

# Animation Cel Preservation Engineering Framework

A Coupled Kinetic Model for Cellulose Triacetate Substrate  
Degradation

*An independent engineering framework extending published preservation science (Curran et al.,  
2019; Image Permanence Institute)*

CelNexus

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This document presents an engineering framework intended to extend and interpret published preservation science for animation cels. Where the framework introduces new mathematical relationships or engineering constructs, these should be regarded as proposed models requiring continued experimental validation.

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## Executive Summary

An animation cel is the original artwork of hand-drawn animation. From the mid-1930s through the late 1990s, every frame of traditional theatrical and television animation was produced by photographing hand-painted transparent plastic sheets — composited in layers against static painted backgrounds, one frame at a time. A single scene might require hundreds of individual cels, each one hand-traced from an animator's drawing and individually painted by artists working in specialized production pipelines that employed hundreds of people at the major studios. The object carries a provenance that licensed merchandise cannot replicate: a production cel is the physical artifact that was in front of the camera. The image it depicts is not a reproduction of the artwork — it is the artwork.

The transition away from this process began in the early 1990s. Computer-assisted ink-and-paint eliminated the manual painting stage first, driven by cost reduction, production speed, and the ability to composite effects that were impractical with physical cels. Fully digital workflows followed. By the early 2000s, the major American and Japanese animation studios had converted their pipelines entirely. The industrial process that had produced tens of millions of unique hand-painted artifacts over six decades ended permanently. What had been routine production output became a closed category with a fixed and irreplaceable supply.

That supply is now aging. Recognition of production cels as collectible objects — as primary artifacts from a documented creative process rather than as fan merchandise — has grown substantially as the generation that encountered the theatrical and television animation of the 1970s through the 1990s reaches peak collecting age. The properties most prized by the contemporary collector community span the golden era of American theatrical animation, the parallel renaissance of Japanese theatrical and television production, and the dominant action and adventure animation of Saturday morning and weekday afternoon television. These are not nostalgia items. They are original works of art from a manufacturing process that no longer exists, increasing in institutional recognition

and market value at precisely the moment when their chemical lifespan is becoming a material concern.

Most animation cels were manufactured on cellulose triacetate film, a polymer with a finite chemical lifespan measurable in decades, not centuries. That lifespan is now actively running out for a significant portion of the collectible market. Some of the earliest CTA-era productions have already reached or crossed the 50-year degradation threshold established by the Image Permanence Institute. See the “IPI Threshold Application” subsection of Model Assumptions for discussion of how this baseline is applied to animation cels. Productions from the mid-to-late 1980s are within one decade of it. The television and theatrical animation of the 1990s — the era most directly prized by the contemporary collector community — sits within a 10 to 25-year intervention window that is narrowing in real time.

This document presents a quantitative engineering framework for understanding why CTA animation cels degrade, how fast, and what specific interventions actually slow it down. It does not provide reassurance that careful storage eliminates the risk. It provides the model that explains which interventions work, why they work, how much each one buys, and how much runway remains to implement them for each production era.

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### *Survivorship Bias and the Community's Hidden Assumption*

For the past three decades, the animation collecting community has operated under an implicit assumption: that vinegar syndrome is primarily a consequence of improper storage — a preventable outcome driven by individual negligence rather than by the underlying chemistry. This assumption may be incomplete in light of current polymer science. The error follows a predictable pattern. Cels that developed vinegar syndrome in the early decades of the secondary market were dismissed as failures of custodianship: poor temperature control, wrong storage materials, excessive humidity, inadequate ventilation. Cels that survived that period in apparent good condition were attributed to good practice:

archival enclosures, climate control, careful handling. Neither attribution is primarily correct.

Both populations are products of the same chemistry. The cels that failed early were in conditions that accelerated a process that was always going to happen. The cels that appear healthy today have not escaped that process. They have not yet reached the threshold at which the damage becomes externally visible.

This distinction carries a specific, testable meaning. The colorimetric indicators most widely deployed in the hobby — A-D strips — cannot register any visual change until internal proton concentration has already increased by approximately 40 times above baseline levels. A bright blue reading is not evidence of a stable cel. It is evidence that the internal chemistry has not yet crossed the indicator's detection threshold. These are not the same thing, and treating them as equivalent is the mechanism by which survivorship bias sustains itself.

A collector who has maintained cels for 30 years without visible degradation has not demonstrated that their approach prevents vinegar syndrome. They have demonstrated that their approach has not yet been tested by the timeline that vinegar syndrome operates on.

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### *What Is Coming*

As productions from the late 1980s and 1990s age through the 30- to 50-year mark over the next two decades, cases of deteriorating cels in carefully maintained collections will increase substantially. Collectors who have stored their work responsibly will encounter degradation they believed their practices had prevented. The instinct will be to identify what was done wrong.

In many cases, nothing was done wrong. The material is following its own chemistry on its own timeline. The storage history determined whether that timeline was accelerated or extended — not whether it exists.

This shift will be challenging for a community that has built its preservation culture around the premise that visible results validate the approach. It will require separating the question of "am I doing the right things?" from the question of "have I yet reached the point where the wrong outcomes are visible?" The second question has a time-structured answer that has not yet arrived for most of the core collectible market. It will.

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### *What This Framework Provides*

This framework develops a coupled two-state kinetic model for CTA animation cel degradation that tracks two physically distinct quantities independently: cumulative structural deacetylation ( $D$ ), representing the permanent chemical history of the polymer, and internal vapor-phase acid concentration ( $P_{int}$ ), representing the current dynamic state of the microenvironment. This formulation is the framework's principal original contribution: it distinguishes between effects that can be managed (vapor pressure, enclosure geometry, temperature) and effects that cannot be reversed (structural bond cleavage).

The framework extends, rather than replaces, existing preservation literature. It shares the autocatalytic premise independently identified by Curran et al. (2019) — who demonstrate that the IPI's 50-year guideline overestimates VS onset by a factor of four or more under typical room conditions — and introduces additional mechanistic elements: a damage-dependent hydrophilic amplification model  $H(D)$ , an enclosure transport resistance term  $R_{tot}$ , and a two-track conservation system that allows a cel's structural damage state and its current vapor environment to be assessed independently.

The practical consequence of this independence is significant. A cel that has been actively scavenged — reducing its vapor-phase acid reading to a safe blue — may simultaneously carry substantial accumulated structural damage that the A-D strip cannot detect. Free acidity and cumulative deacetylation are not equivalent quantities. Only the two-track framework can distinguish between them.



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## *Key Findings*

**Within the framework developed here, enclosure geometry can have a larger influence than ambient room conditions alone.** The physical resistance of a cel's immediate storage environment to vapor transport — its enclosure transport resistance,  $R_{\text{tot}}$  — has a larger effect on degradation trajectory than ambient temperature or relative humidity in isolation. Two cels from the same production run, stored in the same room at the same temperature and humidity, can diverge in preservation outcome based solely on whether they are stored openly or sealed behind thick paint within a polypropylene sleeve and non-vented frame. Room climate management is necessary; it is not sufficient. (See Model Assumptions, IPI Threshold Application: the Disney Mactac® lamination case, 1974–1991, provides documented field validation of this transport resistance relationship.)

**The framework predicts that cold storage becomes the dominant practical intervention for high-odometer cels.** Room-temperature dehumidification reduces the fuel supply for the hydrolysis reaction, but it cannot compensate for the expanded moisture sensitivity of a structurally damaged substrate. The calculation in this framework shows that an aged cel with significant accumulated deacetylation would need to be maintained at approximately 26% relative humidity at room temperature to age at the same rate as a pristine cel — a condition that could desiccate and fracture paint layers before it achieved the intended effect. Only temperature reduction can override the structural moisture penalty without causing mechanical damage.

**The available intervention window varies by production era.** Under the IPI's optimistic 50-year model, productions from the late 1980s retain roughly one to two decades of manageable runway before reaching the autocatalytic threshold under unmanaged conditions. Productions from the 1990s have somewhat more. The actions taken within that window — particularly cold storage and enclosure management — determine the trajectory of the material for the remainder of its lifespan. Late intervention is better than no intervention; early intervention is substantially more effective than late.

**Vinegar syndrome is a phase change, not a death sentence.** Crossing the 0.5% deacetylation threshold does not destroy a cel — it changes which preservation levers remain effective. A cel that has entered Regime 2 can no longer be managed with room-temperature climate control alone. But it can be stabilized through cold storage, and that stabilization is real and quantifiable. The goal of this framework is to give collectors the tools to understand where on the degradation curve any given piece sits, what that means for available interventions, and what timelines are realistic for each approach.

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*This document is a component of the CelNexus Preservation Framework. Companion documents address condition assessment methodology, preservation risk tiers, and field diagnostic workflows.*

## Introduction

Animation cels represent a unique intersection of art and material science. Unlike static prints or paintings, traditional animation cels are composed of polymeric film substrates (primarily cellulose nitrate or triacetate) combined with applied paint layers and, in some cases, adhesive or xerographic elements. These materials are inherently unstable over long time horizons and are subject to a range of chemical and physical degradation mechanisms.

The purpose of this document is to establish a structured, engineering-based framework for understanding and managing the preservation of animation cels. Rather than relying on generalized archival guidance, this document focuses specifically on the mechanisms that govern degradation, and how environmental and storage conditions influence those mechanisms.

This framework is designed to:

- Define what preservation means in a technical context.
- Identify primary degradation pathways affecting animation cels.

- Provide a quantitative framework for evaluating preservation risk and internal mass-transport limits.
- Establish the mathematical foundation for controlled storage, microenvironmental display configurations, and active scavenging environments.

While this document focuses primarily on cellulose triacetate (CTA), the most common material used in late-era animation production, it also references other materials where relevant. A more detailed breakdown of cel materials and identification methods is provided in a separate reference document.

This document is structured as a living engineering framework. Early sections focus on stable-condition preservation, where degradation is slow and predictable. Advanced sections model the non-linear kinetics of autocatalytic runaway, microenvironmental stagnation (the Sleeve Isolation Trap), the physical speed limits of solid-state diffusion, and the exact thermodynamic mass and rate requirements for active vapor-phase molecular scavenging networks

## Scope and Definitions

This document addresses the technical preservation of:

- Hand-painted animation cels
- Xerographic animation cels
- Multi-layer cel assemblies

Primary focus is placed on:

- Chemical stability of the film substrate
- Environmental control (temperature, moisture, vapor-phase contaminants)
- Mechanical handling and storage configuration

The following topics are acknowledged as outside the quantitative transport scope of this revision:

- Paint-related aesthetic degradation and visual failures (excluding structural delamination driven by substrate shrinkage).
- Detailed plasticizer chemical degradation and leaching mechanics
- Invasive restoration techniques, paint consolidation, and chemical repair.
- Full destructive analytical characterization workflows (e.g., FTIR protocols or titration sequences).

## Operational Definitions

To establish clear peer-to-peer technical alignment, the structural health of a collection is evaluated across three interconnected engineering dimensions. These metrics translate abstract chemical decay into an actionable preservation ledger:

- **The Generation Engine (R):** The instantaneous chemical reaction rate at which acetyl ester bonds are cleaved via hydrolysis inside the bulk polymer matrix, releasing volatile acetic acid.
- **The Emission Speedometer (J):** The physical mass transport flux of free acetic acid vapor migrating out of the plastic substrate, crossing any applied paint barriers, and escaping across the surface boundary layer.
- **The Structural Odometer (D):** The time-integrated record of cumulative material damage, defined as the exact percentage of historically broken acetyl bonds.

## Model Assumptions and Calibration

This document presents a first-order engineering framework for modeling the preservation of cellulose triacetate (CTA) animation cels. The governing equations are intended to estimate relative degradation behavior and identify dominant preservation mechanisms rather than provide exact lifetime predictions for individual objects.

## Application of the IPI 50-Year Threshold to Animation Cels

The 50-year vinegar syndrome onset threshold cited throughout this framework was established by the Image Permanence Institute for cellulose triacetate motion picture film stored under controlled archival conditions, not for animation cels. This distinction requires a brief structural argument before the threshold is applied as a calibration baseline.

Motion picture film is wound onto reels and stored in sealed cans. The IPI's methodology measured acid accumulation in this geometry — a tightly wound configuration where acetic acid migrates slowly between layers before reaching the surrounding atmosphere, and where an additional hydrophilic emulsion layer contributes a second degradation pathway. The result is a system with structurally elevated emission resistance, in which internal acid builds against measurable environmental resistance before onset is observed.

A bare or lightly-painted animation cel stored flat in an open binder sleeve presents lower geometric emission resistance than a film reel by construction. The cel surface has relatively direct atmospheric access, acid clears the boundary layer more readily, and the absence of an emulsion layer removes a secondary accumulation pathway. Under these conditions, the 50-year figure is likely conservative and overestimates time to onset for cels.

The situation reverses for heavily-painted or encapsulated cels, and the reversal can be severe. A cel with impermeable paint coverage presents transport resistance that may equal or exceed that of motion picture film on a per-unit-area basis. The extreme case is documented in the historical record. Disney applied Mactac® polyester lamination to production cels from 1974 through 1991 — encapsulating the CTA substrate in a solvent-based adhesive/polyester sandwich that sealed the cel against vapor transport. The visual and structural outcomes of this practice, described by conservator Ron Barbagallo in a peer-reviewed publication (Topics in Photographic Preservation, Vol. 6, 1995, American Institute for Conservation) and documented in surviving condition examples, are

consistent with what this framework's transport model predicts at maximum  $R_{\text{tot}}$ : acid generation without emission relief, accelerating autocatalytic feedback, and structural failure on a timeline substantially shorter than the IPI baseline would indicate for the same CTA substrate under open conditions.

The 50-year threshold is retained in this framework as the calibration baseline because it represents the most rigorously established reference point in the published literature. It should be read as neither a floor nor a ceiling for animation cels specifically, but as the central reference point from which the transport resistance term  $R_{\text{tot}}$  scales outcomes in both directions: conservatively long for open-storage bare substrates, and potentially dramatically shorter for sealed or heavily-painted configurations.

### Primary Assumptions

The framework is developed under the following assumptions:

- The model applies primarily to the pre-autocatalytic preservation regime (approximately  $D \leq 0.5\%$ ), unless otherwise noted.
- Environmental conditions are assumed to be spatially uniform unless enclosure transport effects are explicitly modeled.
- The CTA substrate is treated as chemically homogeneous, with paint and applied layers represented through effective transport resistance.
- Reactant depletion of acetyl groups is neglected within the preservation regime because only a small fraction of the total bond inventory has been consumed.
- Plasticizer migration, mechanical creep, and restoration effects are treated qualitatively and are not explicitly modeled.
- Moisture transport is represented through lumped parameters rather than a full transient diffusion solution.

### Model Calibration

Several parameters serve as calibration anchors derived from published literature or first-principles chemistry rather than cel-specific experimental fitting.

- $R_0 = 0.01 \text{ \%}\cdot\text{yr}^{-1}$  is anchored to the Image Permanence Institute's approximately 50-year baseline for cellulose triacetate motion picture film.
- $\kappa = 2.0$ , the Hydrophilic Amplification Factor, is an engineering estimate informed by published cellulose acetate moisture sorption behavior.
- $\beta = 10.0 \text{ PPM}\cdot\text{\%}^{-1}$ , the stoichiometric conversion factor, is derived from CTA monomer chemistry and the Hackney acidity calibration.
- $\phi = 0.5 \text{ PPM}^{-1}$ , the autocatalytic acceleration coefficient, is an initial engineering estimate requiring experimental validation.

### **Validation Status**

The governing structure of the model—including the coupled generation and transport framework—is physically motivated by reaction kinetics, diffusion theory, and conservation of mass.

The principal original contributions of this framework include:

1. the H(D) hydrophilic amplification model,
2. the coupled two-state damage and vapor transport formulation,
3. the enclosure transport resistance framework ( $R_{tot}$ ),
4. and the preservation-oriented Damköhler interpretation.

These developments extend, rather than replace, existing preservation literature. In particular, the framework shares the same fundamental autocatalytic premise identified independently by Curran et al. (2019), although it reaches this conclusion through a different modeling approach and introduces additional transport-based mechanisms.

Accordingly, the numerical parameter values presented in this framework should be interpreted as engineering calibration anchors suitable for comparative risk assessment. Future revisions are intended to refine these parameters through FTIR measurements, controlled exposure studies, and additional experimental validation.

## Part I: Foundations

Animation cel preservation is fundamentally a **coupled generation–transport–accumulation system**, not a static storage problem. Cellulose triacetate (CTA) substrates possess a finite, historical inventory of acetyl groups that slowly undergo hydrolysis when exposed to moisture, generating volatile acetic acid.

While preservation is often thought of as using acid free materials and having time-based venting strategies, true preservation is defined as balancing this system: minimizing internal generation (R), maximizing outward emission flux (J), and preventing harmful vapor accumulation. Based on the stoichiometric framework developed later in this document, the transition to autocatalytic behavior is predicted to occur when approximately 0.5% of the original acetyl inventory has been lost. Relying on visual inspection or scent for detection is therefore a mathematical trap. By the time degradation becomes externally noticeable, the model predicts that the internal reaction rate may already have increased by several orders of magnitude.

### What Is Preservation?

Preservation with respect to animation cels is often described in general terms such as “keep it cool,” “keep it dry,” or “use archival materials.” While directionally correct, these statements do not explain why degradation occurs or how to systematically control it. For the purposes of this framework, preservation is defined as: *The control of chemical, physical, and environmental processes that drive material degradation, with the goal of minimizing the rate of change over time*

### Degradation as a System

Animation cel degradation is not a single process; it is a coupled system of interacting mechanisms. The most critical of these include:

- Chemical reactions
  - Hydrolysis of cellulose acetate
  - Formation of acetic acid



- Plasticizer loss
- Mass transport processes
  - Diffusion of acetic acid out of the film
  - Ingress of moisture from the environment
  - Accumulation of vapor-phase contaminants
- Physical responses
  - Warping and curling
  - Embrittlement
  - Paint layer stress and delamination

These processes are interconnected. For example, increased moisture accelerates hydrolysis, which generates acetic acid. Acetic acid lowers internal pH and accelerates further degradation, while accumulated acid in the surrounding environment can further shift equilibrium. This creates a feedback structure that can be understood as a generation–transport–accumulation system.

### The Preservation Control Loop

At a high level, preservation requires managing a coupled system. For the purposes of this framework, we divide these challenges into the core thermodynamic transport loop and the external environmental stressors that act upon it:

#### The Mass Transport Core:

1. Generation: The rate at which degradation byproducts (e.g., acetic acid) are produced
2. Transport: The movement of those byproducts through the material and into the surrounding environment
3. Accumulation: The buildup of those byproducts in the local environment
4. Removal / Mitigation: The ability of the system to remove or neutralize those byproducts (e.g., ventilation, scavengers)

#### External System Constraints:

- **Radiation (UV / Light):** High-energy wavelengths that trigger photo-oxidation, fracturing polymer chains independently of moisture.
- **Mechanical Stress:** Physical forces—such as compression from framing, gravity-induced sagging, or localized shearing from substrate shrinkage—that cause delamination.
- **Contamination:** Particulate matter, biological hazards (mold), or external atmospheric pollutants that introduce reactive chemical agents to the cel surface.

Effective preservation does not eliminate degradation; it balances this system such that generation is minimized, transport does not lead to harmful accumulation, accumulation is controlled or reduced, and removal mechanisms are sufficient for the expected load.

### Preservation vs. Perfection

***It is critical to recognize that no storage method can stop degradation entirely.*** All polymeric materials will degrade over time. The goal of preservation is not to achieve permanence, but to extend usable life, maintain visual and structural integrity, and delay the onset of accelerated (autocatalytic) degradation.

This distinction is important, as it shifts the focus from: “**Is this safe?**” to “**How does this condition change the rate of degradation?**”

### Why a Structured Approach Matters

Without a structured understanding of degradation mechanisms, preservation decisions are often inconsistent or contradictory. For example:

- **The Sealed Enclosure Trap:** Sealing a storage container blocks external moisture ingress ( $a_w$ ) and can trap generated acetic acid vapor inside the microenvironment ( $P_{int} > 0$ ), increasing the likelihood of autocatalytic acceleration under unfavorable transport conditions.
- **The Episodic Ventilation Fallacy ("Letting it Breathe"):** Passive manual venting only establishes a temporary, short-lived drop in vapor density ( $P_{int} \approx 0$ ) during the actual breathing event. In the extended intervals *between* these events,

accumulation immediately resumes ( $P_{\text{int}} > 0$ ), while the continuous open-air exposure invites unregulated atmospheric relative humidity and light exposure directly into the substrate.

A proper preservation strategy requires identifying dominant degradation drivers, understanding how each control method affects the system, and balancing trade-offs rather than optimizing a single variable. This framework builds on that foundation—treating animation cel preservation not as a set of rules, but as a system that can be analyzed, controlled, and improved.

## The Substrate: A History of Unstable Plastics

The animation industry adopted transparent plastics for production speed and efficiency, not for long-term archival stability. Over time, several materials were used:

- **Cellulose Nitrate (1920s–1930s):** Highly transparent but chemically unstable and flammable. Degradation produces nitric acid, aggressively damaging both the substrate and paint layers.
- **Cellulose Diacetate (1930s–early 1980s):** Introduced as a safer alternative. While less hazardous, it is highly susceptible to hydrolysis, producing acetic acid and initiating vinegar syndrome.
- **Cellulose Triacetate (CTA) (1980s–2000s):** A more highly substituted acetate with improved initial stability. However, it remains fundamentally vulnerable to hydrolytic degradation and ultimately exhibits the same failure mode as diacetate.
- **Polyester (PET / Mylar):** Chemically inert and resistant to hydrolysis. While ideal for archival enclosures, it was rarely used for production due to poor paint adhesion.

This document focuses on CTA, as it represents the dominant material in collectible animation cels and defines the primary preservation challenge.

## Internal Chemistry: Plasticizers and Mobility

In addition to the polymer substrate, animation cels contain a mobile plasticizer system (e.g., triphenyl phosphate and phthalates) that governs mechanical flexibility and long-term behavior. Plasticizers do not directly affect acid generation (R). However, they strongly influence transport behavior (J) by altering polymer mobility and diffusion pathways, as well as the mechanical response, including stress relaxation and deformation.

As plasticizers migrate or deplete, the polymer stiffens, shrinkage increases, and warping and embrittlement accelerate. Plasticizer loss does not initiate degradation—but it significantly amplifies how that degradation manifests.

## The Applied Layers: Paint and Linework

The substrate is only part of the system. The applied layers introduce additional mechanical and transport constraints.

- **Paint Layers:** Typically more brittle than the substrate. As the underlying film shrinks or expands, the paint cannot accommodate the strain, leading to cracking, cupping, and delamination.
- **Line Art (Ink vs. Xerography):** Hand-inked lines and xerographic toner introduce different aging behaviors, surface adhesion properties, and abrasion risks.

These layers also act as **diffusion barriers**, directly influencing the emission term (J).

## Archival Lifecycle Context: Preservation, Conservation, and Restoration

Animation cels pass through three distinct phases of technical care:

- 1) Preservation
  - a. The process of controlling environmental and physical conditions to minimize the rate of material degradation over time.
  - b. Operates on the principle of rate control—maintaining conditions that prevent the material from entering accelerated degradation regimes.
- 2) Conservation

- a. Intervention initiated at the absolute limit of macro-detection, typically signaling that the core material has already spent its internal chemical stabilization buffer. Focus shifts from passive monitoring to aggressive kinetic suppression using deep thermal controls and active molecular vapor scavenging to prevent the system from dropping into exponential Regime 2 failure.
- b. Includes controlled conditioning environments and acid-reduction strategies.
- c. Stabilization methods to restore favorable system conditions.

### 3) Restoration

- a. Active intervention to correct visible or structural damage.
- b. Includes paint repair, correction of warping/brittleness, and structural reinforcement.

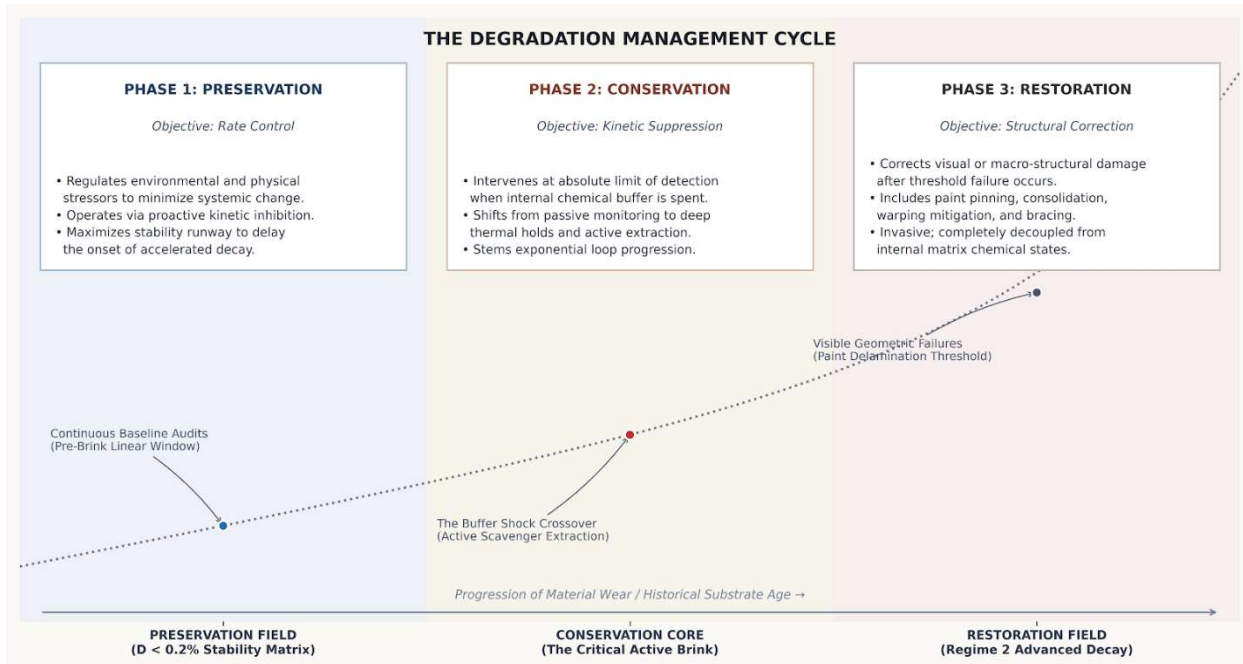


Figure 1: The Degradation Management Cycle

Having established that preservation is fundamentally a rate-control problem — not a question of permanence, but of how quickly a cel moves through its own lifecycle — the next question is mechanical: what physically sets that rate? Answering it requires getting

precise about acidity itself, not as a warning label on a strip of paper, but as the variable that determines how fast the clock runs.

## Part II: The Physics of Decay

### Demystifying Acidity and pH

In preservation, "acid" is a specific chemical reactant that influences the speed of destruction. To manage a collection, one must understand the logarithmic relationship between the amount of acid present and the resulting pH level.

#### The Logarithmic "Redline"

Acidity is measured on the pH scale, which is the negative logarithm of the hydrogen ion concentration  $[H^+]$ .

$$pH = -\log_{10}[H^+]$$

*Equation 1*

Because the scale is logarithmic, the transition from "safe" to "catastrophic" happens much *faster* than most collectors realize:

- A drop of 1.0 pH unit (e.g., from pH 5 to pH 4) represents a **10-fold increase** in acid concentration.
- A drop of 2.0 pH units represents a **100-fold increase** in acid concentration.

In animation cels, this means that by the time you can visually or olfactorily detect a shift in an A-D strip, the internal "redline" of the reaction has already moved several orders of magnitude.

### Acid Generation vs. Acid Emission (The Two Axes of Preservation)

Preservation is governed by two coupled processes: the internal generation of acid and the external emission of that acid.

## Axis 1: Generation (R) – The Internal Engine

Cellulose triacetate (CTA) contains acetyl groups through an acetylation process that makes the film or cel clear and processable. Over time, moisture in the air slowly breaks these acetyl ester bonds in a reaction called hydrolysis. Each time a bond breaks, one molecule of acetic acid is produced.

The rate of internal generation (R) acts as the Engine of decay, controlled strictly by:

- Temperature: The reaction energy (the gas pedal).
- Moisture: The water availability (the fuel).
- Autocatalysis: Internal trapped acid (the chemical turbocharger).

Early on—especially in cool, dry storage—this internal engine is merely idling.

## Axis 2: Emission (J) – The Speedometer

In preservation science, we use the term *emission* to describe the transport pathway: the physical movement of acetic acid vapor from inside the CTA film, through any paint or backing layers, and out into the surrounding environment.

This is where we find our **Speedometer**:

- **The Measurement:** Our tools (like A-D strips or digital PPM sensors) only measure *emitted* acid vapor. They are reading the speedometer.
- **The Measurement Gap:** The speedometer only tells you what has successfully escaped across the surface boundary layer. If a cel is heavily painted, tightly framed, or sealed in a protective sleeve, the escape pathway can be choked.

**The Blind Spot:** Your speedometer (A-D strip) might read "0 PPM / Blue" because no acid is escaping, while the internal Engine (R) is actually redlining due to trapped heat and moisture. Generation happens *inside* the polymer; emission happens *across* the surface.

## The Boundary Layer Problem

Once acid reaches the surface, it encounters the *boundary layer*—a thin, stagnant region of air directly touching the cel.

- Inside this layer, gas exchange is incredibly slow, and diffusion dominates over bulk airflow.
- If a cel is poorly ventilated, packaged in a tight sleeve, or framed, the boundary layer thickens. Local parts-per-million (PPM) of acetic acid skyrocket right at the surface, forcing the paint and line art to live in a highly aggressive microenvironment.

## Cumulative Damage (D) as the Odometer

In this framework, Damage is not a binary state (i.e., "warped" or "not warped"). Instead, it is the cumulative percentage of Deacetylation—the irreversible loss of acetyl groups from the cellulose triacetate (CTA) base.

- 1) The Baseline: Every cel begins with a fixed inventory of acetyl groups (roughly 2.8 groups per monomer unit).
- 2) The Scale: Damage starts the moment the first acetyl bond is broken.
- 3) The Invisible Clock: A cel can have significant internal damage ( $D = 0.4\%$ , which represents approximately 80% of the damage to autocatalytic behavior), and still appear physically "perfect" to the eye.
- 4) The Penalty: Higher damage (D) permanently increases the material's moisture sensitivity, acting like a chemical "sponge" that absorbs more humidity from the air.

## The Autocatalytic Transition

The ultimate state of the cel is determined by how the Odometer (D) and the Speedometer/Emission (J) interact over time. The core question is: *Can emission keep up with generation?*

- **The Balanced Regime:** Early in life, deacetylation (D) is low. The small amount of acid generated by the engine is safely emitted across the boundary layer ( $R \leq J$ ). The odometer ticks up incredibly slowly.
- **The Autocatalytic Brink:** Once the odometer crosses a critical threshold ( $D \approx 0.5\%$ ), the internal chemistry fundamentally shifts.



- **The Feedback Loop:** If emission cannot clear the acid fast enough, the free acid accumulates inside the matrix. Because acid acts as a catalyst for its own creation, this sudden drop in internal pH causes the engine (R) to accelerate exponentially. At this point, the cel enters a runaway feedback loop: *Acid creates more acid*, and the odometer begins spinning uncontrollably toward physical warping, paint delamination, and total structural failure.

## Establishing the Baseline Deacetylation Rate

To translate degradation chemistry into a usable preservation model, we establish a baseline deacetylation rate for cellulose triacetate (CTA) under stable, unmanaged storage conditions. This model serves as a practical, first-order engineering approximation for the pre-autocatalytic regime, anchoring our reference degradation clock before environmental correction factors are applied.

### The 0.5 Acidity Brink

The Image Permanence Institute (IPI) established that the "brink" of the autocatalytic stage occurs at an empirical free acidity level of **0.5**. This is measured via laboratory titration as the milliliters of 0.1M NaOH required to neutralize the free acid extracted from 1 gram of film. Visually, this 0.5 mark is the exact inflection point on a degradation curve where the slope shifts from linear (Regime 1) to exponential (Regime 2).

### The Stoichiometry of Failure

Commercial cellulose triacetate has a baseline Degree of Substitution (DS) of approximately 2.8. We can use the underlying chemistry to estimate what an IPI score of 0.5 means for the structural integrity of the polymer matrix:

1. **The Monomer Inventory:** The molar mass of a CTA monomer unit is roughly 280 g/mol. Therefore, 1 gram of pristine CTA contains a specific mole density of monomer units:

$$\frac{1 \text{ g}}{280 \text{ g/mol}} \approx 0.00357 \text{ moles of monomers}$$

*Equation 2*

2. **The Total Acetate Pool:** With 2.8 acetyl groups per monomer unit, 1 gram of film contains a total initial pool of target bonds:

$$0.00357 \text{ mol} \cdot 2.8 = 0.010 \text{ moles of acetate groups}$$

*Equation 3*

3. **The Free Acid At The Brink:** An IPI free acidity titration value of 0.5 equates to the presence of an estimated 0.00005 moles of free acetic acid per gram of film.

By dividing the free acid present at the threshold by the total initial acetate inventory, we find the critical threshold for the onset of Vinegar Syndrome ( $D_{VS}$ ):

$$D_{VS} = \left( \frac{0.00005 \text{ moles}}{0.010 \text{ moles}} \right) \cdot 100 = 0.5\%$$

*Equation 4*

## Divergence Across Regimes

This stoichiometry suggests a striking reality about CTA degradation: **The model suggests that the transition toward catastrophic degradation begins long before significant bulk chemical depletion occurs.** The model predicts that transition toward runaway degradation begins when a mere **0.5%** fraction of the total acetyl content is lost.

- **Regime 0 & 1 (The Stable Period):** Total structural damage ( $D$ ) remains below 0.5%. While moisture sensitivity increases linearly with each broken bond, the volume of internal acid generated is low enough to safely diffuse across the boundary layer and exit the matrix ( $R \leq J$ ). The baseline model remains highly predictive here.
- **Regime 2 (The Autocatalytic Collapse):** The moment  $D$  crosses the 0.5% threshold; the volume of internal free acid overwhelms the diffusion pathway. The

system transitions from a predictable linear decay to a non-linear, self-accelerating chain reaction.

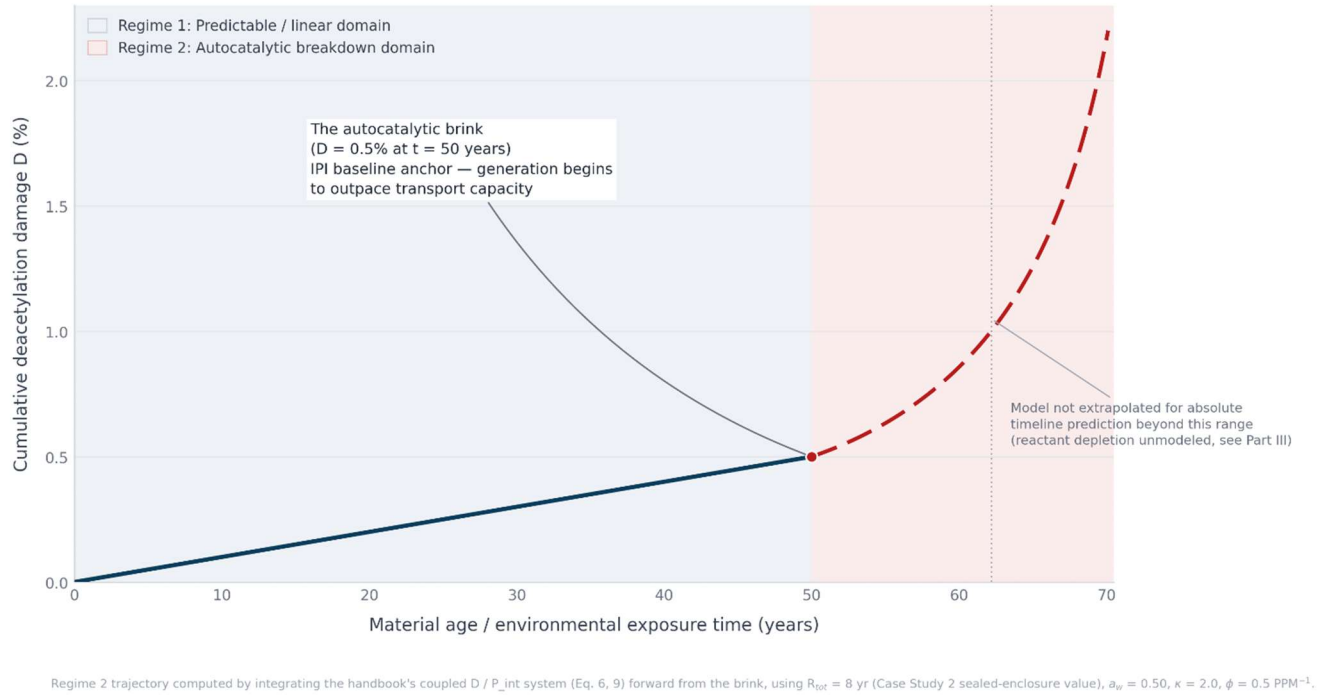


Figure 2: The Regime Trajectory — From Predictable Decay to Autocatalytic Collapse

## The Baseline Preservation Clock

If a stable, unmanaged CTA cel stored under standard room conditions reaches this critical vinegar syndrome threshold ( $D_{VS} \approx 0.5$ ) after approximately 50 years, we define the baseline deacetylation rate ( $\dot{D}_{base}$ ) as:

$$\dot{D}_{base} = \frac{D_{VS}}{t_{VS}} = \frac{0.5\%}{50 \text{ years}} = 0.01\% \text{ per year}$$

Equation 5

This value (0.01% / year) serves as our foundational calibration anchor. While individual cels will experience variance based on their unique paint layers, frame sealing, and manufacturing variables, this baseline rate gives us a rigorous mathematical starting point from which macro-environmental variables can be calculated.

**A note on reference conditions.** The 50-year vinegar-syndrome figure appears in the literature under two slightly different stated conditions: IPI's accelerated-aging basis of 70°F / 40% RH ( $a_w = 0.40$ ), and the ~68°F / 50% RH ( $a_w = 0.50$ ) condition used in the A-D strip guidance and in Curran et al. (2019). This framework adopts the 70°F / 40% RH anchor. Because the 50-year onset is an estimate anchor rather than a measured constant, pinning it to the cooler-drier condition is the more conservative choice: it back-solves to a higher intrinsic thermal velocity ( $R_0 = 0.025$  %/yr, versus 0.020 %/yr if anchored at 50% RH) — that is, a faster baseline rate. The framework's own calculations retain the 40% RH anchor throughout. Readers who prefer to reference results to 50% RH (or any other humidity) can apply a simple correction factor: because the moisture term is linear in water activity ( $a_w^n$  with  $n = 1$ ) and all other terms cancel when only humidity is re-referenced, any baseline generation rate or outgassing figure can be re-referenced by multiplying by ( $a_{w,target} / 0.40$ ) — for example  $\times 1.13$  at 45% RH,  $\times 1.25$  at 50% RH,  $\times 1.38$  at 55% RH, and  $\times 1.50$  at 60% RH. This scales the baseline (environmental) term only; the accumulated-damage ( $\kappa \cdot D$ ) and autocatalytic ( $\Phi \cdot P_{int}$ ) penalties are unaffected, since those are expressed as ratios in which the environmental terms cancel.

Two important context notes on this baseline. First, the 50-year reference timeline derives from IPI accelerated-aging experiments on cellulose triacetate motion picture film — material that includes a gelatin emulsion layer. Gelatin is a known passive acid scavenger (Curran et al., 2019, Table 9), meaning the Adelstein data IPI extrapolated from may have been partially buffered by the emulsion. Cel base without an emulsion layer has no equivalent buffer, which suggests the IPI timeline may be optimistic even as an uncatalyzed baseline for cels specifically.

Second, peer-reviewed modeling by Curran et al. (2019) — working from the same Adelstein dataset — demonstrated that when autocatalysis is properly incorporated, VS onset at 21°C / 40% RH is predicted at 12.1 years rather than the IPI-stated 50 years: a 75% overestimation by guidelines that do not account for autocatalytic feedback. At 4°C / 40%

RH the gap widens further — IPI predicts 450 years, Curran et al. predict 71.2 years. This framework adopts a similar autocatalytic premise and extends the model further to account for enclosure geometry ( $R_{\text{tot}}$ ) and accumulated damage state  $H(D)$ , neither of which appear in the Curran et al. framework.

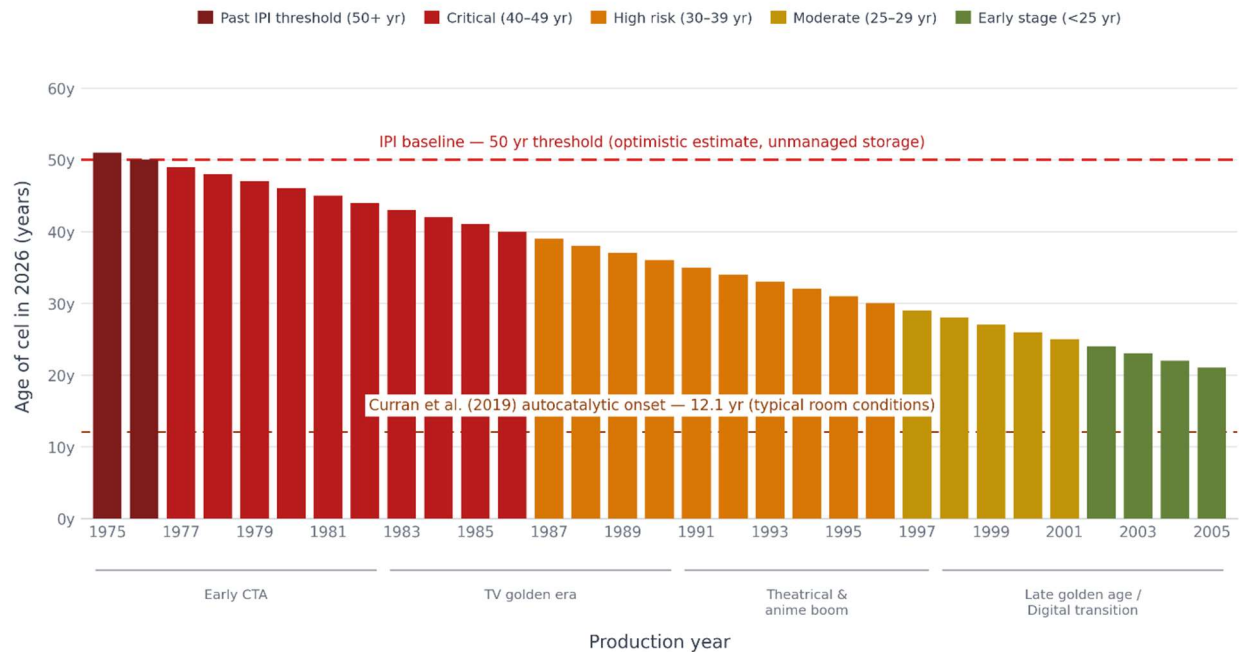


Figure 3: Baseline Preservation Clock

## Preservation Timing: Rate vs State

The interaction between generation ( $R$ ), emission ( $J$ ), and cumulative damage ( $D$ ) creates an important reality in animation cel preservation: **Preservation effectiveness depends heavily on *when intervention begins*.**

Because cellulose acetate degradation is cumulative and irreversible, environmental controls (like cold storage, humidity reduction, acid scavenging, or ventilation) primarily act on the *future degradation rate* of the material—not on the damage already accumulated within the polymer.

## Connecting Hydrolysis to the Odometer

To understand this system, we must explicitly link the chemical reaction to physical structural loss.

- **The Mechanism:** Hydrolysis is the physical action of water splitting the acetyl ester bonds.
- **The Result:** Every single instance of hydrolysis permanently removes an acetyl group, replacing it with a hydrophilic hydroxyl (-OH) group.

Therefore, **more hydrolysis directly equals more cumulative damage (D)**. Every hour a cel spends undergoing hydrolysis, the odometer turns.

### Rate vs. State

To properly diagnose a collection, a conservator must separate the material's current *rate* of decay from its existing *state*.

- **The Current Rate (R):** Driven entirely by temporary environmental variables like current temperature and ambient humidity.
- **The Existing State (D):** The total mileage on the odometer. This is the permanent, historical record of deacetylation.

As the odometer climbs, the physical nature of the polymer permanently alters. The newly introduced hydroxyl (-OH) groups turn the plastic into a chemical sponge, increasing its internal water capacity and shifting its diffusion behavior. These physical transformations remain permanently stamped into the plastic, even if the cel is later moved to a pristine archival vault.

### The Preservation Asymmetry

This split creates a stark asymmetry between early and late intervention:

- **Early Intervention (Low D):** Prevents damage from accumulating. A cel placed in cold storage shortly after production has its hydrolysis rate suppressed *before* significant deacetylation occurs. It preserves a wide stability margin.
- **Late Intervention (High D):** Slower, uphill damage management. A cel entering preservation after 40 years of warm room-temperature storage already possesses

high cumulative damage, increased moisture sensitivity, and a razor-thin stability margin.

### The "Suppressed, Not Corrected" Dilemma

When a degraded cel is placed into deep freeze conditions, it may appear completely cured: vinegar odors vanish, A-D strips return to a safe blue, and physical warping halts.

However, this is an environmental illusion. The underlying cumulative damage (D) remains entirely unchanged. If that cel is ever returned to room temperature, its elevated moisture sensitivity and existing chemical degradation mean the internal engine (R) will immediately fire back up at a much higher baseline rate than a pristine cel. **Environmental controls suppress the reaction rate; they do not reset the material state.**

## Part III: Governing Physics

To project longevity and model intervention outcomes, this section translates chemical decay pathways into a system of **coupled first-order differential equations**. By tracking two distinct states simultaneously—Solid Matrix Damage (dD/dt) and Vapor Phase Gas Balance (dP<sub>int</sub>/dt)—the model isolates how structural wear amplifies environmental vulnerability.

### The Unified Kinetic Law (Acid Generation Rate)

Under conditions where autocatalytic behavior develops, cellulose acetate degradation transitions from approximately linear behavior to a self-accelerating chemical feedback process. To transform these mechanics into an actionable field framework, we intentionally linearize our state-dependent variables directly within this unified equation:

$$\dot{G} = \beta \cdot R_0(T) \cdot H(D) \cdot \left( 1 + \phi \cdot P_{int} \right)$$

*Equation 6*

Where the fundamental temperature-dependent Arrhenius velocity (R<sub>0</sub>) is defined as:

$$R_0 = A \cdot e^{\frac{-E_a}{R_{gas} \cdot T}}$$

Equation 7

where:

- $G$  = Absolute Outgassing Rate ( $\text{PPM} \cdot \text{yr}^{-1}$ ) — the vapor-phase equivalent of  $R$ , scaled by the stoichiometric conversion factor:  $G = \beta \cdot R$ .
- $\beta$  = Stoichiometric Conversion Factor,  $\text{PPM} \cdot \%^{-1}$
- $R_0$  = Intrinsic Arrhenius Rate ( $\% \cdot \text{yr}^{-1}$ )
- $H(t)$  = Hydrophilic Multiplier (dimensionless)
- $(a_w)$  = Internal Water Activity (dimensionless, 0–1)
- $n$  = Reaction Order with Respect to Water (dimensionless)
- $\phi$  = Autocatalytic Acceleration Coefficient ( $\text{PPM}^{-1}$ )
- $P_{int}$  = Internal Partial Pressure of Acetic Acid (PPM)
- $A$  = Pre-Exponential Frequency Factor ( $\% \cdot \text{yr}^{-1}$ , same units as  $R_0$ )
- $E_a$  = Activation Energy ( $\text{J} \cdot \text{mol}^{-1}$ )
- $R_{gas}$  = Universal Gas Constant ( $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ )

Each of the four terms below is a multiplicative gate, not an additive one. A cel does not degrade faster because temperature, moisture, and trapped acid add up — **it degrades faster because they compound**. That distinction is what separates a linear nuisance from a runaway, and it is why each term is walked through individually below before they are combined.

### I. $\beta \cdot R_0(T)$ : The Thermal Engine

This represents the fundamental Arrhenius base rate.  $R_0(T)$  defines the probability of ester bond cleavage at a given temperature ( $T$ ).  $\beta$  acts as the stoichiometric scaling factor, converting the percentage of bond cleavage ( $D$ ) into the potential volume of released acetic acid gas. This term assumes a "pristine" system with no environmental or chemical interference.



Note on activation energy: Two  $E_a$  regimes are relevant to this model. The induction-phase  $E_a$  of approximately  $105 \text{ kJ}\cdot\text{mol}^{-1}$  (derived from IPI / Adelstein zero-order fits) governs  $R_0(T)$  above and sets the temperature sensitivity of the baseline, uncatalyzed hydrolysis rate. Curran et al. (2019) report a lower  $E_a$  of  $70.7 \text{ kJ}\cdot\text{mol}^{-1}$  fitted specifically to the autocatalytic regime. A lower  $E_a$  means temperature reduction provides proportionally less rate suppression once autocatalysis is active — consistent with this framework's finding that cold storage alone cannot arrest State 3 degradation. For induction-phase storage planning (States 1–2),  $105 \text{ kJ}\cdot\text{mol}^{-1}$  is the appropriate value. Where a cel is at or near the autocatalytic regime, Curran et al.'s  $70.7 \text{ kJ}\cdot\text{mol}^{-1}$  better characterizes the remaining temperature sensitivity of active VS progression.

## **II. $H(D)$ : The Hygroscopic Feedback**

$$H(D) = (1 + \kappa * D) * a_w^n$$

As deacetylation progresses ( $D$  increases), the cellulose acetate matrix loses hydrophobic acetate groups, becoming increasingly hydrophilic.  $H(D)$  captures this state-dependency: the more degraded the cel, the more efficient it becomes at adsorbing atmospheric water ( $a_w$ ). This term effectively quantifies how a "damaged" cel creates its own micro-moisture environment, independent of the external ambient relative humidity.

## **III. $(1 + \Phi * P_{int})$ : The Autocatalytic "Acid Trap"**

This is the most critical term for stability. In a stable system,  $P_{int}$  (internal acid partial pressure) is minimized by your storage transport mechanisms ( $J$ ). However, when generation ( $G$ ) exceeds the transport capacity ( $J$ ),  $P_{int}$  accumulates.

### **Chemical Significance:**

- **pH Drop:** The accumulation of acetic acid ( $P_{int}$ ) dissociates into protons ( $H^+$ ), effectively lowering the internal pH of the polymer matrix.

- **Activation Energy (E<sub>a</sub>) Reduction:** The presence of concentrated protons acts as a powerful catalyst. Physically, this lowers the activation energy (E<sub>a</sub>) required to break the remaining cellulose acetate ester bonds.
- **Non-Linear Acceleration:** Because  $(1 + \Phi * P_{int})$  is a **multiplicative factor**, the system transitions from "environmentally dominant" (governed by T, RH) to "acid dominant" (governed by its own internal concentration). Once this term becomes the primary driver of G, the cel enters the **Autocatalytic Phase**, where it will degrade rapidly even in a cold, dry environment, because the "catalyst" is now contained within the film itself.

### Mechanistic Focus: The Hydrophilic Amplification Factor ( $\kappa$ )

To isolate structural wear within an actionable field framework, the model characterizes macro-scale polymer lattice collapse through the constant  $\kappa$ . In pure transport physics,  $\kappa$  is defined as the **Hydrophilic Amplification Factor** or the **Matrix Cooperation Index**. It is the scaling constant that explicitly quantifies how aggressively the solid polymer matrix expands its internal moisture capacity as hydrophobic acetyl shields are lost. When combined with the environmental moisture term ( $a_w^n$ ), it dictates the total hygroscopic load driving the system.

### The Molecular Bait Switch

Pristine cellulose triacetate (CTA) is naturally hydrophobic; its polymer chains are shielded by bulky, non-polar acetyl groups that repel water vapor. However, each individual hour of hydrolysis cleaves an ester bond, stripping away an acetyl shield and leaving behind a highly polar **hydroxyl group (-OH)** pinned to the cellulose backbone. These newly exposed hydroxyl groups become highly favorable sites for hydrogen bonding with water molecules.

### The Cooperative Matrix Effect

If degradation occurred in an isolated, ideal system, the relationship would scale strictly 1:1. However, real animation cels are dense composite materials. When a localized cluster of neighboring acetyl bonds break, a localized cooperative structural changes occur:

- **Free Volume Expansion:** The loss of bulky acetyl groups alters the steric packing of the polymer chain, increasing internal free volume.
- **Plasticizer Displacement:** The sudden, localized spike in matrix polarity chemically repels hydrophobic plasticizers (e.g., triphenyl phosphate), forcing them to migrate or weep out of the immediate zone.
- **Micro-Void Pooling:** This displacement creates sub-microscopic physical voids within the plastic matrix.

Consequently, the generation of hydroxyl groups does not merely attract isolated water molecules; it creates localized, microscopic "pockets" that allow clusters of ambient water vapor to wedge themselves deep into the reaction zone.

$$\kappa = \frac{H(t) - 1}{D}$$

Equation 8

The parameter  $\kappa$  mathematically captures this cooperative structural vulnerability. It reflects the chemical reality that as an animation cel sustains historical chemical damage, the surrounding physical matrix cooperates to expand the internal "chemical sponge," permanently accelerating the material's sensitivity to ongoing ambient humidity ( $a_w^n$ ).

Discretizing the Sensitivity Index ( $\kappa$ ) for Field Testing

While the Hydrophilic Amplification Factor ( $\kappa$ ) represents an internal structural value that requires destructive laboratory analysis to isolate directly, field operations can cleanly discretize the index into three distinct engineering tiers. Bounding this coefficient allows collectors to select an appropriate sensitivity slider based on the era, layer configuration, and observable physical stress of the artwork:

Table 1: Hydrophilic Sensitivity Tiers ( $\kappa$ )

| Sensitivity Tier | Index Value ( $\kappa$ ) | Physical Material Profiles & Production Context |
|------------------|--------------------------|-------------------------------------------------|
|------------------|--------------------------|-------------------------------------------------|

|                      |                |                                                                                                                                                                                                                                    |
|----------------------|----------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Low Sensitivity      | $\kappa = 1.0$ | <b>High-Stability Substrates:</b> Unpainted clear margins, sheets displaying exceptionally high native plasticizer retention, or premium-grade late-era production substrates possessing advanced stabilizers.                     |
| Moderate Sensitivity | $\kappa = 2.0$ | <b>Standard Production Baseline:</b> The baseline calibration anchor representing standard commercial mid-to-late era animation cels subjected to typical multi-layer paint environments.                                          |
| High Sensitivity     | $\kappa = 4.0$ | <b>Stressed Composite Systems:</b> Heavily painted cels with thick-pooled hydrophilic pigment boundaries, sheets suffering from severe historical plasticizer leaching, or assemblies subjected to continuous framing compression. |

### The Transport Model (Acid Emission Flux)

The physical evacuation of free acetic acid vapor out of the cel and across the surface boundary layer is modeled as a steady-state mass transfer resistance network driven by a partial pressure gradient:

$$J = \frac{P_{int} - P_{env}}{R_{tot}}$$

Equation 9

where:

- $J$  = Outward Emission Flux, PPM \* yr<sup>-1</sup>
- $P_{env}$  = Environmental Partial Pressure of Acetic Acid, PPM
- $R_{tot}$  = Total Cumulative Mass Transfer Resistance, yr

### The Unified Mass Balance System

By combining our kinetic generation law with our mass transport resistance network, we establish a unified, two-state dynamic mass balance system. This coupled system cleanly separates structural material damage (the Odometer) from volatile chemical vapor density (the Speedometer):

$$\text{Track 1 ( Solid Matrix Damage Progress) : } \frac{dD}{dt} = R$$

Equation 10

$$\text{Track 2 ( Vapor Phase Gas Balance) : } \frac{dP_{int}}{dt} = \dot{G} - J$$

Equation 11

Substituting our expressions for R and J yields the complete, coupled conservation equation:

$$\frac{dD}{dt} = R_0(T) \cdot H(D) \cdot (1 + \phi \cdot P_{int})$$

Equation 12

$$\frac{dP_{int}}{dt} = \beta \left[ R_0(T) \cdot H(D) \cdot (1 + \phi \cdot P_{int}) \right] - \left( \frac{P_{int} - P_{env}}{R_{tot}} \right)$$

Equation 13

Note on reactant depletion: This framework treats the acetyl bond inventory as effectively inexhaustible within the survival range of collection objects ( $D \leq 0.5\%$ ). Curran et al. (2019) demonstrate that substrate depletion — the gradual exhaustion of unreacted acetyl groups [ROAc] and available water [H<sub>2</sub>O] — becomes mechanistically significant at higher free acidity values, eventually slowing the autocatalytic rate as reactants are consumed. This effect is not modeled here: cels approaching  $D = 0.5\%$  are classified as State 3 and treated as requiring immediate stabilization rather than long-horizon lifetime prediction.

Incorporating substrate depletion would require tracking [ROAc] and [H<sub>2</sub>O] as explicit state variables and fitting those parameters to experimental data. This is an acknowledged gap for future model development and the primary motivation for the planned FTIR calibration study.

where:

- $R$  = Instantaneous Generation Rate ( $\% \cdot \text{yr}^{-1}$ ): the structural bond-cleavage rate that drives  $dD/dt$ .
- $dD/dt$  = Damage Accumulation Velocity,  $\% \cdot \text{yr}^{-1}$
- $dP_{\text{int}}/dt$  (Net Vapor Accumulation Rate,  $\text{PPM} \cdot \text{yr}^{-1}$ ): The instantaneous rate of change of free acid gas trapped inside the cel matrix.

This conservation of mass system can be used to estimate the physical state of the cel based on the performance of its transport network ( $J$ ):

- **The Acid-Controlled Boundary Condition (Regime 1):** When  $R_{\text{tot}} \rightarrow 0$  due to active scavenging,  $J \geq R$ . Free acid is removed rapidly relative to its generation rate, forcing  $P_{\text{int}} \rightarrow 0$ . The autocatalytic term collapses, simplifying the damage rate exclusively to the linear progression of the moisture-driven odometer:  $dD/dt = R_0 \cdot a_w \cdot (1 + \kappa \cdot D)$ .
- **The Transport-Limited Boundary Condition (Regime 2):** When a cel is entombed behind thick paint or sealed enclosures ( $R_{\text{tot}} \gg 0$ ),  $J < R$ . Free acid cannot escape, meaning  $P_{\text{int}} > 0$ . This promotes state-dependent feedback where trapped vapor directly accelerates its own generation rate ( $R_{\text{runaway}}$ ), triggering an exponential autocatalytic collapse.

## The Logarithmic Stakes and Weak Acid Dissociation

To map the transition from structural loss to environmental acidity, the model must account for the behavior of acetic acid ( $\text{CH}_3\text{COOH}$ ) within a liquid or vapor phase. Acetic acid is a weak organic acid, meaning it does not dissociate completely into free hydrogen ions when exposed to moisture. Instead, its behavior is governed strictly by its thermodynamic acid dissociation constant ( $K_a$ ):



Equation 14

At standard room temperature (25 degC / 298.15K), this equilibrium is defined by the law of mass action:

$$K_a = \frac{[H^+]^2}{C_a - [H^+]}$$

Equation 15

where:

- $K_a$  = the acid dissociation constant,  $1.75 \times 10^{-5}$  ( $pK_a = 4.76$ ).
- $H^+$  = concentration of active free protons (hydrogen ions) in solution
- $C_a$  = total analytical concentration of acetic acid generated by the polymer substrate.

Because the system is a weak acid — one that only partially dissociates — the production of destructive free protons scales non-linearly with the total mass of acid generated. Solving this equilibrium quadratic equation allows us to mathematically predict the precise moment internal pH will crash, long before bulk chemical depletion occurs.

## Part IV: Applied Physics

This section bridges high-level transport theory with non-destructive field operations.

Because internal matrix vapors cannot be measured directly without destroying the artwork, field diagnostics rely on colorimetric indicators (A-D strips) to read emitted environmental vapor pressures ( $P_{env}$ ) as an operational proxy. Due to the weak dissociation kinetics of acetic acid and the narrow active window of bromocresol green dye, a stark **40x measurement gap** exists before an A-D strip can register its first visual change.

Furthermore, predictive modeling across real-world field scenarios confirms that for high-odometer cels nearing or passing the autocatalytic brink, **room-temperature dehumidification alone is mathematically incapable of halting degradation**. Once structural changes have occurred, dropping the ambient kinetic energy via **deep thermal cold storage** is the only operational lever capable of overriding the matrix damage penalty and locking the preservation clock in place.

## Technical Metric Dashboard

Use this upfront matrix as a quick-reference guide to balance rates, track states, and identify localized material bottlenecks before executing storage interventions. The table below is a forward reference: each ratio is built term-by-term across Sections I–III.

Bookmark this page and return to it once  $R$ ,  $J$ ,  $D$ , and  $\kappa$  are defined — it will read very differently the second time.

*Table 2: Technical Metric Dashboard*

| Quantity             | Equation                      | Purpose                                      | Used In          |
|----------------------|-------------------------------|----------------------------------------------|------------------|
| $R_0(T)$             | Arrhenius equation            | Baseline hydrolysis rate                     | Generation Model |
| $H(D)$               | $1 + \kappa D$                | Historical moisture amplification            | Generation Model |
| $aw^n$               | Water activity term           | Environmental moisture influence             | Generation Model |
| $(1 + \phi P_{int})$ | Autocatalytic term            | Internal acid feedback                       | Generation Model |
| $G$                  | $\beta \cdot R$               | Converts bond cleavage into vapor generation | Vapor Balance    |
| $J$                  | $(P_{int} - P_{env})/R_{tot}$ | Vapor emission rate                          | Transport Model  |
| $dD/dt$              | Damage ODE                    | Tracks cumulative deacetylation              | State Equation   |
| $dP_{int}/dt$        | Vapor ODE                     | Tracks internal acid accumulation            | State Equation   |



|                      |                        |                                             |                   |
|----------------------|------------------------|---------------------------------------------|-------------------|
| <b>H<sup>+</sup></b> | Weak acid dissociation | Converts total acid to proton concentration | pH Interpretation |
|----------------------|------------------------|---------------------------------------------|-------------------|

### The Logarithmic Matrix: Mapping A-D Strips to Acidity Deltas

A-D strips are paper indicators dyed with a pH-sensitive chemical (bromocresol green). They do not measure the solid plastic substrate directly; instead, they rely on a gas-liquid-solid equilibrium where free acetic acid vapor escapes the cel, builds up in a sealed microenvironment, and protonates the dye embedded in the paper strip.

The visual endpoints of this field diagnostic scale are directly dictated by the protonation kinetics of the dye:

- **The Indicator Constant (pK<sub>in</sub>):** Bromocresol green has an intrinsic indicator constant (pK<sub>in</sub>) of 4.8.
- **The Active Window:** An indicator dye’s visible transition band is bounded by pH = pK<sub>in</sub> ± 1.0. For this system, the active color change spans precisely from pH 5.4 down to pH 3.8.

Because acidity is measured on a logarithmic pH scale (pH = -log<sub>10</sub>[H<sup>+</sup>]), linear steps on an A-D strip mask massive, exponential surges in active proton density. By pairing the dye’s visual indicators with our weak acid dissociation equations (K<sub>a</sub>), we can map out the precise acidity intervals across the diagnostic spectrum:

Table 3: A-D Strip Level to Acidity Delta Mapping

| A-D Strip Level | Visual Color State | Vapor Exposure (PPM) | Titrateable Acidity (ml of 0.1M NaOH/g film) | Estimated Local pH | Free Proton Acidity Delta       |
|-----------------|--------------------|----------------------|----------------------------------------------|--------------------|---------------------------------|
| AD 0            | Bright Blue        | 0 to 0.5 PPM         | 0 to 0.1                                     | > 5.4              | 1x (Baseline Background Level)  |
| AD 0.5          | Blue-Green         | 0.5 to 1 PPM         | 0.1 to 0.2                                   | 4.9 to 4.6         | 2.5x increase in proton density |
| AD 1.0          | True Green         | 1 to 2 PPM           | About 0.2                                    | 4.5 to 4.1         | 10x increase (The Warning Gate) |

|               |                    |              |                       |            |                                              |
|---------------|--------------------|--------------|-----------------------|------------|----------------------------------------------|
| <b>AD 1.5</b> | <b>Light Green</b> | 3 to 5 PPM   | About 0.5 (The brink) | 4          | <b>30x increase (Autocatalytic Ignition)</b> |
| <b>AD 2.0</b> | Lime Yellow        | 6 to 8 PPM   | About 1               | 3.8 to 3.5 | <b>100x increase</b> in proton density       |
| <b>AD 3.0</b> | Bright Yellow      | 18 to 20 PPM | About 2 or above      | < 2.8      | <b>500x to 1000x increase (Freefall)</b>     |

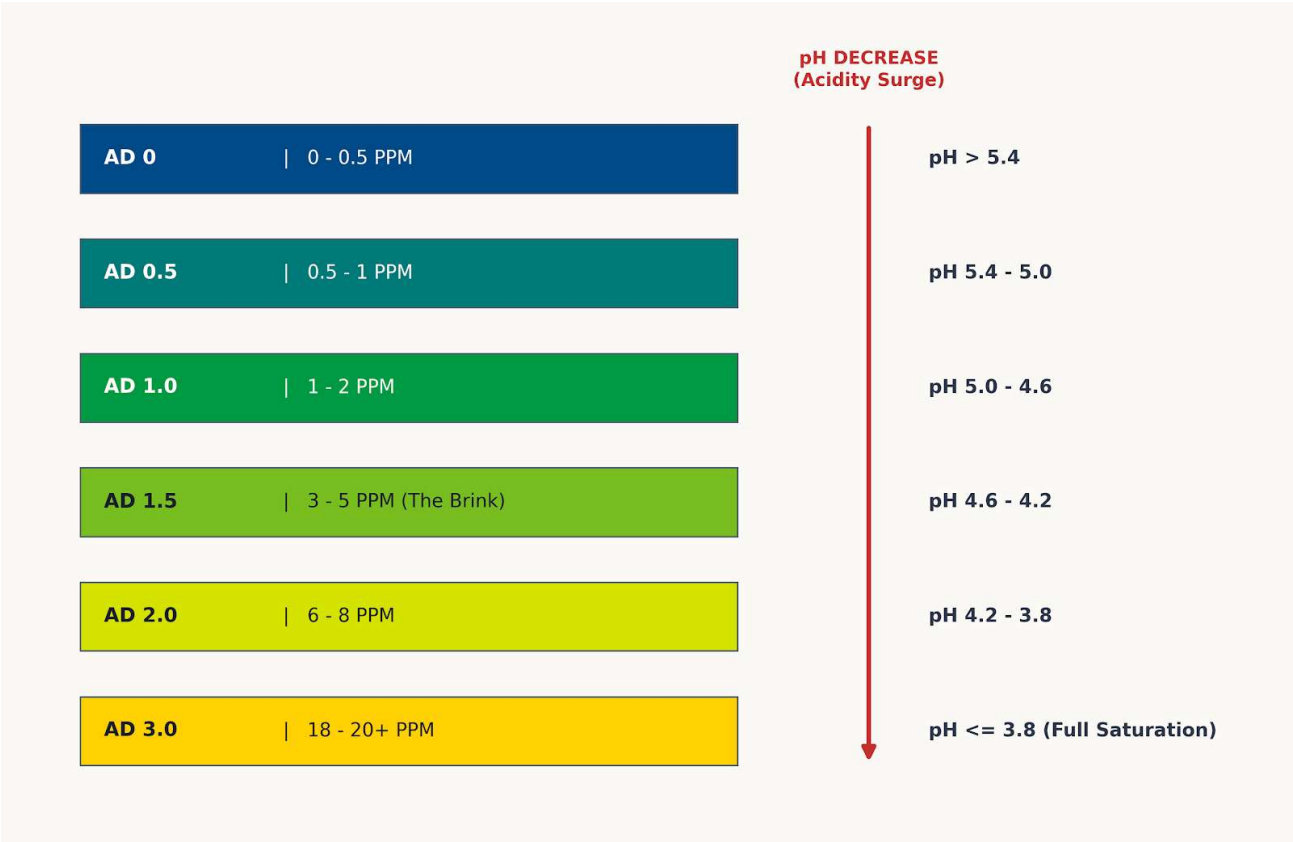


Figure 4: A-D Strip Color Progression and Corresponding Acidity Range

The quantitative mapping of vapor-phase organic acid exposure across colorimetric paper matrices in this framework is calibrated directly against the spectrophotometric workflows established by Hackney (2016).

When deploying standard alkali-stabilized bromocresol green indicator strips to detect volatile outgassing within collection microenvironments, field operations must account for three critical thermodynamic parameters verified by this reference:

- **Reagent Boundary Constraints:** The visible halochromic transition window of the embedded indicator dye is strictly bounded by chemical equilibria between a stable blue ionized state at pH > 5.4 and a fully protonated un-ionized yellow state at pH ≤3.8. Consequently, an A-D Level 3 reading denotes complete indicator color saturation, meaning the underlying core matrix acidity may continue to intensify past pH 3.8 without displaying further visual hue variations
- **Thermal Independence Boundaries:** Empirical climate chamber testing confirms that temperature fluctuations within standard museum display and storage bounds (16.5°C to 27.5°C) exert a negligible impact on the strip's internal colorimetric equilibrium kinetics. This physical independence isolates temperature as a clean control variable, confirming that any detected colorimetric drift is a direct, uncoupled function of volatile organic acid vapor accumulation or shifting relative humidity.

### Quantifying the Early-Stage Measurement Gap

To illustrate the true danger of relying on visual metrics, we calculate the invisible chemical transition that occurs between a perfectly pristine baseline (pH 7.0) and the strip's very first threshold of detection (pH 5.4).

Using our logarithmic proton expression ( $[H^+] = 10^{-pH}$ ):

- At Pristine Neutral (pH 7.0):  $[H^+] = 10^{-7} = 1.0 \cdot 10^{-7} \text{ mol/L}$
- At Detection Limit (pH 5.4):  $[H^+] = 10^{-5.4} = 3.98 \cdot 10^{-6} \text{ mol/L}$

$$\text{Acidity Jump} = \frac{3.98 \cdot 10^{-6} \text{ mol/L}}{1.0 \cdot 10^{-7} \text{ mol/L}} \approx 39.8x$$

*Table 4: Proton Concentration Scaling from Pristine Baseline to Sensor Saturation*

| Substrate Matrix State | Absolute Molar Concentration $[H^+]$ | Cumulative Acidity Scaling (vs. Pristine Baseline) | Visual Reagent Field State (A-D Strip Match) |
|------------------------|--------------------------------------|----------------------------------------------------|----------------------------------------------|
|                        |                                      |                                                    |                                              |

|               |                             |                                 |                                                          |
|---------------|-----------------------------|---------------------------------|----------------------------------------------------------|
| pH 7.0        | $1.00 \times 10^{-7}$ mol/L | 1x ( <i>Pristine Baseline</i> ) | Deep Archival Blue ( <i>AD 0 Background</i> )            |
| pH 6.0        | $1.00 \times 10^{-6}$ mol/L | 10x increase                    | Deep Archival Blue ( <i>AD 0 Background</i> )            |
| <b>pH 5.4</b> | $3.98 \times 10^{-6}$ mol/L | 39.8x increase                  | True Blue-Green ( <i>AD 0.5 Threshold Entry Point</i> )  |
| pH 5.0        | $1.00 \times 10^{-5}$ mol/L | 100x increase                   | True Green ( <i>AD 1.0 Critical Alert Gate</i> )         |
| pH 4.0        | $1.00 \times 10^{-4}$ mol/L | 1,000x increase                 | Light Green / Lime ( <i>AD 1.5 to AD 2.0 Boundary</i> )  |
| <b>pH 3.8</b> | $1.58 \times 10^{-4}$ mol/L | 1,585x increase                 | Vivid Yellow ( <i>AD 3.0 Entry / Sensor Saturation</i> ) |
| pH 3.0        | $1.00 \times 10^{-3}$ mol/L | 10,000x increase                | Vivid Yellow ( <i>Total Saturation Flatline</i> )        |
| pH 2.0        | $1.00 \times 10^{-2}$ mol/L | 100,000x increase               | Vivid Yellow ( <i>Total Saturation Flatline</i> )        |
| pH 1.0        | $1.00 \times 10^{-1}$ mol/L | 1,000,000x increase             | Vivid Yellow ( <i>Total Saturation Flatline</i> )        |

This suggests that a cell's internal active free acidity must increase by nearly **40 times** (a 3,900% surge in proton concentration) **before an A-D strip can register any visual change** at all. *A bright blue strip (AD 0) does not indicate a complete lack of chemical activity; it*

*merely indicates that the exponential curve has not yet breached the strip's physical entry gate.*

## Quantifying the Upper-Bound Sensor Saturation

A secondary measurement gap occurs at the hyper-acidic end of the spectrum. When an enclosed cel experiences severe, advanced autocatalytic decay, it can release enough volatile gas to spike headspace concentrations well past 20 PPM down to 50+PPM inside of a few minutes.

On a standard visual test, the bromocresol green dye is completely protonated and turns entirely yellow at a local solution value of pH 3.8, matching an exposure of roughly 18 to 20 PPM (AD 3.0). Because the dye cannot change color any further, an AD 3.0 reading does not represent a static maximum level of deterioration—it represents the functional saturation limit of the indicator paper.

To track freefall velocity accurately past this limit without destructive testing, field workflows must swap out passive indicator strips for active sampling tools like colorimetric gas tubes, which draw fixed volumes of air through a reagent column to measure absolute parts-per-million volume concentrations directly up to the true chemical limits of the collapse.

## Field Scenarios: Applied Kinetics & Multi-Variable Stress Tests (Comparing the same cel)

To deploy this engineering framework successfully in the field, diagnostics must transition from static visual observations to dynamic mass-transport modeling. Because an archivist cannot directly measure internal polymer variables without executing destructive testing sequences, we map the coupling of solid-matrix wear and vapor accumulation through field-ready metrics.

The following background matrix evaluates the absolute outgassing generation rate ( $G = \beta \cdot R$ ) across a calibrated baseline environment to isolate how historical structural damage and real-time gas trapping interact.

## The Baseline Parametric Matrix

The baseline calculations below are simulated under common indoor collection conditions (70F and 40% RH, yielding an internal water activity of  $a_w = 0.40$ ). To determine a way to estimate the influence of the increased hydrophilicity, deacetylation state, and internal vapor pressure, Equation 6 is used and compared against the same cel in pristine condition; that is a cel that has no accumulated damage and has no internal vapor pressure loading. Environmental constants mathematically cancel, and the relative penalty is isolated for rapid field screens as seen in Equation 16. The system equations utilize the absolute engineering parameters calibrated from the framework's baseline values:

$$\frac{\dot{G}_{\text{degraded}}}{\dot{G}_{\text{pristine}}} = \frac{\beta \cdot R_0 \cdot (1 + \kappa \cdot D) \cdot a_w^n \cdot (1 + \phi \cdot P_{\text{int}})}{\beta \cdot R_0 \cdot (1 + \kappa \cdot 0) \cdot a_w^n \cdot (1 + \phi \cdot 0)}$$

Variation between two states can be seen by:

Equation 16

$$\text{Relative Penalty} = (1 + \kappa \cdot D) \cdot (1 + \phi \cdot P_{\text{int}})$$

- **Intrinsic Thermal Velocity ( $R_0$ ):** 0.025% structural bonds broken per year.
- **Stoichiometric Conversion Factor ( $\beta$ ):** 10.0 PPM %<sup>-1</sup>.
- **Hydrophilic Amplification Factor ( $\kappa$ ):** 2.0 (Standard Production Baseline).
- **Autocatalytic Constant ( $\Phi$ ):** 0.5 PPM<sup>-1</sup>.

Table 5: Room Temperature Kinetic Matrix (70F at 40% RH)

| Damage Odometer State (D) | Internal Vapor Pressure (Pint) | Hygroscopic Loading (H) | Autocatalytic Multiplier | Absolute Outgassing ( $G^\cdot$ ) | Kinetic Acceleration Factor ( $G^\cdot / G^\cdot \text{pristine}$ ) |
|---------------------------|--------------------------------|-------------------------|--------------------------|-----------------------------------|---------------------------------------------------------------------|
| 0.0% (Pristine Control)   | 0.0 PPM                        | 0.40                    | 1.00                     | 0.100 PPM * y <sup>-1</sup>       | 1.00x                                                               |

|                                   |         |      |      |                             |              |
|-----------------------------------|---------|------|------|-----------------------------|--------------|
| <b>0.2% (Evolving Wear)</b>       | 0.0 PPM | 0.56 | 1.00 | 0.140 PPM * y <sup>-1</sup> | <b>1.40x</b> |
| <b>0.5% (Autocatalytic Brink)</b> | 0.0 PPM | 0.80 | 1.00 | 0.200 PPM * y <sup>-1</sup> | <b>2.00x</b> |
| <b>0.0% (Pristine Blueprint)</b>  | 2.0 PPM | 0.40 | 2.00 | 0.200 PPM * y <sup>-1</sup> | <b>2.00x</b> |
| <b>0.5% (Autocatalytic Brink)</b> | 2.0 PPM | 0.80 | 2.00 | 0.400 PPM * y <sup>-1</sup> | <b>4.00x</b> |
| <b>0.0% (Pristine Blueprint)</b>  | 5.0 PPM | 0.40 | 3.50 | 0.350 PPM * y <sup>-1</sup> | <b>3.50x</b> |
| <b>0.5% (Autocatalytic Brink)</b> | 5.0 PPM | 0.80 | 3.50 | 0.700 PPM * y <sup>-1</sup> | <b>7.00x</b> |

### Kinetic Stress Test: Structural Damage (D) vs. Vapor Pressure (P<sub>int</sub>)

Evaluating the independent parameters in this grid resolves a critical debate regarding conservation priorities: **Which variable drives a more severe threat to material stability—permanent lattice damage (D) or local vapor trapping (P<sub>int</sub>)?**

While structural damage (D) is the most fundamentally devastating factor *conceptually* because it permanently alters the matrix packing into an irreversible, water-loving sponge, **trapped vapor pressure (P<sub>int</sub>) is mathematically far more impactful as a kinetic acceleration driver.**

- **The D Limitation Window:** Because a cellulose triacetate cel shifts into catastrophic geometric collapse the moment a mere 0.5% fraction of its total acetyl bonds are destroyed, the absolute scope of the damage modifier (1 + κ \* D) is physically bounded between 1.0x and 2.0x for surviving collection objects.
- **The P<sub>int</sub> Turbocharging Potential:** Conversely, gas phase accumulation (P<sub>int</sub>) has no physical ceiling inside an unventilated enclosure. In stagnant storage conditions, P<sub>int</sub>

routinely scales to 2.0 PPM, 5.0 PPM, or higher. This unrestricted growth allows the autocatalytic multiplier  $(1 + \Phi \cdot P_{\text{int}})$  to easily drive kinetic velocity surges of 3.5x, 7.0x, or higher, completely overriding the influence of the solid-state structural state.

**Conservation Alignment:** Structural wear (D) constructs the vulnerability profile, but vapor retention ( $P_{\text{int}}$ ) acts as the high-velocity catalyst that triggers autocatalytic collapse. Managing the vapor footprint is the most high-leverage option available to an engineer seeking to slow down an aging collection.

### *Edge-Case Field Studies: Stress-Testing the Boundary Equations*

The following case studies present extreme scenario profiles designed to stress-test the mass balance boundaries of the unified kinetic equation against real-world enclosure configurations.

#### **Case Study 1: The Passive Acid-Controlled Bound ( $J > G$ )**

- **Asset Profile:** Production cel nearing the vinegar syndrome threshold ( $D = 0.4$ , yielding a high moisture capacity score of  $H = 0.72$  under 40% RH).
- **Storage Configuration:** The item is housed inside an open-air archival storage rack equipped with active molecular vapor-phase scavenging networks. Active scavenging maintains the external boundary layer at an ideal state ( $P_{\text{env}} \approx 0$  PPM), lowering the total mass transfer resistance of the path to a highly efficient level ( $R_{\text{tot}} = 1.25$  yr).
- **Diagnostic Entry Point:** A localized colorimetric tube registers an active, elevated internal outgassing footprint ( $P_{\text{int}} = 1.0$  PPM).

#### **Mathematical Stress Test Evaluation:**

1. Compute the absolute generation profile (G):

$$G = 10.0 \cdot 0.025 \cdot 0.72 \cdot (1 + 0.5 \cdot 1.0) = 0.27 \text{ PPM} \cdot \text{yr}^{-1}$$



2. Compute the outward evacuation flux (J):

$$J = \frac{1.0 \text{ PPM} - 0 \text{ PPM}}{1.25 \text{ yr}} = 0.800 \text{ PPM} \cdot \text{yr}^{-1}$$

3. Evaluate the dynamic mass balance boundary condition:

$$\frac{dP_{\text{int}}}{dt} = 0.27 - 0.800 = -0.530 \text{ PPM} \cdot \text{yr}^{-1}$$

**Field Outcome:** Because the designed transport framework keeps mass transfer resistance exceptionally low ( $R_{\text{tot}} \rightarrow 0$ ), the outward emission flux easily overpowers internal generation ( $J > G$ ). The net vapor accumulation rate is negative. Free acid is stripped away the instant it exits the film, forcing the internal vapor profile toward a safe baseline and stabilizing the asset within a slow, predictable decay trajectory.

#### **Case Study 2: The Transport-Limited Boundary & Core Runaway Trap ( $G > J$ )**

- **Asset Profile:** An identical high-odometer production cel from the same sequence ( $D = 0.4\%$ ,  $H = 0.72$  under 40% RH).
- **Storage Configuration:** The item is sealed inside a thick protective polypropylene display sleeve and mounted behind a non-ventilated frame. The heavy paint layer combined with the stagnant boundary layer of the enclosure locks the system behind an intense cumulative mass transfer barrier ( $R_{\text{tot}} = 8 \text{ yr}$ ).
- **Diagnostic Entry Point:** The initial internal vapor concentration mimics the companion piece ( $P_{\text{int}} = 1.0 \text{ PPM}$ ).

#### **Mathematical Stress Test Evaluation:**

1. Compute the absolute generation profile (G):

$$G = 10.0 \cdot 0.025 \cdot 0.72 \cdot (1 + 0.5 \cdot 1.0) = 0.27 \text{ PPM} \cdot \text{yr}^{-1}$$

2. Compute the outward evacuation flux (J):

$$J = \frac{1.0 \text{ PPM} - 0 \text{ PPM}}{8.0 \text{ yr}} = 0.125 \text{ PPM} \cdot \text{yr}^{-1}$$

3. Evaluate the dynamic mass balance boundary condition:

$$\frac{dP_{\text{int}}}{dt} = 0.27 - 0.125 = +0.145 \text{ PPM} \cdot \text{yr}^{-1}$$

**Field Outcome:** This scenario triggers the catastrophic **Transport-Limited Boundary Condition**. Even though both cels share identical room environments and internal odometer states, the high mass-transfer resistance traps acid gas within the matrix faster than it can diffuse outward ( $J < G$ ). The net accumulation velocity turns positive, driving  $P_{\text{int}}$  upward.

As  $P_{\text{int}}$  intensifies, it systematically lowers internal pH and drops the reaction's activation energy, forcing the generation velocity ( $G$ ) to multiply exponentially. The object is locked inside a self-accelerating loop where it will collapse into severe warping and delamination entirely from the inside out, proving that high enclosure resistance makes environmental room controls obsolete.

Set side by side, these two case studies make the single most persuasive argument in this framework: two cels from the same production run, sharing the same room, the same temperature, and the same starting odometer reading, arrive at opposite fates purely because of enclosure resistance ( $R_{\text{tot}}$ ). Ambient room control did nothing to protect Case Study 2 — the sleeve and frame around it determined its trajectory more than the climate of the room it sat in. This is why this framework treats transport resistance, not ambient temperature or humidity alone, as the variable a collector has the most leverage over at the point of framing or sleeving a cel.

A critical distinction from closed-system models: In the Curran et al. (2019) framework and in IPI guidelines, free acidity is used as a direct proxy for accumulated structural damage —

because their systems are assumed fully sealed, every molecule of acetic acid generated remains in the film, making [HOAc] and D proportional by definition. In open or scavenged storage, this equivalence breaks down entirely. A cel with active scavenging history may show a blue A-D strip and low free acidity while having undergone substantial cumulative deacetylation — the acid was removed, but the bond cleavage it represents was not reversed. This is precisely why this framework tracks D (cumulative structural damage) and P<sub>int</sub> (current vapor-phase acid concentration) as independent variables on two separate tracks. Free acidity alone cannot distinguish between a pristine cel and a scavenged one. D can.

## Field Scenarios: Quantifying the Hydrophilic Multiplier

To look at how permanent structural deacetylation changes a cel's vulnerability to its storage room, we isolate our environmental variables to compare two distinct items—Cel A and Cel B—housed in the exact same macro-climate. The four scenarios that follow isolate one variable at a time, building toward a single practical question: why can't a degraded cel simply be dehumidified back to safety, and what intervention actually works instead?

To make this clean, let's apply a standard **Perfect Sink Approximation**—meaning we assume the enclosure air paths, ventilation, or chemical molecular sieves are so infinitely efficient that they strip away every molecule of acid vapor the exact instant it leaves the film surface, allowing us to drop the internal acid partial pressure to zero (P<sub>int</sub> = 0).

If we pull back our complete, unified kinetic Equation 6 from Part III:

$$R = R_0 \cdot H(D) \cdot (1 + \phi \cdot P_{int})$$

Because we assume a perfect sink where P<sub>int</sub> = 0, that entire autocatalytic multiplier term collapses straight down to 1:

$$(1 + \phi \cdot 0) = 1$$

*Equation 17*

This leaves us strictly with the linear, pre-autocatalytic structural moisture-penalty equation ( $R_1$ ):

$$R_1 = R_0 \cdot a_w^n \cdot (1 + \kappa \cdot D)$$

Equation 18

Because both cels share a room, their surrounding temperature (T) and humidity fuel ( $a_w$ ) are identical. When dividing the generation rate of Cel B by Cel A to evaluate the relative degradation penalty, the environmental thermal parameter ( $R_0$ ) and the water activity variable ( $a_w$ ) mathematically cancel out of the fraction:

$$\frac{R_{1,B} = R_0 \cdot a_w^n \cdot (1 + \kappa \cdot D_B)}{R_{1,A} = R_0 \cdot a_w^n \cdot (1 + \kappa \cdot D_A)} = \frac{1 + \kappa \cdot D_B}{1 + \kappa \cdot D_A}$$

Equation 19

This mathematical proof isolates the environmental noise. It confirms that when external storage conditions are held completely constant, any variance in the internal acid generation speed is driven entirely by the difference in the cels' accumulated odometer damage (D).

### Scenario 1: The Parity Check (Identical Structural States)

**Conditions:** Two fresh production cels from the same animation sequence are stored together in an unmanaged space kept at 50% RH ( $a_w = 0.50$ ). Both cels exhibit an identical initial odometer reading of  $D_A = D_B = 0.025\%$ .

**Calculation:** To compute the baseline degradation velocity, we assign a standard **Moderate Sensitivity Index ( $\kappa = 2.0$ )** to the production run. We calculate the individual localized moisture multipliers ( $H_A$  and  $H_B$ ) explicitly:

$$1 + (\kappa \cdot D_A) = 1 + (2.0 \cdot 0.025) = 1.05$$

$$1 + (\kappa \cdot D_B) = 1 + (2.0 \cdot 0.025) = 1.05$$

(Note: For the purposes of baseline environmental calibration, this first-order engineering approximation utilizes a baseline model anchor of  $H = 1.05$  to establish a standardized reference clock before environmental correction factors are applied.)

Next, we evaluate the absolute pre-autocatalytic generation values ( $R_1$ ) under our enforced perfect sink room environment ( $R_0 = 1.00$  at standard room temperature):

$$R_{1,A} = R_0 \cdot H_A = 1.00 \cdot 0.50 \cdot 1.05 = 0.525$$

$$R_{1,B} = R_0 \cdot H_B = 1.00 \cdot 0.50 \cdot 1.05 = 0.525$$

Finally, we construct the comparative degradation ratio to check for structural parity between the items:

$$\text{Comparative Velocity Ratio} = \frac{R_{1,B}}{R_{1,A}} = \frac{0.525}{0.525} = 1x$$

**Field Outcome:** The comparative ratio calculates to 1x. Both items degrade at an identical, predictable speed, successfully establishing our foundational calibration baseline score of 0.525 for macro-environmental comparison.

#### *Scenario 2: The Treated Cel Dilemma (The Speedometer Blind Spot)*

**Conditions:** A heavily degraded cel, Cel B, has successfully undergone an active chemical vapor extraction treatment. The treatment successfully vents all volatile acid from the container, resetting its external speedometer reading to approximately 0 PPM (AD 0 / Blue). However, the chemical hydrolysis reaction is completely irreversible; the structural acetyl bonds that were historically destroyed remain permanently replaced by water-loving hydroxyl groups. The cel's structural odometer remains permanently trapped right at the edge of the autocatalytic brink ( $D_B = 0.50\%$ ). It is placed back into the same 50% RH room right next to the fresh Cel A ( $D_A = 0.025\%$ ).

**Calculation:**

We compute the localized moisture multiplier for the degraded cel ( $H_B$ ) utilizing its permanent odometer damage ( $D_B = 0.50\%$ ) and divide it directly by the established fresh baseline value ( $R_{1,A} = 0.525$ ):

$$H_B = 1 + (\kappa \cdot D_B) = 1 + (2.0 \cdot 0.50) = 2.00$$

$$\text{Relative Rate Ratio} = \frac{R_{1,B}}{R_{1,A}} = \frac{R_0 \cdot H_B}{0.525} = \frac{1.00 \cdot 0.50 \cdot 2.00}{0.525} = 1.9x$$

**Field Outcome:** Even though the treated cel produces a "safe blue" indicator on a standard strip, its underlying structural damage causes the polymer to act as a permanent sponge. It absorbs significantly more water from the room air, causing its internal engine to run nearly **twice as fast** as the fresh piece sitting beside it. For a collector, this introduces a severe preservation trap: **high-odometer cels possess an elevated hidden baseline and will try to fall back into Regime 2 runaway much faster than fresh cels**, requiring entirely different preservation levers

### *Scenario 3: The Dehumidification Intervention*

**Conditions:** Realizing that the high-odometer Cel B is running too fast at room temperature, a collector initiates an intentional climate mitigation by moving Cel B into a dry microenvironment set to a strict 40% RH ( $a_w = 0.40$ ).

**Calculation:** The relative velocity of this mitigated cel is compared back to the fresh reference standard from Scenario 1:

$$\frac{R_{1,B, \text{mitigated}}}{R_{1,A, \text{baseline}}} = \frac{0.4 \cdot 2.00}{0.525} = 1.52x$$

**Field Outcome:** Restricting the relative humidity successfully chokes the reaction's fuel supply, dropping the generation penalty down from 1.90x to 1.52x. However, room-temperature dehumidification alone is mathematically incapable of neutralizing the structural risk. While you can alter the ambient water activity ( $a_w$ ), you cannot alter the physical size of the internal sponge ( $H$ ). To find the exact relative humidity required to bring

this degraded cel into true aging parity (1x) with the fresh cel at room temperature, we solve the mass conservation ratio for  $a_{w,B}$ :

$$a_{w,B} = \frac{H_A}{H_B} = \frac{0.50 \cdot 1.05}{2.00} = 0.2625$$

Maintaining an animation cel at a sustained 26% RH at room temperature is an archival challenge; it can desiccate, embrittle, and fracture the applied paint layers and binders. This supports that standard consumer dehumidification lines are operationally insufficient to safeguard degraded cels. To pull a high-odometer cel below the decay velocity of a fresh piece, a collector must drop the final remaining variable in our mass equation—the thermal kinetic multiplier ( $R_0$ )—making deep archival cold storage an absolute structural mandate to maintain nominal deacetylation rate for survivors.

#### *Scenario 4: The Combined Thermal-Hygroscopic Intervention (The Preservation Runway)*

**Conditions:** Realizing from Scenario 3 that dehumidification alone cannot force a heavily degraded piece down to a safe aging velocity, the collector implements a combined environmental intervention. The degraded Cel B ( $D_B = 0.50\%$ ,  $H_B = 2.00$ ) is maintained inside a dry microenvironment at 40% RH ( $a_w = 0.40$ ), but the storage temperature is systematically lowered across four benchmark testing tiers: 70 degF, 65 degF, 60 degF, and 55 degF.

**Calculation:** To isolate the exact preservation benefit of adding thermal control, we reintroduce the Arrhenius temperature correction multiplier ( $R_0$ ) into our mass conservation ratio. The net decay velocity for the cooled, degraded piece is calculated continuously against our fixed standard reference from Scenario 1—a fresh Cel A ( $D_A = 0.025\%$ ,  $H_A = 1.05$ ) sitting unmanaged at 70 degF and 50% RH ( $a_w = 0.50$ , baseline value = 0.525):

Comparative Velocity Ratio =

$$\frac{R_0(T) \cdot H_B}{R_0(\text{baseline}) \cdot H_A} = \frac{1 \cdot 0.40 \cdot 2.00}{0.525} = 1.52x$$

By substituting the validated Arrhenius thermal multipliers (1.00x at 70 degF, 0.664x at 65 degF, 0.438x at 60 degF, and 0.286x at 55degF), the structural matrix yields the following performance values:

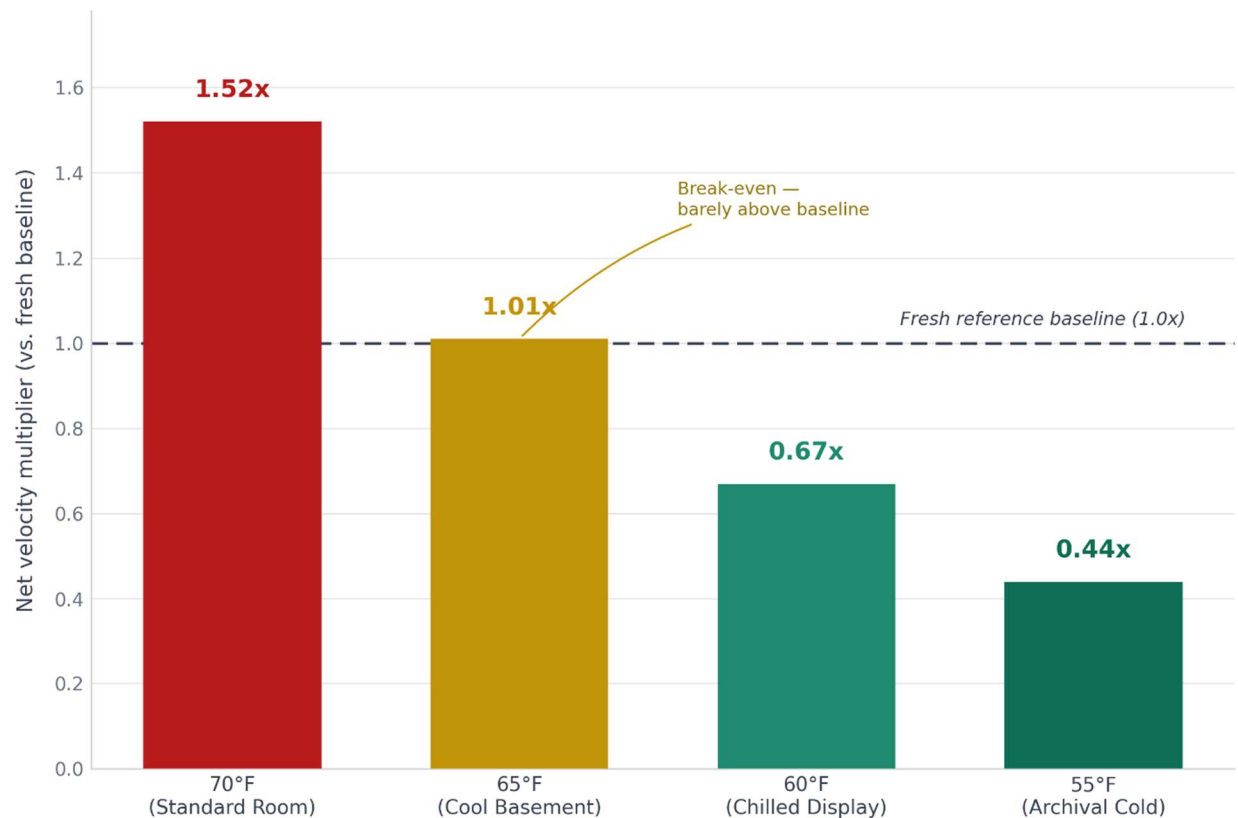
Table 6: Thermal Intervention Results for a Degraded Cel (D = 0.50%, 40% RH)

| Storage Temperature(at 40% RH) | Thermal Multiplier R0(T) | Absolute Generation Value(R0·aw ·H) | Net Velocity Multiplier(vs. Fresh Room-Temp Baseline) | Engineering & Archival Reality                                                                                                                                                                                   |
|--------------------------------|--------------------------|-------------------------------------|-------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 70 degF (Standard Room)        | 1.00x                    | 1 * 0.4 * 2 = 0.8                   | <b>1.52x penalty</b>                                  | <b>Room Temperature Defeated.</b> Even with low moisture fuel, the large physical size of the internal sponge dominates the reaction. The cel ages 52% faster than a fresh piece.                                |
| 65 degF (Cool Basement)        | ≈ 0.664x                 | 0.664 * 0.4 * 2 = 0.5312            | <b>1.01x penalty</b>                                  | <b>The High-Odometer Boundary.</b> Dropping the ambient room temperature by 5 degF dramatically cuts kinetic energy, bringing the cel within striking distance of parity with a fresh room-temperature baseline. |
| 60 degF (Chilled Display)      | 0.438x                   | 0.438 * 0.4 * 2 = 0.35              | <b>0.67x benefit</b>                                  | <b>The Break-Even Threshold.</b> Halving the thermal rate completely neutralizes the structural damage penalty. The cel finally ages <b>23% slower</b> than a fresh production                                   |



|                                 |                  |                           |                      |                                                                                                                                                                                                                                     |
|---------------------------------|------------------|---------------------------|----------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                 |                  |                           |                      | piece sitting in a standard room.                                                                                                                                                                                                   |
| 55 degF<br>(Archival Cold Room) | $\approx 0.286x$ | $0.286 * 0.4 * 2 = 0.229$ | <b>0.44x benefit</b> | <b>Active Preservation.</b><br>Crushing the absolute kinetic energy allows the system to run at a heavily suppressed velocity. The remaining chemical runway is effectively doubled, buying decades of absolute physical stability. |

**Field Outcome:** This progressive stress test reveals the absolute power of thermal levers in material preservation. Because a high-odometer cel suffers from an irreversible structural shift, you are physically incapable of shrinking its expanded chemical moisture capacity. However, by lowering the ambient storage temperature, you apply a structural restrictor plate to the entire kinetic engine.



Degraded cel ( $D = 0.50\%$ ), dehumidified to 40% RH — 1.52x anchor from the dehumidification scenario. Thermal multipliers computed at  $E_a = 105$  kJ/mol.

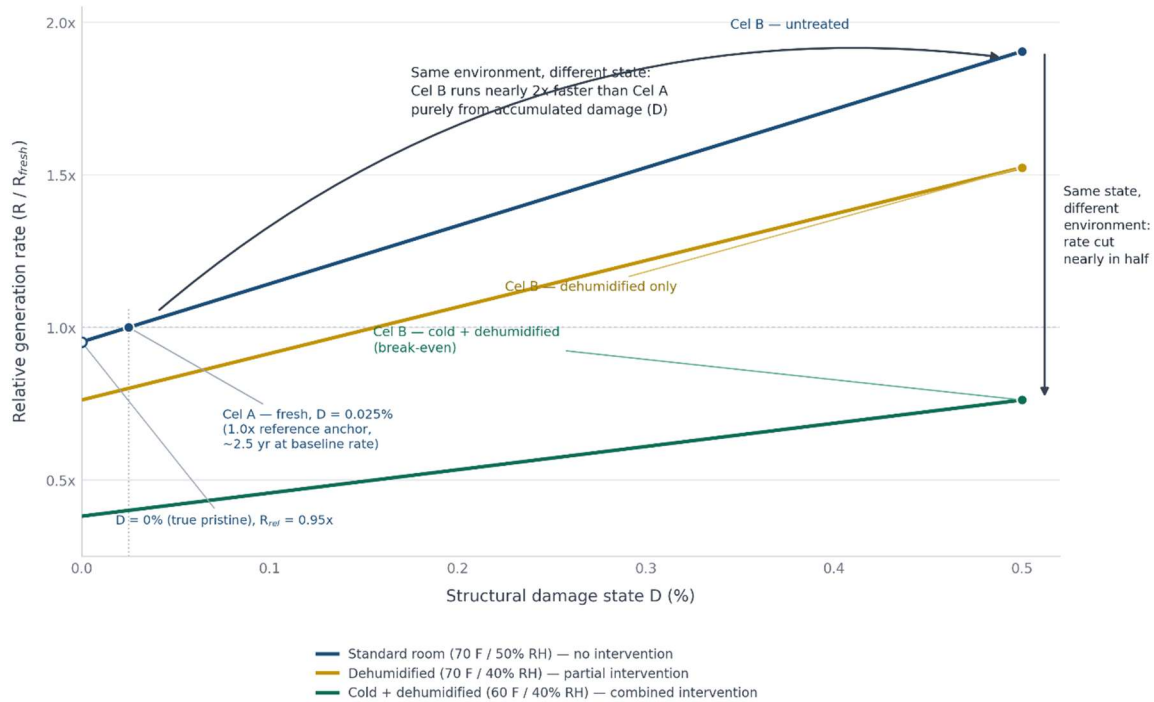
Figure 5: Net Velocity Multiplier for a Degraded Cel Under Thermal and Humidity Intervention

When combining a strict 40% RH microclimate with a chilled 60 degF environment, the system crosses its critical break-even threshold. At this junction, the thermal velocity drop overpowers the material's structural wear, compressing the active deacetylation rate below that of a brand-new cel and is supportive of why temperature control is the ultimate baseline safety mandate for highly vulnerable collections.

## Redefining Vinegar Syndrome: An Operational Phase Change

For decades, the term "Vinegar Syndrome" has been treated by the collecting community as a terrifying, binary death sentence—a sudden terminal illness that marks the immediate end of an artwork's lifecycle. Materials science reveals a far more manageable reality.

Vinegar Syndrome is not the death of a cel; it is simply a predictable **thermodynamic phase change**.



$R_{ref}(D) = a_{ref} \cdot (1 + \kappa D) / [a_{ref,ref} \cdot (1 + \kappa D_{ref})]$ ,  $\kappa = 2.0$ , normalized to  $D_{ref} = 0.025\%$  (Scenario 1 anchor). Reproduces Scenarios 1-4 exactly: 1.00x, 1.90x, 1.52x, 0.76x. Domain capped at  $D = 0.5\%$  (model val

Figure 6: Rate vs. State — Isolating the Effects of Structural Damage and Environment

When a substrate crosses the critical 0.5% deacetylation threshold, the reaction ceases to be a slow, linear erosion process (Regime 1) and transitions into a self-accelerating, non-linear chain reaction (Regime 2). The material has fundamentally rewritten its own internal rules, transforming from an uncatalyzed system into an autocatalytic loop.

Crossing this threshold does not mean the cel is lost; it means **the available preservation control levers have permanently changed**.

- In **Regime 1 (Pre-Brink)**, the material's internal engine is idling. Passive room-temperature climate management and standard humidity reductions are completely sufficient to maintain a long stability runway.
- In **Regime 2 (Post-Brink)**, the internal engine is actively redlining. Because the physical size of the internal chemical sponge has expanded, standard consumer dehumidification and room-temperature air filtration are mathematically incapable of stopping the runaway loop.

To salvage a survivor that has transitioned into Regime 2, passive monitoring must be completely abandoned in favor of aggressive **kinetic suppression**. Because you cannot shrink the permanent internal sponge, you are forced to change the final remaining variable in the mass balance equation: the absolute thermal kinetic multiplier ( $R_0$ ). By executing a systematic drop in temperature—moving the asset into dedicated cold or sub-freezing storage environments—you apply a structural restrictor plate to the reaction kinetics.

*Vinegar Syndrome doesn't mean game over; it simply dictates that the artwork has officially graduated out of basic household display conditions and now mandates deep thermal control to safely lock its operational clock in place.*

## References

- Ahmad, I. R., Cane, D., Townsend, J. H., Triana, C., Mazzei, L., & Curran, K. (2019). Are we overestimating the permanence of cellulose triacetate cinematographic films? A mathematical model for the vinegar syndrome. *Polymer Degradation and Stability*, 172, 109050. <https://doi.org/10.1016/j.polymdegradstab.2019.109050>
- Hackney, S. (2016). Colour measurement of acid-detector strips for the quantification of volatile organic acids in storage conditions. *Studies in Conservation*, 61(sup1), 55–69. <https://doi.org/10.1080/00393630.2016.1140935>
- Reilly, J. M. (1993). *IPI Storage Guide for Acetate Film*. Image Permanence Institute, Rochester Institute of Technology.
- Adelstein, P. Z., Reilly, J. M., Nishimura, D. W., & Erbland, C. J. (1995). Stability of cellulose ester base photographic film: Part V — recent findings. *SMPTE Journal*, 104, 439–447.
- Barbagallo, R. (1995). Mickey, Donald, Goofy & Pluto — What's Breaking Up That Old Gang of Mine? *Topics in Photographic Preservation*, 6, Article 6 (pp. 98–105). American Institute for Conservation.

*Note: this list reflects the principal sources informing the framework's calibration anchors and is not exhaustive. Readers seeking the complete accelerated-aging dataset underlying the IPI storage guidelines should consult the full Adelstein, Reilly, Nishimura, and Erbland "Stability of Cellulose Ester Base Photographic Film" series (Parts I–VI), published in the SMPTE Journal between 1992 and 2002.*