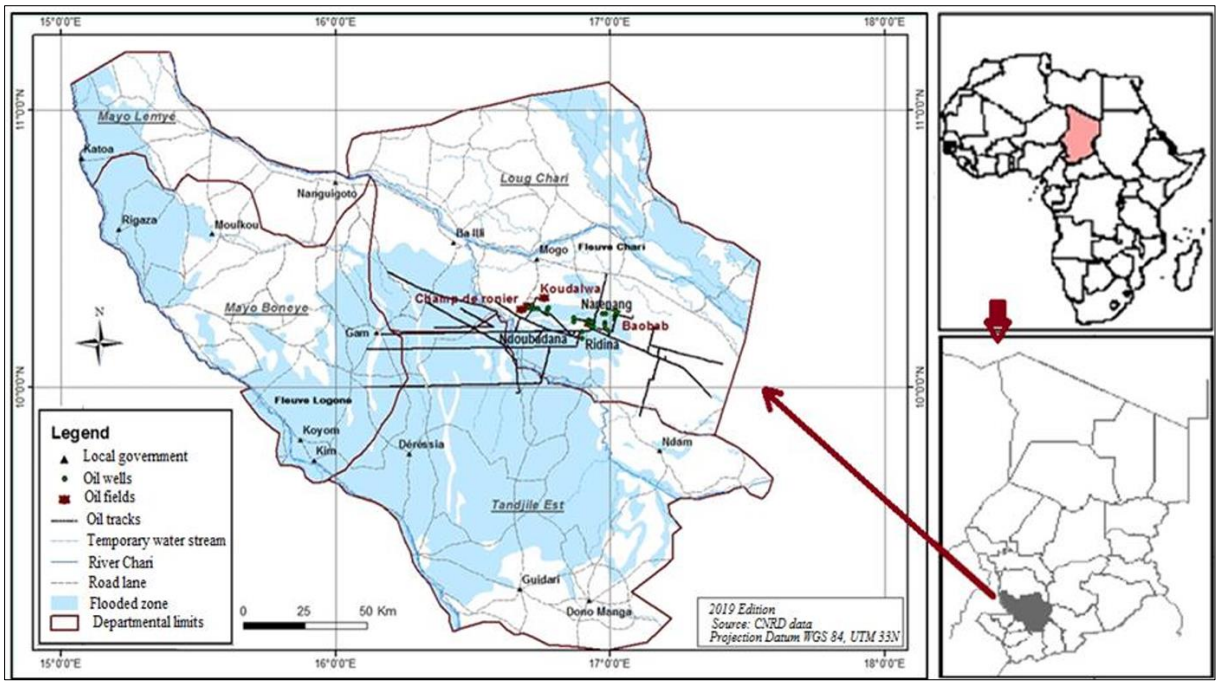

Figure 1 Geographic location of the Bongor Basin of Block H in Chad

2.2. Site Description

- Location: Logone Oil Basin (example inspired by Chad or Cameroon)
- Type of Facility: 12-inch pipeline transporting undesalted crude oil
- Service Life: Several years
- Climate: Semi-arid tropical climate, with alternating wet/dry seasons

2.3. Problems Observed

- Spot leaks detected in certain buried sections
- Internal perforations caused by under-deposit corrosion
- Presence of sulfide-rich black sludge during inspection
- Traces of acid attack due to the presence of CO_2 dissolved in the crude

2.4. Cause Analysis

- Factor: Impact on Corrosion
- Formation Water (>5%)
- Promotes Electrochemical Corrosion
- Dissolved CO_2
- Form of Carbonic Acid, Lowering pH
- H_2S
- Sulfurous Corrosion + Risk of Cracking
- Temperatures > 60°C
- Accelerated Reactions
- Lack of Regular Pigging
- Accumulation of Deposits

2.5. Diagnostic Methodology

- Internal Inspection Using a Smart Pigging Tool
- Electrochemical Potential Measurements (Corrosion Probes)
- Internal Deposit Sampling and Chemical Analysis
- Microbiological Study: Presence of Sulfate-Reducing Bacteria (SRB)

2.6. Corrective Actions Implemented

- Regular Injection of Corrosion Inhibitors (Dosage Adjusted According to Season)
- Monthly Pigging Operations
- Replacement of Critical Sections with Internally Coated Pipes
- Program online monitoring of corrosion rate

3. Results and Discussions

3.1. Results of Electrochemical Corrosion Mechanisms

These mechanisms result from a set of reactions that occur at the metal-solution interface and involve electrons and chemical species. They can be described in a simplified manner:

Anodic reaction of metal dissolution (M)

$$\boldsymbol{M \rightarrow Mn+ + n}\text{é}$$

Cathodic reduction reaction of a species of the electrolyte (Ox)

$$Ox + n\text{é} \rightarrow Red$$

The species susceptible to reduction must be present in sufficient quantity in the medium. When a metal comes into contact with an aggressive solution, the following behaviors may occur: [13]

- Corrosion of the metal;
- Immunity of the metal;
- Passivity of the metal;
- Covering of the metal with a mineral compound.

3.1.1. Mechanism and parameter influencing CO2 corrosion

Dissolving CO_2 in water leads to the formation of carbonic acid, which reacts with low-alloy carbon steels to form iron carbonates and hydrogen carbonates.

Dissolving carbon dioxide (CO_2) gas (CO_2) liquid

Formation of carbonic acid: $CO2 + H2O \rightarrow H2CO3$

First dissolution of carbonic acid: $H2CO3 \rightarrow H+ + HCO3-$

Second dissolution of carbonic acid: $HCO3- \rightarrow H+ + CO3\,2-$

Iron corrosion reaction: $H2CO3 + Fe \rightarrow Fe\,2+ + CO3\,2- + H2$

Formation of iron bicarbonate: $Fe\,2+ + 2(HCO3-) \rightarrow Fe(HCO3)2$

Formation of iron carbonate: $Fe\,2+ + CO3\,2- \rightarrow FeCO3$

3.2. Mechanisms and parameters influencing H_2S corrosion

The sulfur content in crude oil ranges from 1.8 to 2.6%. If the H2S concentration in the gas is greater than 0.5 ppm/mol and greater than 5 ppm in water, H_2S corrosion is caused. The following reactions are described: [7]

Dissolution of hydrogen sulfide (H_2S) gas (H_2S) liquid

First acid dissociation: (H_2S) liquid → $H^+ + HS^-$

Second acid dissociation: $HS- \rightarrow H+ + S2-$

Iron oxidation: $Fe \rightarrow Fe2+ + 2e$

Proton reduction: $H+ + é \rightarrow H0$

Formation of iron sulfide: $Fe2+ + S2- \rightarrow FeS + 2H+$

3.2.1. Mechanism of chloride hydrolysis corrosion

For inorganic salts, the reaction of formation of HCl by hydrolysis starts from 130°C as shown in the figure according to the following equations:

$MgCl2 + 2H2O \rightarrow 2HCl + Mg(OH)2$ Taux d'hydrolyse 250°C = 80%

$CaCl2 + 2H2O \rightarrow 2HCl + Ca(OH)2$ Taux d'hydrolyse 300°C = 50%

$NaCl + H2O \rightarrow HCl + NaOH$ Taux d'hydrolyse 300°C = 0,1%.

3.2.2. Corrosion by concentrated hydrochloric acid

The corrosion products formed by hydrochloric acid are highly soluble in the liquid phase, resulting in linear corrosion rates as a function of time. In the refinery, this acid can form at the top of the distillation, fractionation or stripper column. It is corrosive in the concentrated liquid state or dissolved in a liquid aqueous phase. In the gaseous state it is not corrosive.

Mechanism of corrosion by concentrated hydrochloric acid

Corrosion mechanisms are electrochemical, with the anodic reaction being the oxidation of the metal and the cathodic reaction being the reduction of hydrogen.

For steels, the overall reaction is:

$$Fe + 3HCl \rightarrow FeCl3 + 3/2H2$$

For organic salts, the hydrochloric acid formation reaction by hydrolysis remains at 130°C according to the reactions above

3.2.3. Corrosion by concentrated acids

Corrosion by sulfuric acid (H2SO4)

Concentrated sulfuric acid is used as a catalyst in some alkylation processes and can be formed during the condensation of sulfurous fumes. It is generally corrosive in its concentrated liquid state or dissolved in a liquid aqueous phase.

Mechanism of corrosion by concentrated H_2SO4

- The following equation describes the mechanism of the reaction: $Fe + H2SO4 \rightarrow FeSO4 + H2$
- Corrosion is generalized if the acid covers all of the metal parts or localized when there is condensation of acid droplets.

3.2.4. The parameters governing corrosion by H_2SO4

The parameters that govern this corrosion are:

- Temperature: an increase in temperature up to a vaporization temperature leads to increased corrosion;
- Acid concentration: a high concentration directly leads to this form of corrosion.
- Hydrodynamic corrosion rate: For alloys protected by the formation of a protective layer of metal sulfates, excessively high flow rates can cause it to peel off and thus generate high corrosion rates;
- Presence of contaminants and oxidizing agents: the presence of liquid sulfuric acid, contaminants such as chlorine, and oxidizing agents such as O2, Fe^{3+}, and Cu^{2+} cause an acceleration of the corrosion rate.

3.2.5. Corrosion by naphthenic acids in crude oil

Carboxylic or naphthenic acids are present in some crude oils. These acids are corrosive at temperatures close to their boiling point: corrosion has occurred from 179°C. The materials affected are carbon and low-alloy steels, stainless steels and certain nickel alloys.

3.2.6. Corrosion mechanisms by naphthenic acids

For corrosion due to naphthenic acids, three types of mechanisms have been proposed:

- Type I, a corrosion mechanism due solely to naphthenic acids, where sulfur compounds have little or no effect if present;
- Type II, in which sulfurization is accelerated by the presence of acids;
- Type III, in which corrosion by naphthenic acids is inhibited to some extent by sulfur compounds. There is competition between the attack caused by naphthenic acids and that caused by hydrogen according to the following equations:

Direct attack on steel: $Fe + 2RCOOH \leftrightarrow Fe(RCOO)2 + H2$

Corrosion due to hydrogen sulfide: $Fe + H2S \leftrightarrow FeS + H2$

Attack of iron naphthene by H2S: $Fe(RCOO)2 \leftrightarrow FeS + 2RCOOH$

For the latter reaction, the naphthenic acid is in this case regenerated by the reaction, which can once again fuel corrosion [18].

3.2.7. Corrosion by soda (NaOH)

$2NaOH + H2S \rightarrow Na2S$ (disulfure de sodium) + $2H_2O$

$NaOH + R - SH \rightarrow R - S - Na$ (mercaptide) + H_2O

$NaOH + CO2 \rightarrow NaHCO3$ (bicarbonate de sodium)

$NaOH + NaHCO3 \rightarrow Na2CO3$ (carbonate de sodium)

3.2.8. Description of the mechanism of corrosion by soda

Attack of the protective layer of steel (iron oxide/hydroxide) for the Fe/H2O system at a temperature of 150°C.

$$Fe(OH)2 + 2NaOH \leftrightarrow Na2FeO2 + 2H2O$$

"Direct" attack of steel (high concentrations), according to the following reaction:

$$Fe + NaOH + 2H2O \leftrightarrow NaHFeO2 + H2$$

3.3. Results of the bibliographic analysis on the Fundamental Principles of Electrochemical Corrosion

We review the basic principle of aqueous corrosion: the formation of an electrochemical cell with microanodes (metal dissolution) and microcathodes (reduction, often of oxygen or H^+ ions).

3.3.1. Crucial role of oxygen

In the bibliography, the authors explain the mechanism of rust on iron. The initial cathodic reaction (reduction of H^+ ions) is quickly blocked by polarization due to the adsorption of hydrogen gas. Depolarization by dissolved oxygen is essential for corrosion to continue. The overall process is summarized as follows:

$$Fe + H_2O + \frac{1}{2} O_2 \qquad Fe\,2 + + 2OH -$$

Cathodic Protection: The principle is briefly mentioned: by coupling a metal with a more 'active' metal (sacrificial anode such as Zn or Mg), the metal to be protected (e.g., steel) is forced to become the cathode of the pair, thus preventing its dissolution.[16]

3.4. Study of Specific Forms of Corrosion

The article [16-18] stands out for its clear and illustrated explanation of three particularly critical types of localized corrosion.

3.4.1. Pitting Corrosion

- Materials concerned: Passive materials (stainless steels, aluminum, titanium) are the most sensitive.
- Mechanism: The protective passive film fails locally (due to inclusions, scratches). A micro-cell forms between the large cathodic surface (passive metal) and the very small anodic surface (bare metal). The very high anodic current density leads to rapid perforation.
- Aggravating factors: The presence of chloride ions (Cl^-), which compete with oxygen for adsorption on the surface, preventing local repassivation. The article also describes the self-sustaining phenomenon of pitting via the formation of a concentration cell (Evans effect) and the cathodic protection of the surrounding passive surface [16].

3.4.2. Stress Corrosion

- Required Conditions: Combination of a specific corrosive medium, a sensitive (often passive) material, and a tensile stress.
- Proposed Mechanism: The stress causes brittle fracture of the passive film, which cannot deform plastically like the underlying metal. The exposed metal becomes a localized anode, and a crack propagates. Stress concentration at the crack tip accelerates the process.
- Importance: The author emphasizes the importance of this phenomenon for complex alloys used under severe conditions and mentions the increasing use of fracture mechanics for its study. 17

3.4.3. Intercrystalline Corrosion of Stainless Steels

Cause: Improper heat treatment (maintaining or slow cooling between 500 and 800°C) causes the precipitation of chromium carbides ($Cr_{23}C_6$) at the grain boundaries. Consequence: The regions adjacent to the grain boundaries become depleted in chromium (below the 13% threshold required for passivation). An electrochemical cell forms between the sound austenite (cathode) and the depleted zone (anode), leading to selective attack along the grain boundaries.

Solutions

- Use low-carbon steels (L: ≤ 0.03%).
- Stabilize the steel with elements such as titanium (Ti) or niobium (Nb), which have a stronger affinity for carbon than chromium, thus preventing chromium depletion.

3.5. Control Methods: Focus on Corrosion Inhibitors

Article [17-20] devotes a significant section to inhibitors, presented as an effective method for acting on the corrosive environment.

Principle: Add a small amount of a compound that binds to the metal surface and polarizes the anodic and/or cathodic reaction.

3.5.1. Classification by mode of action

- Formation of an insoluble film (e.g., phosphates, carbonates).
- Oxidizers (e.g., chromates, nitrites), which reinforce the natural passive film (but with a risk of pitting in the event of a defect).
- Adsorption of organic compounds (amines, mercaptans), forming a protective barrier.

Advanced search: The author mentions work using infrared spectroscopy to identify the nature of adsorbed inhibitor films (e.g., formation of metal complexes). It also discusses the potential of inhibitors to combat stress corrosion cracking and presents the concept of volatile chemical inhibitors (VCIs) for atmospheric protection during storage[18].

3.6. Context and Challenges

- New technical challenges: The use of materials under more severe conditions (temperature, stress) and the development of high-performance alloys, which are often more susceptible to corrosion.
- Energy challenge: Energy production and storage are identified as areas where corrosion is a major limiting factor (e.g., heat exchangers, hydrogen corrosion, liquid metals) [19].

3.6.1. Measurement of Corrosion Potential (Ecorr)

- Principle: Simple and non-disruptive measurement of the potential difference between the sample and a reference electrode.
- Advantage: No alteration of the system. Useful for identifying thermodynamic stability domains (immunity, corrosion, passivity).
- Major limitation: Does not provide any information on kinetics (corrosion rate) [14-17].

3.6.2. Current-Voltage Curves (I = f(E))

Principle: By applying a polarization, the system is perturbed to obtain a curve that relates the current (linked to the corrosion rate via Faraday) to the potential.

Objectives

- Determine the corrosion rate as a function of the potential.
- Understand the mechanisms (control by charge transfer, diffusion, etc.).
- Applications: Study of localized corrosion (pitting potential, repassivation), passivation, and sensitivity to stress corrosion cracking.
- Limit: Based on the Wagner-Traud principle, which is only approximate (oxidizing species can have a chemical effect in addition to their polarization role)[18-19].

3.6.3. Estimation of corrosion rate by Stern methods

The authors detail two methods for estimating the corrosion current (Icorr), which is directly proportional to the corrosion rate[18].

3.6.4. First Stern Method (Tafel Extrapolation)

- Principle: Extrapolation of the anodic and cathodic linear branches in the Tafel domain (log I vs E plane) to find their intersection at (Icorr, Ecorr).
- Limitations: Very restrictive. Requires well-defined Tafel lines over a wide range, which is rare in practice due to ohmic drops, mass transport, film formation, or changes in the anodic/cathodic area distribution ([17-21]).

3.6.5. Second Stern Method (Linear Polarization)

- Principle: Measurement of the polarization resistance (Rp), slope of the I=E curve at Ecorr. The Stern-Geary relationship links Rp to Icorr: `Icorr = B / Rp`, where B is a constant depending on the anodic (ba) and cathodic (bc) Tafel slopes.
- Advantage: Requires only a weak polarization around Ecorr.

Fundamental Problems

- The constant B (which requires knowledge of ba and bc) is often unknown and estimated.
- Like the first method, it assumes ideal behavior (control by charge transfer only). As soon as other phenomena (transport, inhibition) are involved, Rp is no longer a reliable measure of charge transfer kinetics.

3.6.6. The Decisive Contribution of Electrochemical Impedance Spectroscopy (EIS)

EIS is presented as the most powerful technique for overcoming the limitations of stationary methods.

Principle: Application of a low-amplitude sinusoidal perturbation over a range of frequencies and measurement of the impedance response.

Key Advantages

- Separation of phenomena: It allows distinguishing charge transfer resistance (Rt), related to corrosion kinetics, from other contributions such as solution resistance (Rs), diffusion processes, or film formation, thanks to their different time constants.
- Measurement validation: It allows verifying whether the measurement of Rp using another technique is correct (i.e., whether Rp ≈ Rt) [18-21].

3.7. Results on Practical Applications and Impact Areas

Electrochemical techniques have moved beyond laboratories to industrial applications, particularly thanks to advances in EIS.

- Insulating Coatings (Paints, Anodic Oxides): This is a major application. EIS can be used to characterize:
- The film's dielectric properties and its water absorption.
- The underlying porosity and corrosion mechanisms.
- The quality of protection, by correlating the transfer resistance at the bottom of the pores with corrosion resistance.
- Other areas: Corrosion in concrete, soils, and monitoring of industrial facilities.

4. Conclusion and Synthesis

Our research offers both a fundamental and applied view of corrosion. It is remarkably up-to-date on many concepts (pitting mechanisms, stress corrosion, sensitization of stainless steels) [1]. Its strength lies in the clear physicochemical explanation of complex phenomena and the consistent link established between theory, practical manifestations, and protection methods.

It highlights the fact that corrosion is not inevitable, but a phenomenon that can be understood, predicted to a certain extent, and combated by scientific means (alloy treatments, cathodic protection, inhibitors), a philosophy that remains at the heart of modern materials science. In short, electrochemical techniques are unique and indispensable for studying in situ corrosion and understanding its kinetics. While they have long been criticized for relying on simplistic models, conceptual (particularly with EIS) and instrumental advances in recent decades have clarified their possibilities and limitations, making their use more rational and reliable. The investment required, both human and material, is often more modest than one might think to resolve a large proportion of corrosion problems[22].

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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