CHEMICAL ENGINEERING TRANSACTIONS

VOL. 117, 2025

A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Fabrizio Bezzo, Flavio Manenti, Gabriele Pannocchia, Almerinda di Benedetto

ISBN 979-12-81206-17-5; **ISSN** 2283-9216

DOI: 10.3303/CET25117138

Kinetics of Aluminum and PVC Separation from Pharmaceutical Blisters Using Spent Galvanic Pickling Liquors

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Pharmaceutical ampoules known as blisters are single-use packaging materials. These materials are widely distributed but inefficiently disposed of, as only the manufacturing companies are legally required to ensure proper disposal. This study proposes a process to separate aluminum and PVC from blisters originating from a pharmaceutical company through dissolution in spent pickling solutions from the galvanic industry. Experimental tests yielded sigmoidal-shaped curves, which were fitted to a kinetic model with an R^2 correlation factor in the range of 0.95–0.98. The obtained parameters were used to thermally simulate the separation process of PVC and aluminum using COMSOL Multiphysics software. The model was experimentally validated using a 300 mL reactor. The proposed process will generate a positive environmental impact, providing an alternative to recycle PVC from blisters for additional uses and utilizing waste from the galvanic industry to produce a product with potential use as a coagulant, such as aluminum chloride.

1. Introduction

Pharmaceutical ampoules are produced through thermoforming or cold-forming processes and consist of four main components: formed film, heat-sealing coating, sealing lid, and printing inks. This type of medication packaging offers several advantages over other forms of packaging: it is economical, provides good product protection against moisture, is easier to use, and better preserves the product compared to other containers like jars (Agarwal et al., 2020).

The global cost of pharmaceutical packaging materials increased from \$47.8 billion to \$71 billion in 2018, and it is estimated to reach \$149.3 billion by 2026, with an annual growth rate of 6–8% between 2019 and 2029 (Brooks, 2019). The growing use of these materials has led to a 4% increase in daily waste compared to the volume of packaging material generated (Pilchik, 2000). Various methodologies and processes have been proposed in the literature to recycle this material (Çapkın & Gökelma, 2023; Shukla et al., 2022). However, conventional recycling of blisters cannot be carried out effectively due to difficulties in separating their layers and the toxic vapors emitted during incineration processes used for other polymeric wastes. As a result, tons of waste end up buried in landfills or secure landfills, generating future environmental liabilities.

2. Recycling of Blisters

Blister sheets are primarily made of PVC (polyvinyl chloride), but they can also be manufactured from other polymers such as PP (polypropylene), HIPS (high-impact polystyrene), and PET (polyethylene terephthalate). PVC offers superior properties, including low gas and vapor permeability, thermal stability, printability, and relatively low cost, among others (Yaren Çapkın & Gökelma, 2023). The thickness of the PVC sheet is approximately 250 microns, and for improved performance, a thinner PVDC (polyvinylidene chloride) film of 20–50 microns is sometimes applied, reducing gas permeability by a factor of 5–10 (Haiying Liu, 1999). The lid material is typically aluminum, as it is completely impermeable and mechanically stable. The aluminum film has

Paper Received: 13 December 2024; Revised: 12 March 2025; Accepted: 4 May 2025
Please cite this article as: Suarez O.J., Leon-Molina H.B., 2025, Kinetics of Aluminum and Pvc Separation from Pharmaceutical Blisters Using Spent Galvanic Pickling Liquors, Chemical Engineering Transactions, 117, 823-828 DOI:10.3303/CET25117138

a thickness of 20–25 microns. Its thickness and malleability allow the end user to easily extract the medication from the package. Generally, blister packs consist of 80–85% PVC and 10–20% aluminum.

Despite the advantages of recycling, only a small percentage of PVC derived from blisters is recycled globally due to its structural complexity. These materials are often incinerated or directly disposed of in landfills as solid waste, especially in developing countries (Sadat-Shojai & Bakhshandeh, 2011). The incineration of this material can produce toxic gases such as dioxins and hydrogen chloride, among others (Agarwal et al., 2020). Additionally, if incinerated with other materials, it becomes impossible to recover aluminum, removing it from the circular economy value chain. The separation and recycling of this residual material from the pharmaceutical industry has gained attention in recent years due to the cost and environmental impact of discarded materials. Recycling efforts focus on zero-waste strategies (Zaman & Lehmann, 2013).

2.1 Methods for Separating PVC from Blisters

Given the multilayer composition of these materials, separating their components is essential for effective recovery. The literature highlights three main methodologies for this separation: hydrometallurgical methods, thermal degradation, and mechanical separation.

Hydrometallurgical Separation

Hydrometallurgical methods are the most employed techniques for separating aluminum from PVC in blister waste. Çapkın et al. (Çapkın & Gökelma, 2023) investigated various organic and inorganic acids, as well as solvent mixtures, for material separation. Experiments were conducted at 20, 40, and 60°C with magnetic stirring. It was found that using hydrochloric acid, the average metal dissolution time was approximately 4 hours, while sulfuric acid required up to a week. In the case of solvent mixtures, Shukla et al. (Shukla et al., 2022) utilized acetone and isopropanol combinations with magnetic stirring for 60–120 minutes, successfully separating the metal from the plastic in all cases except with pure ethanol. Reported aluminum recovery rates ranged between 80% and 94%. Wang et al. (Chongging et al., 2015) applied 1.25 M sodium hydroxide solutions at 70°C for 20 minutes, achieving nearly 100% separation efficiency. Sodium hydroxide concentration and temperature were identified as critical factors for recovery.

Thermal Degradation

The incineration of PVC in blisters, along with other waste, can release hazardous pollutants such as nitrous oxide, hydrochloric acid aerosols, and dioxins. Consequently, the incineration of such materials has been restricted in some European countries (Shukla et al., 2022). Klejnowska et al. (Klejnowska et al., 2020) conducted thermal degradation experiments at 400–450°C, producing gases with a calorific value of approximately 20 MJ/m³. Pikon et al. (Pikoń et al., 2021) separated carbonaceous material from metallic material with aluminum recovery efficiencies of 85–90%. The calorific value of the produced gas was estimated at 32 kJ/kg.

Mechanical Separation

Gente et al. (Gente et al., 2003) performed separation processes using cryo-milling followed by electrostatic separation of the metallic fraction. Results indicated approximately 90% separation efficiency for both the metallic and polymeric fractions. However, residual contamination between phases necessitated further refinement. Agarwal et al. (Agarwal et al., 2020) introduced an electrohydraulic separation process, where high-voltage pulses (100–180 kV) at 2–5 Hz were propagated through a liquid medium. The resulting shock wave broke the blister into small fragments, which were subsequently separated by sieving and density differences in zinc chloride solutions. Aluminum recovery percentages ranged from 30% to 70%, depending on the conditions.

Although no single method currently provides a fully satisfactory solution, each has specific advantages and drawbacks that must be considered for different use cases. This study explored the use of waste from the galvanic industry, which contains a high concentration of free hydrochloric acid, as a dissolution agent for extracting aluminum from blisters.

3. Experimental Procedure

The separation procedure involved introducing approximately 0.100 g of blister material into 10.0 mL of an acidic solution. The acidic mixture consisted of spent pickling solution (SS), water, and 37% w/w hydrochloric acid (Sigma Aldrich) in varying proportions, as detailed in Table 1. The pickling solution, characterized by ITYM LTDA company (Colombia), exhibited a free acidity of 1.30 mol/L, a density of 1.27 g/cm³, and a total iron concentration of around 2.8 mol/L, with approximately 14% attributed to Fe^{3+} ions.

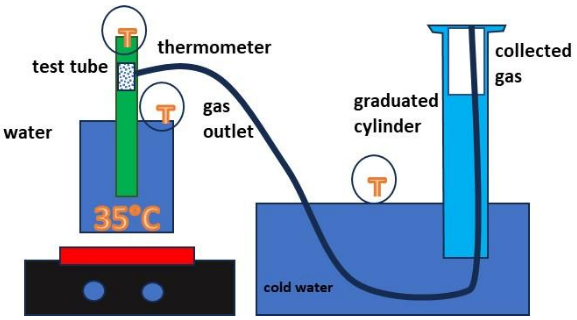

Figure 1: Experimental Setup for Determining the Dissolution Kinetics of Aluminum.

Table 1: Composition of Acidic Mixtures Used for Aluminum Dissolution from Blisters

Solution	SS (% vol)	Water (% vol)	Hydrochloric acid (%vol)	[HCl] calculated	[Fe+3] calculated
1	100	0	0	1.32	0.39
2	80	10	10	1.98	0.31
3	60	20	20	2.65	0.23
4	40	30	30	3.31	0.16
5 (Fe^{3+} depleted)	100	0	0	0.92	0.0

The dissolution process occurs through the following reactions:
Main Reaction:

$$Al_{(s)} + 3\ HCl_{(aq)} \Rightarrow AlCl_{3(aq)} + 1{,}5\ H_{2(g)}\ (\Delta H=-428\ kJ/mol) \quad (1)$$

Secondary Reaction:

$$3\ Fe^{3+} + Al_{(s)} + 3\ Cl^{-} \Rightarrow 3\ Fe^{2+} + AlCl_{3(aq)}\ (\Delta H=-460\ kJ/mol) \quad (2)$$

A test tube with a gas outlet was used as the reactor, which was heated in a water bath at 35°C. The reaction kinetics were evaluated by measuring the volume of gas generated, which was bubbled into a graduated cylinder, as shown in Figure 1. The temperature during the reaction was monitored by inserting a thermometer into the reactor.

3.1 Simulation and Validation

The operation of a pilot process for the separation of PVC and aluminum was modeled using COMSOL Multiphysics software. The process included a 300 mL semi-batch reactor loaded with Solution 2, to which eight batches of 6.3 g of blister material were added. The model was developed using the kinetic parameters obtained, along with thermodynamic data from external sources. The heat transfer coefficient, U, was calculated to be 20 W/(m² K) at an external temperature of 293 K. The simulation data were subsequently validated using a reactor of the same capacity, where the external temperature was recorded using a thermocouple and a data logger.

4. Results

Figure 2 presents the reaction monitoring curves: (a) gas volume collected versus time and (b) temperature versus time for each of the solutions used. It has been reported that several phenomena exhibit sigmoidal (S-shaped) kinetic curves, as seen in Figure 2a. These phenomena include the formation of transition metal nanoclusters, solid-state phase transformations, plant growth, and bacterial growth, among others (Bentea et al., 2017).

The dissolution of aluminum in hydrochloric acid is characterized by an induction period (a slow initial phase), followed by a rapid increase in the heat production rate (Kitabayashi et al., 2016). Initially, the dissolution process involves breaking down the surface oxide passivation layer:

$$Al_2O_3{\cdot}nH2O_{(s)} + 6\ HCl_{(aq)} \Rightarrow 2AlCl_{3(aq)} + (3+n)\ H_2O_{(l)} \quad (3)$$

Although the surface reaction is exothermic, it does not significantly contribute to the system's temperature increase due to its slow reaction rate. Once the surface layer is removed, the underlying solid aluminum reacts directly with HCl(aq) or Fe^{3}+ ions, as described in reactions (1) and (2), producing a significant exothermic effect, as observed in Figure 2b.

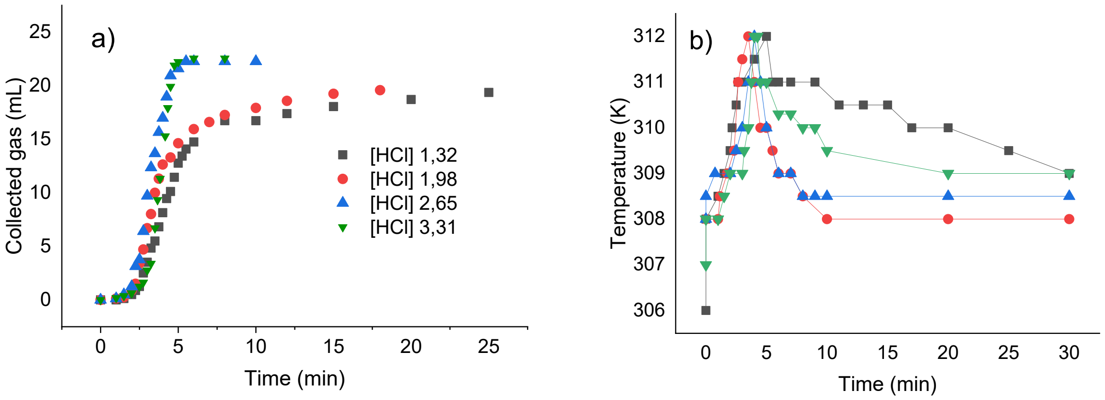

Figure 2: Monitoring of Aluminum Dissolution Reaction in Acidic Solutions a: Gas Volume Collected; b: Reaction Temperature

Bentea et al. (2017) proposed a kinetic model to explain the formation of Ir(0)$_n$ nanoclusters. The model consists of slow and continuous nucleation (A → B) with a rate constant k_1, followed by rapid autocatalytic growth (A + B → 2B), with a rate constant k_2. This approach is known as the two-step Finke-Watzky (F-W) model. The kinetic model uses the concept of two pseudo-elementary steps, allowing the quantitative determination of average rate constants for both the nucleation and autocatalytic or growth stages.

In our case, an adaptation of the model was performed, considering the following equation:

$$-(\frac{\rho_{Al}\cdot\varepsilon}{A_{Al}})\frac{d[Al]_{sup}}{dt} = 1.5\frac{d[H_2]}{dt} + 3\frac{d[Fe^{2+}]}{dt} \qquad (4)$$

Where -d[Al]$_{(sup)}$/dt represents the dissolution rate of aluminum, ρ, ε and A_{Al} are the density, thickness and atomic weight of the aluminum film, respectively, dH_2/dt represents the hydrogen production rate, and dFe^{2+}/dt represents the production rate of Fe^{2+} ions. In our adaptation of the model, it is proposed:

$$\frac{d[H_2]}{dt} = \left[k_1(\frac{\rho_{Al}\cdot\varepsilon}{A_{Al}})[Al]_{sup} + k_2(\rho_{Al}\cdot\varepsilon)[Al]_{sup}[AlCl_3]\right]A_o \qquad (5)$$

Where $[Al]_{sup}$ is the surface concentration of aluminum inside the reactor (cm²/L), $[AlCl_3]$ is the molar concentration of aluminum chloride, and A_o is the fraction of aluminum consumed by the reaction with hydrochloric acid. From the adjustment of the experimental data, a dependency was observed between k_2 and the HCl concentration, as well as between A_o and the Fe^{3+} concentration. Figure 3 shows the values of k_2 and A_o for each solution. Table 2 presents the regression parameters obtained for the adjustment of the adapted F-W model data.

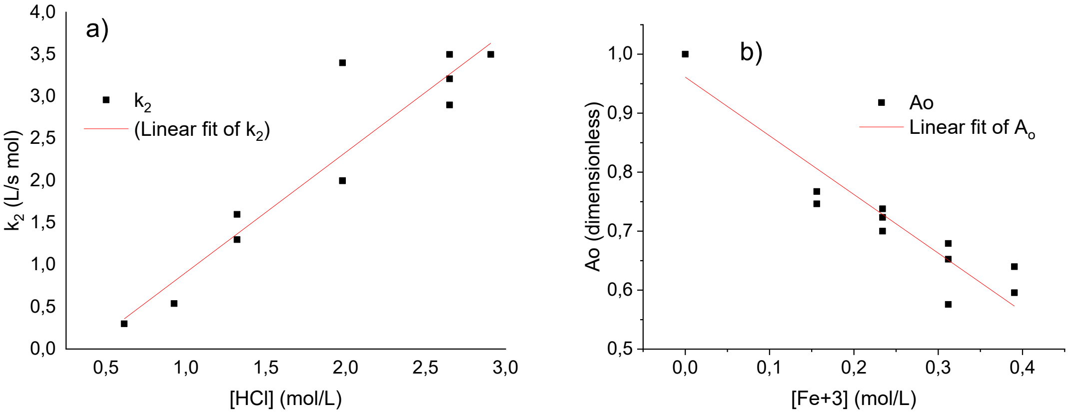

Figure 3: Kinetic Parameters of the F-W Model Adjusted to the Aluminum Dissolution Reaction in Acidic Mixtures a: k_2 vs. Hydrochloric Acid Concentration; b: A_o vs. Fe^{3+} Ion Concentration

Table 2: Parameters of the Adapted F-W Model to aluminum dissolution

Parameter	Equation	a	b	R^2
k_1	constant	0.014±0.007	---	
k_2	y=ax + b	1.427±0.18	-0.518±0.36	0.864
A_o	y=ax + b	-0.994±0.11	0.961±0.0.3	0.891

In Figure 4a, the hydrogen production obtained during the reaction with Solution 2 is presented alongside the curve calculated using the adapted F-W model. A good fit was achieved, with a correlation coefficient of R^2 = 0.95. Table 3 presents the R^2 values for the four solutions used, all around 0.95, indicating a strong fit of the model under the applied conditions.

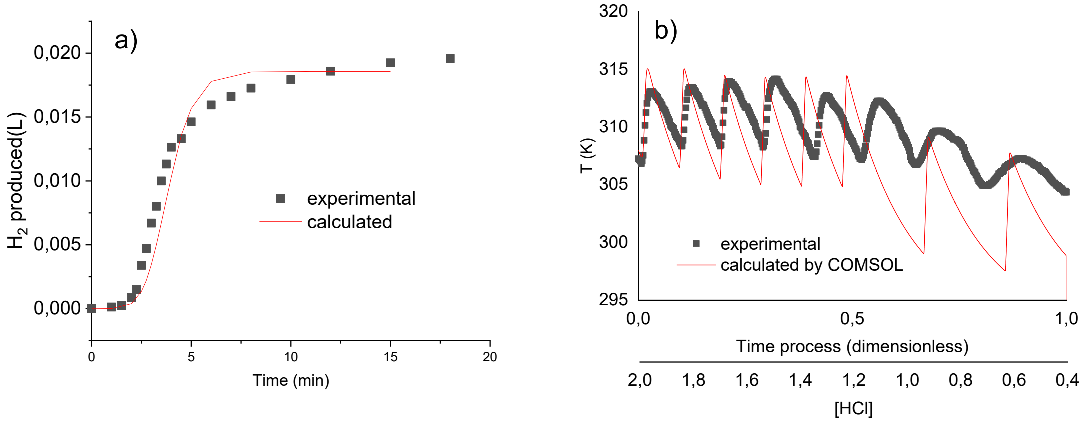

Figure 4: a: Hydrogen Production: Comparison of Calculated and Experimental Data for Aluminum Dissolution Using Solution 2 b: Temperature Profile of a 300 mL Pilot Reactor: Experimental vs. Calculated Data.

Table 3: Adjustment of the Adapted F-W Model for Each Solution.

Solution	1	2	3	4
R^2	0.94	0.95	0.98	0.97

In Figure 4b, the results of the COMSOL simulation are presented. A good agreement is observed between the experimental and calculated data, particularly during the first five reactor batches, where the difference between the experimental and calculated temperatures is approximately 2 K. For the final three batches, the maximum calculated temperature is like the experimental value. However, the temperature increase in the actual reactor is smaller than the model's prediction. These results suggest that the kinetics align well with hydrochloric acid concentrations above 1.2 M, but adjustments are required for lower concentrations.

5. Conclusions

Experiments were conducted to study the dissolution process of aluminum from pharmaceutical blisters in acidic solutions derived from the galvanic industry. The reaction exhibited a sigmoidal curve, which was modeled using an adaptation of the Finke-Watzky (F-W) model for reactions involving an induction period followed by an increase in reaction rate. The kinetic parameters were found to be linearly dependent on the concentrations of hydrochloric acid and Fe^{3+} ions. Using these parameters, the kinetics of hydrogen production were modeled and compared with experimental data, yielding R^2 values between 0.94 and 0.98 for the four solutions. The thermal behavior of a 300 mL pilot reactor was modeled using COMSOL Multiphysics, showing good agreement for hydrochloric acid concentrations above 1.2 M. Adjustments to the model are required for lower concentrations.

Nomenclature

a – Slope of the linear regression
A_o - Dimensionless kinetic parameter
A_{Al} – Atomic weight, g/mol
k_2 – Kinetic parameter, L/ mol min
$[Al]_{sup}$ - Aluminum concentration, cm^2/L
$[AlCl_3]$ - Aluminum chloride concentration, mol/L

b – Intercept of the linear regression
k_1 – Kinetic constant, 1/min

U – Heat transfer coefficient, $W/(m^2\ K)$
ρ - density, g/cm^3
ε – Film thickness, cm

Acknowledgments

Agencia Atenea and their Call for Proposals: ECOCAMBIO-BOGOTA EJEMPLO GLOBAL DE SOSTENIBILIDAD, Universidad ECCI and ITYM LTDA company.

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