

Article

Microchannel Design Facilitates Efficient Tannin–Germanium Deposition

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Abstract

To address the core industrial bottlenecks of conventional batch tannic acid-based germanium precipitation processes—high reagent consumption, long reaction cycles of several hours, severe impurity co-precipitation as well as the common mismatch between single-channel microreactor throughput and industrial production demands. This work combines numerical simulation with experimental validation to investigate microscale two-phase flow regulation, high-throughput microreactor optimization, and tannic acid precipitation intensification. Two-dimensional two-phase flow models are established for straight and zigzag microchannels, with the level set method applied to track interfacial evolution. The regulatory effects of inlet velocity and channel geometry on flow patterns, droplet behavior and mixing performance are clarified. Zigzag channels induce chaotic convection via periodic corners, achieving an order-of-magnitude improvement in mixing efficiency at low Reynolds numbers ($Re < 400$), which lays a fundamental basis for reaction intensification. Taking zigzag channels as core units, a bidirectional symmetric superposition scale-up strategy is proposed to break the throughput limitation of single-channel systems, and a 3D-printed high-throughput microreactor integrating 78 parallel zigzag channels is designed. 3D simulations reveal a three-stage mixing mechanism and uniform flow distribution among parallel channels, with total throughput two orders of magnitude higher than a single channel. Single-channel experiments with industrial germanium-bearing raffinate yield 91.81% precipitation efficiency under optimal conditions, reducing the reaction residence time from hours in conventional batch processes to the second scale. Staged reagent addition and two-stage serial configuration further raise the efficiency to ~98%, realizing deep germanium recovery with significantly improved reagent utilization and reduced impurity co-precipitation. This process achieves efficient intensification of the chelation precipitation process while balancing throughput and mixing performance, providing a novel and technically feasible approach for efficient low-consumption germanium recovery, and offering solid technical support for the industrial application of microreactors in the hydrometallurgy field.



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1. Introduction

Germanium is a critical dispersed strategic metal that underpins the development of high-technology fields including 5G communications, infrared detection, solar cells, and optical-fiber communications [1]. Currently, approximately 70% of global germanium production is derived from the comprehensive recovery of by-products generated during lead-zinc smelting, with hydrometallurgical enrichment routes as the predominant technical approach. The primary processes include the tannic acid complexation precipitation method, solvent extraction, ion exchange, sulfide precipitation, and iron salt co-precipitation, among others [2]. Among these processes, solvent extraction exhibits high processing capacity and facilitates easy continuous operation, yet it is constrained by high extractant costs, along with inherent risks of volatilization loss and organic phase entrainment. Ion exchange features straightforward operation and regenerable, recyclable resin, but is limited by its finite adsorption capacity and susceptibility to interference from impurity ions such as iron and arsenic. Sulfide precipitation and iron-salt co-precipitation are low-cost routes; however, their poor selectivity and considerable difficulty in downstream purification have resulted in their gradual displacement by mainstream processes. By contrast, the tannic acid complexation precipitation method represents the most widely adopted hydrometallurgical germanium extraction technology in industrial practice, attributed to its simple process flow and favorable selectivity [3]. Drzazga et al. [4] investigated the process for the selective precipitation of germanium from tin- and indium-bearing sulfate solutions using tannic acid. It was demonstrated that at a reaction temperature of 90 °C, the adoption of pure tannic acid in powder form for 90 min or as a 20% solution for 5 min achieved a germanium precipitation efficiency exceeding 99%, and reduced the residual germanium concentration in the liquor to below 0.015 g/dm³. However, conventional stirred tank reactors (STRs) rely on macroscopic turbulence to achieve reactant mixing, and the time scale for molecular-scale homogeneous dispersion is on the order of minutes, far exceeding the intrinsic kinetic timescale of the complexation reaction between tannic acid and Ge⁴⁺. This kinetic mismatch necessitates an excessive tannic acid dosage equivalent to 25–35 times the mass of germanium in industrial practice to ensure satisfactory recovery efficiency, giving rise to prominent drawbacks including high reagent consumption, prolonged reaction duration, and severe co-precipitation of impurity ions. These issues not only substantially elevate reagent costs and reduce the purity of downstream germanium concentrate, but also restrict the continuous and automated upgrading of the production process, ultimately constraining the green and efficient development of the germanium recovery industry. Therefore, developing an intensified process that simultaneously achieves high recovery efficiency, low reagent consumption and continuous stable operation is an urgent demand for industrial germanium recovery [5–7].

The timescale mismatch between macroscopic mixing and intrinsic complexation reactions is the root cause of excessive reagent dosage and severe co-precipitation of impurity ions. Against this backdrop, microscale reaction systems represented by microchannel reactors (MCRs) have emerged as an effective technical solution to overcome the performance limitations of conventional STRs. As a revolutionary technology in the field of process intensification, microreactor technology is endowed with an ultra-high specific surface area, extremely short mass-transfer distance, and precise fluid controllability at the micrometer scale, providing a novel paradigm for the intensification of multiphase reaction processes. Having been widely industrialized in sectors including fine-chemical synthesis, continuous pharmaceutical manufacturing, and energy catalytic conversion, microreactor technology, leveraging its superior microscale mass-transfer enhancement and precise process-regulation capabilities, also opens up a new technical avenue for the efficient, low-consumption recovery of dispersed metals in hydrometallurgical systems [8–10].

The process intensification performance of microreactor technology essentially stems from the microscale effects within micrometer-scale channels, while the geometric structure of microchannels serves as the core factor that directly governs the flow field distribution, mixing and mass-transfer efficiency, and reaction performance. Accordingly, optimal structural design of microchannels and systematic investigation of flow mechanisms tailored to specific reaction systems constitute a critical prerequisite for the efficient development of microreactor-based processes [11,12]. Existing microchannel configurations encompass a diverse array of structural forms, including straight reference structures, planar bent structures, three-dimensional spatial structures, and built-in obstacle structures. Among the numerous microchannel geometries, straight microchannels feature simple geometry and stable flow characteristics, serving as the benchmark model for investigating microscale two-phase flow and mass-transfer mechanisms [13,14]. By contrast, zigzag microchannels induce secondary flow and vortex structures via their periodic bends, achieving pronounced mixing intensification under low-Reynolds-number laminar flow regimes. Widely validated as an ideal configuration for the intensification of fast reaction processes, zigzag microchannels constitute the most commonly adopted functional unit configuration in industrial microreactor systems [15,16]. Nevertheless, a long-standing bottleneck restricting the industrial application of microchannel reactors is the inherent trade-off between mixing intensification and processing throughput. The former cannot satisfy the mixing demands of fast reactions, whereas the latter, despite achieving favorable reaction performance, is incapable of supporting large-scale processing throughput [17,18]. Parallel scale-up through multi-channel arrays is a theoretical solution to the throughput shortfall; however, conventional manufacturing techniques face significant challenges in the low-cost, high-precision monolithic fabrication of arrays with complex bent channels. Machining tolerances and assembly misalignments typically induce severe flow maldistribution across parallel channels, which ultimately causes a substantial deterioration in the performance of scaled-up systems [19,20]. Against this backdrop, the inherent monolithic forming advantage of 3D printing technology opens up new avenues to alleviate this predicament. It enables not only the accurate replication of the intensification structures in zigzag channels but also the simultaneous integration of symmetric fluid distributors. While retaining the microscale mass-transfer superiority, this technology achieves linear scaling of processing throughput along with stable and controllable flow distribution, thus providing critical technical support for the engineering scale-up of microreactors [21–23]. Microchannel reactors have been widely recognized as a powerful platform for process intensification of mixing and reaction systems. Benefiting from the characteristic microscale flow dimensions, fluids in microchannels exhibit unique flow and mixing behaviors that differ significantly from macroscopic stirred systems. Microchannel reactors have been widely recognized as a powerful platform for process intensification of mixing and rapid reaction systems. As summarized by Wojnicki et al. [24], fluid flow in micro-geometries is typically dominated by the laminar regime, and pure molecular diffusion is insufficient for efficient mixing. Therefore, various passive intensification strategies, including periodic wall perturbation, split-recombination structures and droplet-based microfluidics, have been developed to induce chaotic advection and shorten the mass-transfer distance, realizing efficient mixing at a millisecond timescale without extra energy input. Built on this theoretical foundation, this work adopts a serrated single-channel structure to intensify the micromixing process of tannic acid and germanium-containing leachate, so as to achieve precise control of the complex precipitation process.

In this study, numerical simulations based on the finite element method (FEM) are performed to systematically investigate the flow-pattern evolution characteristics and mixing intensification mechanism of liquid–liquid two-phase flow in single straight and

zigzag microchannels. On this basis, a high-throughput microreactor integrating 78 parallel zigzag channels is designed and fabricated via 3D printing technology, and its internal flow distribution uniformity, mixing characteristics and flow distribution behavior are analyzed in detail. Finally, experimental validation is conducted using industrial germanium-bearing raffinate as the feed solution, and the effects of key process parameters on germanium precipitation efficiency are explored. This work systematically addresses the two core bottlenecks of insufficient mixing in single channels and difficulty in high-throughput scale-up, and verifies the technical feasibility of the process with actual industrial feedstock. The findings provide a solid theoretical foundation and technical support for the large-scale industrial application of microreactor technology in the field of scattered metal recovery.

2. Methodology

2.1. Numerical Simulation Methods

2.1.1. Two-Phase Flow Simulation in Single Microchannel

(1) Governing Equations

The laminar two-phase flow module was adopted for numerical computation. The governing equations consist of the coupled Navier–Stokes equations, continuity equation, and level-set equation, which are tightly integrated via the velocity field and phase-interface function. The level-set method was employed to capture the spatiotemporal evolution of the liquid–liquid two-phase interface. A reinitialization technique was applied to preserve the signed-distance property of the level-set function in the vicinity of the interface, ensuring the stability and accuracy of numerical calculations. Compared with other interface-tracking approaches, the level-set method has inherent advantages in handling topological changes in the interface (such as breakup and coalescence). In addition, it yields a smooth interface profile, which facilitates the accurate calculation of interface curvature and normal vectors. The density and dynamic viscosity of the fluids were determined by interpolation of the level-set function. The velocity field simultaneously drives the transport of the level-set function and momentum transfer within the fluid.

Navier–Stokes equations [25]:

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \eta \nabla^2 \mathbf{u} + \mathbf{F} \quad (1)$$

where ρ denotes the fluid density; $\mathbf{u} = (u_x, u_y, u_z)$ is the velocity field vector; p represents the fluid pressure; I is the identity diagonal matrix; η corresponds to the dynamic viscosity of the fluid; $\mathbf{F} = (f_x, f_y, f_z)$ is the body force vector acting on the fluid; and t is the time variable.

Continuity equation [26]:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (2)$$

Level set equation [27]:

$$\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = \nabla \cdot \left(\varepsilon_{1s} \nabla \phi - \phi(1 - \phi) \frac{\nabla \phi}{|\nabla \phi|} \right) \quad (3)$$

where ϕ is the level set function. Its value range is defined as follows: $\phi < 0.5$ corresponds to the oil phase region; $\phi > 0.5$ corresponds to the aqueous phase region; and $\phi = 0.5$ characterizes the position of the oil–water two-phase interface. The second term on the right-hand side of the equation is the compression term, which serves to maintain the compactness of the interface transition zone; ε_{1s} is the interface thickness control parameter.

(2) Geometric Model and Mesh Generation

Geometric Model and Mesh Generation Two-dimensional geometric models featuring a T-junction inlet were built for comparative simulation. The hydraulic diameter for both straight and zigzag microchannels was fixed at 0.6 mm. The straight microchannel had a total length of 15 mm to guarantee fully-developed flow at the outlet. The zigzag microchannel contained nine 90° bends, and its overall length was matched to that of the straight counterpart, so that equal fluid residence time could be achieved for the two channel geometries. Triangular unstructured meshes were utilized for domain discretization with refined element sizes. Local mesh refinement was implemented near channel walls, two-phase interfaces and zigzag bends where sharp gradient variations occurred. A mesh independence study was carried out, and the deviation of flow-field results between the present mesh and a further-refined mesh was below 2%, which meets the numerical calculation accuracy criteria. For the straight microchannel, the axial flow-development length under low-Reynolds-number laminar conditions can be evaluated via an empirical correlation [28]:

$$L_e/D = 0.05Re \quad (4)$$

(3) Boundary Conditions and Parameter Settings

Boundary conditions were specified based on the following fundamental assumptions: the effects of temperature and concentration variations on fluid physical properties were neglected, and the fluids were treated as incompressible media; the channel walls were regarded as ideally smooth surfaces subjected to a no-slip constraint; the additional interfacial tension effect at the wall-fluid interface was ignored, as was the feedback effect of interphase mass transfer on the flow pattern. The specific boundary conditions are detailed as follows: both the liquid-phase and aqueous-phase inlets were defined as normal inflow velocity boundaries, with inlet velocities ranging from 0.001 to 0.09 m/s; the outlet was set as a pressure-outlet boundary with a relative pressure of 0 Pa; the channel walls were assigned a wetting-wall condition with a no-slip constraint imposed.

2.1.2. Three-Dimensional Numerical Simulation of High-Throughput Microreactor

(1) Geometric Model and Mesh Generation

The high-throughput microreactor adopts a channel array design with bidirectional symmetric superposition, integrating 78 parallel zigzag microchannels (39 channels per group, arranged symmetrically about the central plane). The entire reactor comprises double-sided circular inlets, a fluid isolation chamber, a mixing chamber, an array of cylindrical flow-distribution pillars, rectangular transition channels, a zigzag microchannel array, and an outlet chamber. It is integrally fabricated via stereolithography (SLA) 3D printing with a manufacturing accuracy of 25–50 µm, enabling precise fabrication of complex internal flow channels. Taking advantage of the reactor's central symmetry, a quarter of the flow domain was selected as the computational domain to reduce the computational cost. Unstructured tetrahedral meshes were employed for spatial discretization, yielding a total of 395,495 elements. Local mesh refinement was applied in regions near the channel walls, zigzag bends, and flow-distribution pillars. A mesh independence test was performed: the deviation between the results obtained with the current mesh scheme and those from a finer mesh (approximately 800,000 elements) was less than 1.5%, which meets the standard numerical accuracy requirements.

(2) Governing Equations

The flow inside the high-throughput microreactor is steady-state incompressible laminar flow. The governing equations consist of the coupled Navier–Stokes equations, continuity equation, and convection–diffusion equation. Since this simulation aims to

investigate the passive mixing characteristics of the reactor, the chemical reaction source term is neglected ($R = 0$).

Continuity and momentum equations [16]:

$$\nabla \cdot \mathbf{u} = 0, \rho(\mathbf{u} \cdot \nabla)\mathbf{u} = -\nabla p + \mu \nabla^2 \mathbf{u} \quad (5)$$

Convection–diffusion equation [14]:

$$\frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = \nabla \cdot (D \nabla c) \quad (6)$$

where c is the molar concentration of the target species (mol/m^3), and D is the molecular diffusion coefficient (m^2/s). A steady-state solver was adopted for computation. The convection term was stabilized using the streamline upwind/Petrov–Galerkin (SUPG) method to eliminate numerical spurious oscillations under high Péclet number conditions.

(3) Boundary Conditions and Physical Properties

Boundary conditions were set based on the following assumptions: the solution is a highly diluted system, and concentration variations do not alter the macroscopic physical properties of the fluid; the channel walls are ideally smooth with no wall slip; interfacial tension effects are neglected, and no substance adsorption or permeation occurs at the walls. The specific boundary conditions are defined as follows: both circular inlets are set as normal inflow velocity boundaries with velocities ranging from 0.00236 to 1.888 m/s, and the inlet concentrations are set to 1 mol/m³ and 0 mol/m³, respectively; the outlet is specified as a free outflow boundary with zero normal stress and a relative pressure of 0 Pa; a no-slip constraint and an insulating concentration boundary are imposed on the channel walls; on the symmetry plane, the normal component of velocity and the normal component of the concentration gradient are set to zero. Typical physical properties of dilute aqueous solution at ambient temperature were used in the simulation: density $\rho = 1000 \text{ kg}/\text{m}^3$, dynamic viscosity $\mu = 0.001 \text{ Pa}\cdot\text{s}$, and molecular diffusion coefficient $D = 1.0 \times 10^{-9} \text{ m}^2/\text{s}$. The inlet velocity specified at the boundary represents the cross-sectional average velocity. Local velocity inside microchannels can differ from this average value due to T-junction impingement and near-wall velocity gradients, which conform to the continuity equation. All velocity contour plots adopt a unified color scale of 0–0.18 m/s for consistent visual comparison.

To further verify the reliability and accuracy of the established numerical model, experimental results were adopted for model validation on the basis of mesh independence verification. The simulated flow-pattern evolution, chaotic advection behavior, and velocity-dependent mixing efficiency variation are highly consistent with the trend of germanium precipitation performance obtained from experimental tests. The optimal inlet velocity range determined by numerical simulation matches well with the experimentally optimized process parameters, which sufficiently validates the rationality and practicability of the present two-phase flow simulation model for serrated microchannels. In addition, the accuracy and inherent limitations of the numerical model are clarified. The current model can accurately characterize the macroscopic flow field distribution, vortex generation mechanism, and micromixing intensification law inside microchannels, providing reliable theoretical guidance for process optimization. However, several idealized simplifications are adopted in the simulation, including smooth channel wall assumptions and the absence of coupled microscopic chelation precipitation kinetics and particle growth behavior. These simplifications lead to minor deviations between simulated hydrodynamic results and actual complex reaction environments. Even so, the model is sufficiently robust to reveal

the essential flow intensification mechanism of zigzag microchannels and support the structural and parametric optimization of the microreactor system.

Although the governing equations and boundary conditions describe the hydrodynamic behavior inside microchannels, certain model simplifications are inevitable for CFD computation according to the practical features of the tannic acid–germanium mixing-precipitation system. In the present CFD model, several reasonable simplifications are adopted. The feed solutions are dilute aqueous streams under a nearly isothermal state; thus, thermophysical parameters including density and viscosity are treated as constant values. Since two inlet streams are completely miscible aqueous phases, no interphase interface emerges, and interfacial mass-transfer terms are omitted. As the germanium–tannic acid chelation is a fast reaction with a high Damköhler number, reaction kinetics are not coupled into the flow simulation, where mixing dominates the overall process. In addition, a constant molecular diffusion coefficient is used for the dilute-solution system. To evaluate the reliability of the above treatments, a sensitivity analysis is further performed to quantify the potential error introduced by these simplifications.

2.2. Experimental Methods

2.2.1. Experimental Materials and Reagents

The germanium-bearing feed solution used in the experiments was collected from the raffinate of the indium extraction process at a smelting enterprise, representing a low-concentration, strongly acidic germanium-containing system. Its chemical composition, determined by inductively coupled plasma optical emission spectrometry (ICP-OES), is presented in Table 1.

Table 1. Chemical composition of the germanium-bearing feed solution.

Component	Concentration (g/L)	Note
Ge	0.12	Target element for recovery
Fe	29.50	Impurity (ferric iron)
Zn	15.34	Major impurity
In	0.26	Scattered metal impurity
Cl [−]	15.28	Complexing anion
H ₂ SO ₄	54.6	Source of solution acidity
pH	≈0.5	Strongly acidic environment

Industrial-grade tannic acid (molecular formula: C₇₆H₅₂O₄₆, molecular weight: 1701.23 g/mol, purity ≈ 60%) was adopted as the precipitant. It was dissolved in deionized water to prepare a stock solution prior to use, and the solution was freshly prepared for each experiment to avoid oxidative degradation. Auxiliary reagents included anhydrous ethanol (analytical grade), deionized water (resistivity ≥ 18.2 MΩ·cm), and 0.22 μm mixed cellulose ester microporous filter membranes.

2.2.2. Experimental Apparatus and Equipment

The experimental system mainly consists of the following components:

Microreactor system: A microchannel module (channel diameter: 800 μm, effective length: 102 mm, substrate material: photosensitive resin); two peristaltic pumps equipped with 18-gauge tubing, with a flow rate range of 0–300 mL/min; a 3D-printed single-channel zigzag microreactor (T-junction inlet, channel diameter: 500 μm, effective length: 120 mm, substrate material: photosensitive resin). Analytical instruments: PerkinElmer Optima 8300 inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer, Waltham, MA, USA); Mettler Toledo FE28 precision pH meter (Mettler-Toledo, Greifensee, Switzerland); Sartorius SECURA analytical electronic balance (Sartorius, Göttingen, Ger-

many); DZF-6050 vacuum drying oven (Shanghai Yiheng Scientific Instrument Co., Ltd., Shanghai, China); Phantom Miro C110 high-speed camera system (Vision Research, Wayne, NJ, USA). Control experiment equipment: IKA RW 20 mechanical stirring device (IKA-Werke GmbH & Co. KG, Staufen, Germany).

2.2.3. Experimental Procedure and Operation Steps

Solution pretreatment: The germanium-bearing feed solution and tannic acid stock solution were transferred into 50 mL glass syringes, respectively. The pH of the germanium-bearing solution was adjusted to 0.5 ± 0.05 , and air bubbles trapped in the tubing were thoroughly removed.

Micro-mixing reaction: The two fluid phases were pumped into the T-junction inlet of the microreactor by a dual-channel precision syringe pump (LSP02-1B, Longer Precision Pump Co., Ltd., Baoding, China) with a relative flow rate accuracy of $\pm 0.5\%$. The two channels operated in an independent constant-flow mode to precisely maintain the preset volume ratio and stable inlet pressure throughout the entire experiment, avoiding flow fluctuation caused by manual operation. Prior to each formal test, the actual outlet flow rate of each channel was calibrated via the gravimetric method to verify that the experimental inlet velocity was highly consistent with the constant velocity boundary condition adopted in the numerical simulation, and to eliminate systematic deviations caused by syringe specification tolerances. The two phases mixed via laminar impinging jets and underwent the coordination precipitation reaction simultaneously.

Solid–liquid separation: The reacted slurry was immediately separated by vacuum filtration through a $0.22\ \mu\text{m}$ microporous filter membrane, and the filtrate was collected in a polyethylene bottle for subsequent analysis.

Precipitate treatment: The filter cake was washed alternately with anhydrous ethanol and deionized water for three cycles, then vacuum-dried at $60\ ^\circ\text{C}$ and $-0.09\ \text{MPa}$ for 12 h until a constant weight was attained.

Analytical measurement: After appropriate dilution, the residual concentrations of Ge, Fe, Zn, and In in the filtrate were determined by ICP-OES. The detection wavelengths were 209.426 nm for Ge, 238.204 nm for Fe, 213.856 nm for Zn, and 230.606 nm for In.

The parameter ranges investigated in the experiments were as follows: tannic acid dosage multiple (mass ratio of tannic acid to Ge) of 10–30, phase volume ratio (germanium-bearing solution:tannic acid solution) of 4:1–10:1, residence time of 0.01–0.2 s, and reaction temperature of $20 \pm 2\ ^\circ\text{C}$.

All precipitation experiments were performed in triplicate under identical operating conditions, and all results are presented as the mean value $\pm$ standard deviation (SD). The concentrations of germanium and impurity elements were determined by ICP-OES, with a relative standard deviation (RSD) of less than 0.3% for germanium detection within the tested concentration range. The error bars in all figures correspond to the standard deviation of three parallel measurements.

3. Results and Discussion

3.1. Flow Pattern Evolution and Mixing Mechanism of Liquid–Liquid Two-Phase Flow in Single Microchannels

3.1.1. Flow Pattern Evolution Law in Straight Microchannels

The inlet velocity is the core operational parameter governing the two-phase flow pattern in straight microchannels. As the inlet velocity increases gradually from 0.001 m/s to 0.1 m/s, the flow pattern sequentially passes through three stages: large wavy flow, transitional flow, and stable parallel laminar flow. This evolution reflects the underlying

ing physical mechanism: as the capillary number rises, viscous forces gradually replace interfacial tension as the dominant factor governing the flow pattern [29].

At low flow velocities, interfacial tension exerts absolute dominance. The shear force applied by the continuous phase to the dispersed phase is weak and insufficient to overcome the Laplace pressure within droplets that preserves the interface geometry. As a result, the two-phase interface exhibits large-amplitude, irregular wavy morphology along the channel axis, forming a typical large-wavy flow regime. In this state, the velocity measured at the channel centerline monitoring point shows highly irregular random fluctuations, consistent with the unstable nature of the flow pattern.

When the flow velocity increases to a moderate level, the enhanced viscous force dampens the amplitude of interface fluctuations, and the flow-pattern transitions to a mixed state where wavy flow and laminar flow coexist. At an inlet velocity of 0.01 m/s, the relatively high velocity and large capillary number in the inlet region allow viscous shear to suppress interface fluctuations, establishing stable parallel-laminar flow. However, wall friction along the channel causes local velocity and pressure decay, reducing the capillary number in the flow direction. The influence of interfacial tension is thereby re-strengthened, and the interface in the downstream region destabilizes again to exhibit wavy characteristics. This behavior demonstrates the axial non-uniformity of flow-pattern stability in finite-length straight microchannels. At this stage, the centerline velocity presents distinct periodic oscillations, corresponding to the propagation of the wavy interface along the channel at a constant wave speed [30].

As the flow velocity is further increased to 0.1 m/s, the capillary number rises markedly, and viscous shear forces fully dominate the flow pattern, completely suppressing fluctuations driven by interfacial tension. Stable parallel laminar flow is formed throughout the channel, with a flat and stationary two-phase interface, and the centerline velocity converges to a constant value [31]. The aforementioned correlation among inlet velocity, flow pattern, and velocity stability provides important guidance for the optimized selection of operating parameters in microreactor systems.

By combining the velocity-fluctuation characteristics depicted in Figure 1a with the flow-pattern evolution profiles shown in Figure 2, the correlation among inlet velocity, flow pattern, and velocity stability is established, as illustrated in Figure 3. Low inlet velocities correspond to a large-wavy flow regime with highly irregular velocity fluctuations; moderate inlet velocities correspond to a wavy-flow regime with periodic velocity oscillations; and high inlet velocities correspond to stable parallel-laminar flow with a constant velocity distribution. This systematic regularity offers important guidance for the optimal selection of operating-velocity parameters in microreactor systems.

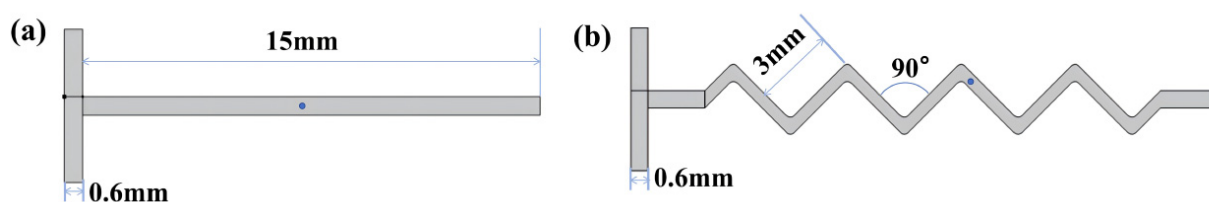


Figure 1. Geometry of simulated microchannels: (a) straight microchannel, (b) zigzag microchannel. Structural dimension labels are provided in the schematic.

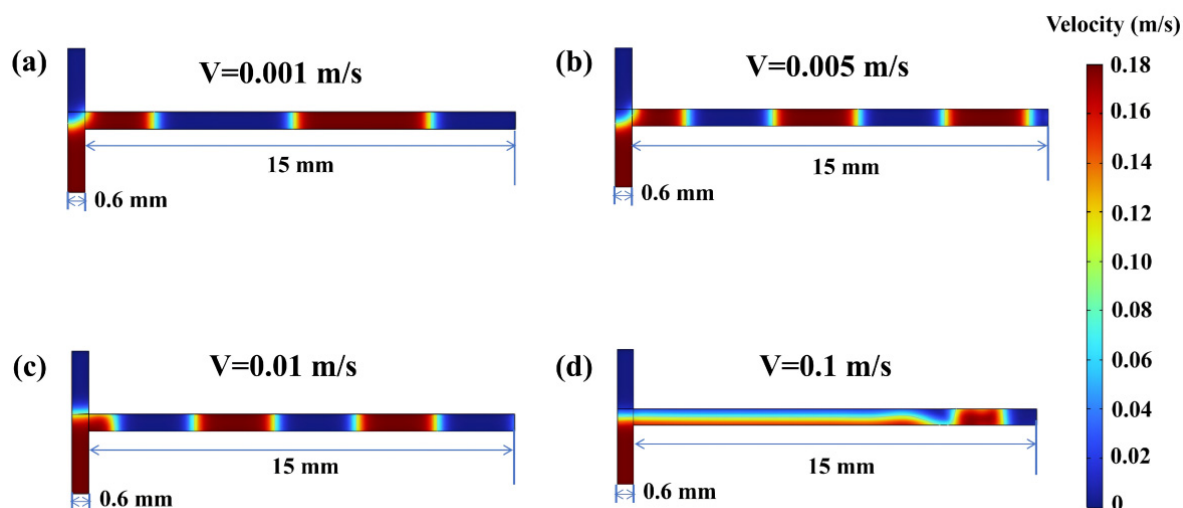


Figure 2. Velocity contours in the straight microchannel under different cross-section-averaged inlet velocities: (a) $V = 0.001$ m/s, (b) $V = 0.005$ m/s, (c) $V = 0.01$ m/s, (d) $V = 0.1$ m/s. A structural dimension scale bar is shown. A unified velocity color scale of 0–0.18 m/s is applied for all sub-plots.

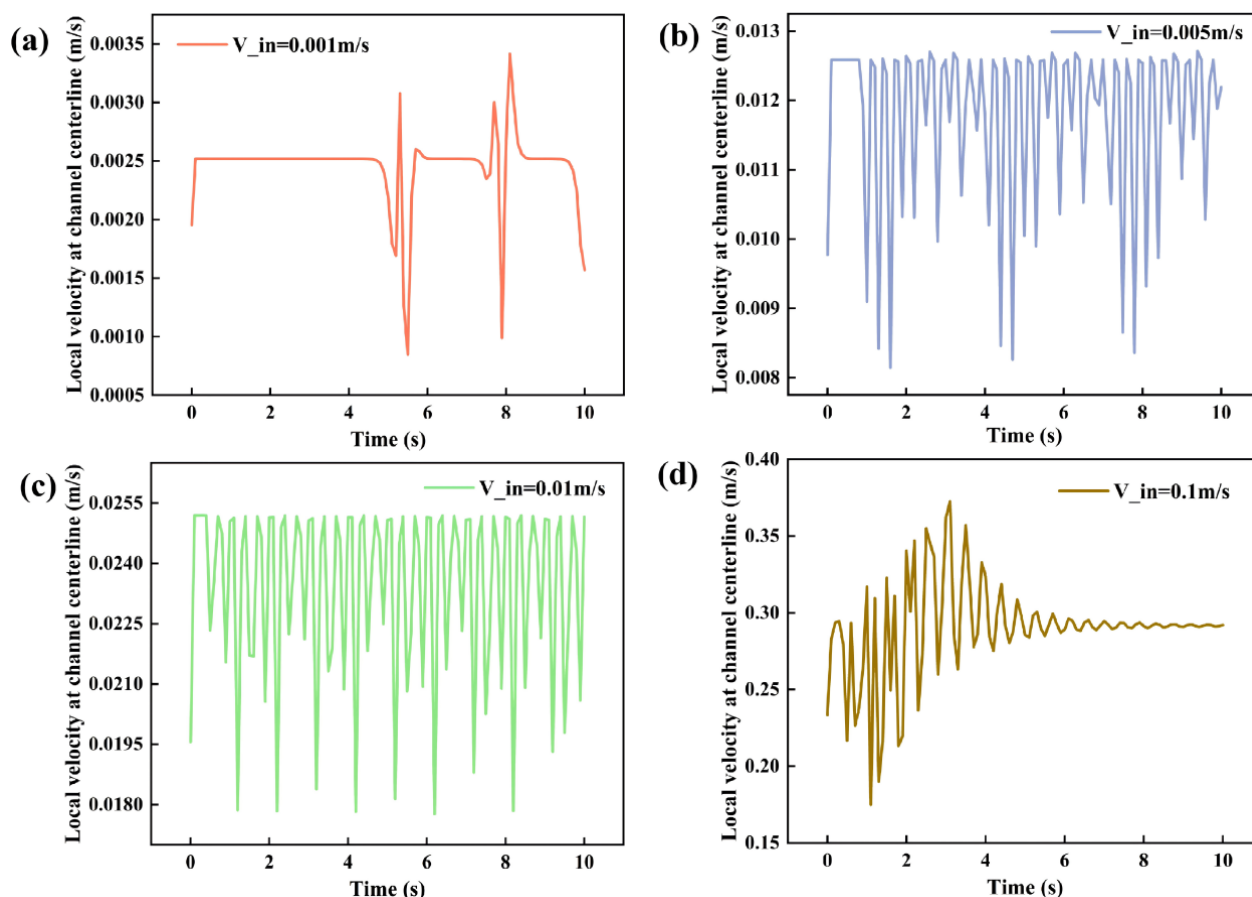


Figure 3. Temporal evolution of local velocity at the channel-centerline monitoring point of the straight microchannel under different cross-section-averaged inlet velocities: (a) $V = 0.001$ m/s, (b) $V = 0.005$ m/s, (c) $V = 0.01$ m/s, (d) $V = 0.1$ m/s. Local point-wise velocity sampled at the channel centerline.

3.1.2. Flow Pattern Characteristics and Mixing Intensification Mechanism in Zigzag Microchannels

As shown in Figure 4, In contrast to straight channels, the flow pattern in zigzag microchannels is strongly governed by the channel geometry. Within the velocity range

examined in this work (0.01–0.075 m/s), stable slug flow is consistently maintained inside the channel, and the droplet size decreases monotonically with increasing flow velocity. The underlying physical mechanism is elucidated as follows: as the flow velocity rises, viscous shear stress gradually exceeds the restoring stress dominated by interfacial tension, inducing large deformation and even breakup of droplets in the strong shear field, which generates smaller droplet units. The bend structure of zigzag channels exerts a remarkable intensification effect on the evolution of droplet size. When fluid passes through the bends, the primary-flow stream deflects toward the outer wall under the action of inertia, forming a low-pressure zone adjacent to the inner wall. The transverse pressure gradient drives the fluid to form secondary-flow vortices; meanwhile, the high shear-stress gradient at the inner wall triggers boundary-layer separation, giving rise to local recirculation regions. The entrainment and stretching effects of the recirculation vortices exert intense shear and tearing forces on the droplets, facilitating further droplet breakup upon each passage through a bend. After successive interactions with nine bends, the droplet size is significantly reduced relative to the initial state, accompanied by a more uniform size distribution [13,32].

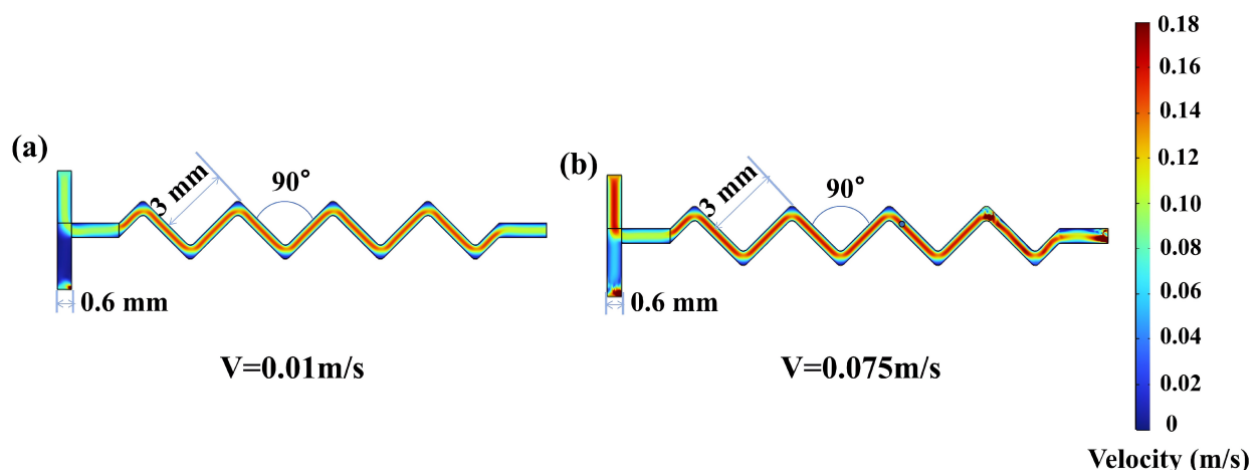


Figure 4. Numerical simulation of flow patterns in the zigzag microchannel under varying inlet velocities: (a) $V = 0.01 \text{ m/s}$, (b) $V = 0.075 \text{ m/s}$. A structural dimension scale bar is shown. A unified velocity color scale of 0–0.18 m/s is applied for both sub-plots.

As shown in Figure 5, from the perspective of velocity-field characteristics, the velocity measured at the centerline monitoring point in the zigzag channel consistently exhibits turbulence-like irregular fluctuations, corresponding to a pseudo-chaotic flow regime induced by geometric perturbations under low-Reynolds-number laminar flow conditions. Chaotic advection subjects fluid elements to repeated stretching, folding and reorientation, rapidly reducing macroscopic concentration inhomogeneity to microscopic scales where molecular diffusion can operate effectively. In contrast to the quadratic scaling law followed by the mixing characteristic time in straight channels, chaotic advection in zigzag channels compresses the mixing characteristic time into a logarithmic scaling law, achieving an order-of-magnitude enhancement in mixing efficiency. Notably, this study achieves efficient chaotic mixing within the low Reynolds number range of $Re < 400$, which effectively circumvents the inherent physical constraint that the critical Reynolds number for laminar-turbulent transition is difficult to attain at the microscale. This provides a high-performance pathway for microscale mixing intensification independent of turbulent flow [33,34].

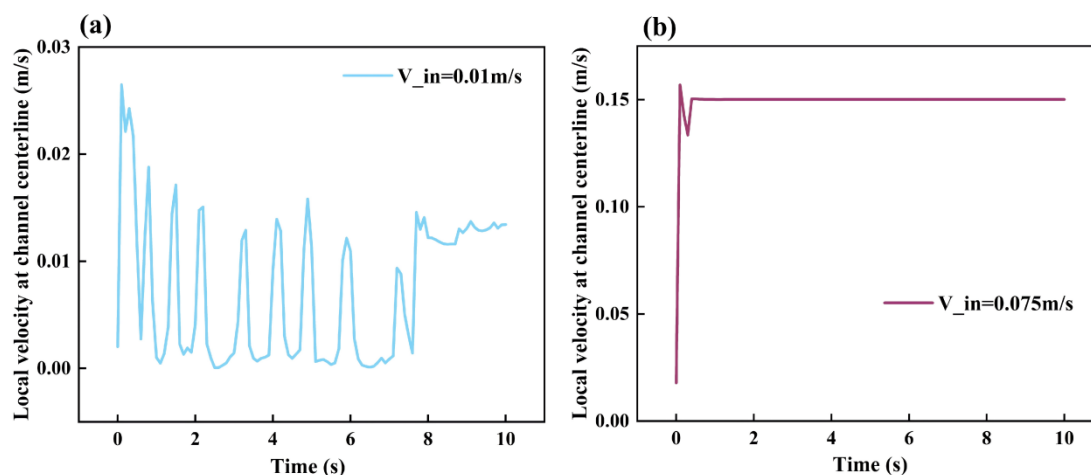


Figure 5. Temporal evolution of the local maximum velocity at the serrated contraction throat under different inlet average velocities: (a) 0.01 m/s; (b) 0.075 m/s. A vertical axis represents local point-wise velocity sampled at the contraction throat.

3.1.3. Comparative Analysis and Comprehensive Discussion of Two Channel Configurations

In terms of flow-pattern characteristics, the flow pattern in straight microchannels undergoes a three-stage evolution with increasing inlet velocity, exhibiting high sensitivity to operating conditions; axial flow-pattern non-uniformity tends to emerge within the medium-velocity range. In contrast, the flow pattern in zigzag channels is more strongly governed by channel geometry: stable slug flow is maintained throughout the investigated velocity range, with only droplet size varying with flow velocity, granting superior flow-pattern controllability and operational stability. From the perspective of the mixing mechanism, straight channels rely on molecular diffusion and weak interfacial perturbations to achieve mixing. The flow becomes stable at high velocities, yet mixing efficiency remains low, which cannot satisfy the demands of fast-reaction systems. Zigzag channels induce secondary flow and chaotic advection via their bend structures, synergistically enhancing convective and diffusive mixing. Efficient mixing can be achieved even at low Reynolds numbers, making them more suitable for scenarios such as fast chemical reactions, nanoparticle synthesis, and emulsion preparation. Regarding engineering applicability, straight channels feature simple structures, low fabrication difficulty, and low flow resistance, and are suitable for extraction operations requiring stable stratified interfaces or mass-transfer measurement experiments. Zigzag channels deliver excellent mixing performance but come with considerably higher flow resistance, operational energy consumption, and fabrication cost. In practical microreactor design, a combined configuration can be adopted according to process requirements—for instance, embedding local zigzag perturbation units into straight channels to achieve a balance between mixing efficiency and pressure drop [13,35,36].

Based on the above flow-field and mixing results for both channel geometries, sensitivity analysis is further performed. To quantitatively assess the magnitude of deviations originating from the aforementioned modeling simplifications, sensitivity analysis was implemented to evaluate how model assumptions affect simulated hydrodynamic results. Thermophysical properties were perturbed within a reasonable fluctuation range, the diffusion coefficient was varied over a representative interval, and a comparative simulation incorporating a fast homogeneous reaction was also conducted. The simulation results reveal that these parameter variations only induce minor deviations in the velocity-field distribution and outlet mixing efficiency. All observed deviations fall within generally accepted engineering error ranges. Therefore, these results demonstrate that the above sim-

plifications have no remarkable influence on velocity-field distribution, mixing-efficiency prediction and reactor-performance evaluation for serrated microchannels.

3.2. Flow Field Distribution and Mixing Characteristics of High-Throughput Microreactor

3.2.1. Overall Structure and Scale-Up Principle of High-Throughput Microreactor

Based on the mixing-intensification mechanism of Dean vortices in zigzag microchannels, this work proposes a channel-array scale-up strategy with bidirectional symmetric superposition, and designs a high-throughput microreactor integrating 78 parallel zigzag microchannels. As shown in Figure 6, in this design, two symmetrically arranged sets of zigzag microchannels are superposed about the central plane. Each channel receives uniform inlet conditions through the upstream distribution chamber, and the reacted fluids converge into the downstream outlet chamber prior to discharge. This integrated design eliminates fluid maldistribution among individual reactors in conventional external-parallel configurations, while greatly reducing the reactor footprint and the complexity of connecting pipelines. Numerical results demonstrate that, while maintaining laminar-flow conditions within every single channel, the total processing throughput of the reactor is increased by two orders of magnitude compared with a single channel. Large-flow processing can be realized at millisecond-scale residence time, which satisfies the industrial-scale demands of fast-reaction systems such as tannic acid-mediated germanium precipitation.

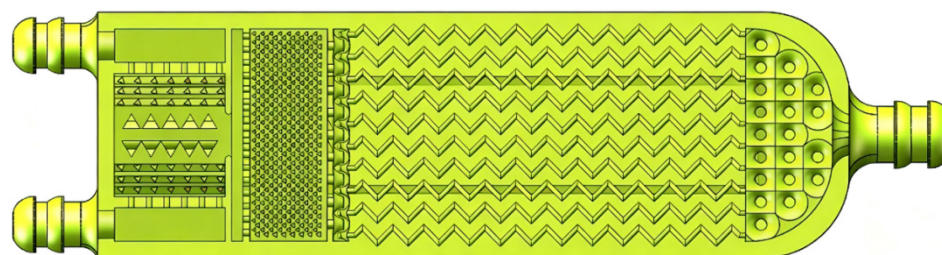


Figure 6. Schematic design of the high-throughput microreactor. This schematic shows the overall structure of the zigzag microchannel reactor, consisting of inlet and outlet ports, pre-distribution zone, zig-zag chaotic mixing units and outlet collecting chamber.

3.2.2. Internal Flow Field Structure and Three-Stage Mixing Mechanism of the Reactor

Numerical simulation results reveal a three-stage mixing mechanism inside the high-throughput microreactor, which fully combines the advantages of macroscopic-chamber pre-mixing and fine-scale microchannel mixing. First stage: inlet convective shearing. After entering through double-sided inlets, the two fluids travel in relatively independent laminar states within the rectangular mixing channel. The two-phase interface is stretched and thinned under shear action, laying a solid foundation for subsequent mixing. Second stage: chaotic pre-mixing in the distribution chamber. When the fluid enters the distribution chamber, the coupling of large spatial scale and cylindrical flow-distribution pillars disrupts the inherent laminar structure. Stable symmetric recirculation-vortex pairs and complex three-dimensional vortex motions form inside the chamber. Central reverse flow impinges on and entrains ambient fluid, generating intense chaotic mixing, which greatly enhances lateral mass exchange among fluid elements and achieves macroscopic uniform distribution. Third stage: microscale intensification in zigzag channels. The fluid uniformly distributed by the distribution chamber flows into each parallel zigzag microchannel, where bend-induced Dean vortices further achieve molecular-level homogeneous mixing.

3.2.3. Fluid Distribution Characteristics and Uniformity Analysis

In parallel multi-channel reactors, the uniformity of fluid distribution directly determines the consistency of overall treatment performance. Simulation results reveal that the

inlet velocity of each microchannel follows a distribution pattern of “faster in the center and slower at the edges”: microchannels near the central region of the distribution chamber are guided more directly by the flow-guiding structures and hence possess higher inlet velocities. In contrast, channels located at edge positions undergo greater flow deflection and deceleration, yielding relatively lower flow velocities. This non-uniformity arises from the fluid-inertia effect within the distribution chamber. Velocity-distribution non-uniformity becomes more pronounced as the total inlet velocity rises. Under high-throughput operating conditions, special attention should be paid to deteriorated mixing efficiency or incomplete reactions inside edge channels induced by excessively low flow velocity. Further improvement in fluid-distribution uniformity can be realized by tuning the arrangement density of flow-distribution pillars and optimizing the geometric profile of the distribution chamber. Furthermore, single-channel simulation results demonstrate that increasing flow velocity amplifies the intensity of Dean vortices and enhances secondary-flow mixing, yet it simultaneously shortens fluid residence time and narrows the molecular-diffusion window. Accordingly, an optimal operating-velocity range exists, which should be optimized combined with the kinetic characteristics of the target reaction system [37,38].

3.2.4. Reynolds Number Effect and Wall Pressure Distribution

Calculated from the simulated velocity field data, the Reynolds number in the microchannels within the reactor operating range is 0.129–253.85, covering a wide interval from Stokes-flow to the laminar transition regime. At low Reynolds numbers ($Re < 1$), viscous forces fully dominate interfacial behavior, and droplet deformation and breakup are severely suppressed. At high Reynolds numbers ($Re > 100$), inertia effects gradually emerge, promoting droplet shear breakup and interphase contact, which exerts a positive effect on mass-transfer intensification [13]. For the tannic acid–germanium precipitation system, the selection of flow velocity conditions must balance mixing intensification and interfacial stability. Analysis of wall pressure distribution shows that high-pressure zones are concentrated in the fluid distribution chamber and its transition connection regions with the microchannels. The sharp flow turning and vortex dissipation in the distribution chamber cause significant local pressure loss, and the wall bears considerable stress from the conversion between hydrostatic and dynamic pressure. This result suggests that the structural design of the reactor must ensure sufficient mechanical strength in the distribution chamber region, especially under high-throughput operation conditions, to avoid wall deformation or even structural failure caused by excessive internal pressure [39].

3.3. Experimental Results and Analysis of Tannic Acid Germanium Precipitation in Single-Channel Microreactor

Using industrial germanium-bearing raffinate as the raw material, single-factor experiments were systematically conducted to investigate the effects of raffinate flow rate, operating temperature, tannic acid dosage multiple, dosing mode, and number of serially connected reactors on germanium precipitation efficiency, so as to optimize process parameters and verify the intensification effect of the microreactor on germanium precipitation. With a tannic acid dosage of 25 times (a tannic acid dosage of 25 times the mass of germanium in the leachate), ambient temperature, and a single reactor, the germanium precipitation performance was investigated at raffinate flow rates ranging from 100 to 600 mL/min. As shown in Figure 7a, the germanium precipitation efficiency first increases and then decreases with increasing flow rate. When the flow rate rises from 100 mL to 300 mL, the fluid Reynolds number inside the microchannel increases, enhancing liquid–liquid two-phase mixing and interfacial mass transfer, and facilitating sufficient progression of the chelation reaction between tannic acid and germanium ions. Accordingly, the germanium precipitation efficiency gradually increases from 89.33% to 91.81%.

When the flow rate exceeds 300 mL, the hydraulic residence time is significantly shortened, providing an inadequate time window for the complexation reaction. Meanwhile, the shear effect induced by high flow velocity suppresses the aggregation and sedimentation of tannic acid–germanium complexes, ultimately leading to a continuous decline in precipitation efficiency, which decreases to 86.66% at a flow rate of 600 mL. Overall, 300 mL is the optimal raffinate flow rate within the experimental range, at which the mass-transfer intensification effect and reaction residence time achieve an optimal balance. With other process parameters kept constant, the precipitation performance was investigated over a temperature range of 20–60 °C. As shown in Figure 7b, the germanium precipitation efficiency decreases slowly with increasing temperature: it reaches 91.14% at the ambient temperature of 20 °C, decreases slightly at 30 °C, and drops to 89.24% at 60 °C. This downward trend is the real thermodynamic characteristics of the weakly exothermic chelation reaction, rather than random measurement fluctuations. This mild and steady decreasing trend is consistent with the thermodynamic characteristics of the weak exothermic chelation reaction between tannic acid and Ge^{4+} . The insignificant temperature dependence demonstrates that the coordination precipitation process has approached thermodynamic equilibrium within the millisecond-scale residence time in the microchannel, which benefits from the intensified chaotic mixing and interfacial mass transfer in the serrated channel structure. The underlying mechanism behind this trend is that the five-membered chelate complex formed by tannic acid and germanium exhibits poor thermal stability, and elevated temperatures weaken the binding strength of coordination bonds. Meanwhile, high temperature accelerates the oxidative degradation of phenolic hydroxyl groups in tannic acid molecules, reducing the concentration of effective complexing groups in the system and ultimately impairing precipitation capacity. This finding indicates that efficient germanium precipitation can be realized under ambient temperature conditions without auxiliary heating, which helps reduce process energy consumption and operational costs, making the process well-suited for practical industrial operating conditions. Based on metallic germanium mass, the precipitation performance was investigated at tannic acid dosage multiples ranging from 10 to 30. As shown in Figure 7c, the precipitation efficiency presents a two-stage variation characteristic of “rapid growth followed by slow growth” with increasing tannic acid dosage. When the dosage multiple rises from 10 to 25, abundant phenolic hydroxyl complexing sites provided by tannic acid enable more free germanium ions to be fully converted into insoluble chelates, thereby driving a sharp improvement in precipitation efficiency from 56.10% to 90.95%. At this stage, reagent concentration acts as the dominant rate-limiting factor for the chelation reaction. When the dosage multiple further increases from 25 to 30, the vast majority of germanium in the solution has already undergone precipitation, and reagent dosage is no longer the reaction bottleneck. The marginal benefit of excessive reagent addition becomes negligible, with the precipitation efficiency rising by merely 0.48 percentage points to 91.43%. Considering both precipitation performance and reagent economic cost, a 25-fold dosage is determined as the optimal economic dosage of tannic acid.

In order to further improve the utilization rate of reagents and strengthen the precipitation effect of germanium, this study adopted a two-stage tannic acid dosing mode to explore the precipitation performance under different dosing ratios between the first and second stages. This is a process optimization strategy based on the single-channel reactor. The tannic acid solution is introduced into two different axial positions of the single microchannel (the main inlet and the side feed inlet in the middle of the channel), while the mainstream channel remains a single continuous channel. The flow field characteristics and mixing law obtained by single-channel simulation can be fully applied to the two-stage casting process. The addition of the second inlet will not change the channel structure, the

vortex evolution mode, or the mixing strengthening mechanism in the channel. As shown in Figure 7d, the precipitation efficiency first increases and then decreases with an increase in the first-stage dosing proportion, reaching a peak of 91.14% at an 80% first-stage/20% second-stage ratio. The superiority of staged dosing is that the high-concentration tannic acid supplied in the first stage rapidly accomplishes complexation precipitation of bulk germanium to guarantee reaction kinetics, while the supplementary low dosage in the second stage enables deep capture of low-concentration residual germanium in the primary effluent, further lowering the germanium concentration in the final tail solution. An excessively low first-stage proportion causes insufficient reagent supply during the main reaction stage and restricts the overall precipitation efficiency. In contrast, an excessively high first-stage dosage proportion leads to inadequate supplementary dosing in the second stage, failing to activate the synergistic deep-precipitation effect. Therefore, the 80%/20% staged dosing ratio is determined as the optimal scheme. To break the precipitation limitation of a single microreactor, multi-stage serial microreactor experiments were conducted to explore precipitation performance under different serial configurations. As shown in Figure 7e, the germanium precipitation efficiency of a single-stage reactor ranges from 90.38% to 91.52%, which is consistent with the aforementioned single-factor experimental results. Upon adopting a two-stage serial-reactor configuration, precipitation efficiency exhibits a substantial improvement, ranging from 96.67% to a maximum of 98.09% under optimal conditions. This indicates that the secondary reactor can realize efficient secondary complexation-precipitation of residual germanium within the primary effluent and significantly enhance germanium recovery. When a three-stage serial-reactor setup is employed, no statistically significant difference in precipitation efficiency is observed relative to the two-stage configuration, with no further tangible performance gain. This demonstrates that a two-stage serial connection can already achieve deep germanium precipitation from the raffinate. Further increasing the number of reactor stages delivers only limited marginal gains in precipitation efficiency, while raising equipment investment and system flow resistance. Considering both technical performance and economic benefits, the two-stage serial microreactor arrangement is identified as the optimal process configuration [33,40,41]. Under the optimal condition with a germanium precipitation efficiency of 98.09%, the final precipitate is mainly composed of germanium–tannic acid chelates with ultra-high selectivity. Although the original germanium-bearing raffinate contains Zn, In, and Cl^- , these components scarcely enter the solid phase under strongly acidic precipitation conditions. Specifically, in the pH-controlled strong acid environment, Zn^{2+} and In^{3+} have negligible complexing ability with tannic acid and cannot form stable insoluble precipitates. Chloride ions only act as supporting electrolyte ions in the solution and remain completely in the aqueous phase without participating in solid-phase formation. Therefore, the final precipitate contains no Zn, In, or chloride impurities. Only a small amount of Fe^{3+} undergoes slight chelation co-precipitation, with a co-precipitation rate as low as 1.8% under optimal conditions, demonstrating the excellent impurity suppression performance of the microchannel-intensified precipitation process. Despite the extremely low impurity content, the obtained precipitate still contains trace iron and residual organic components. For industrial high-purity germanium production, further conventional purification procedures are still required to obtain ultra-pure germanium products.

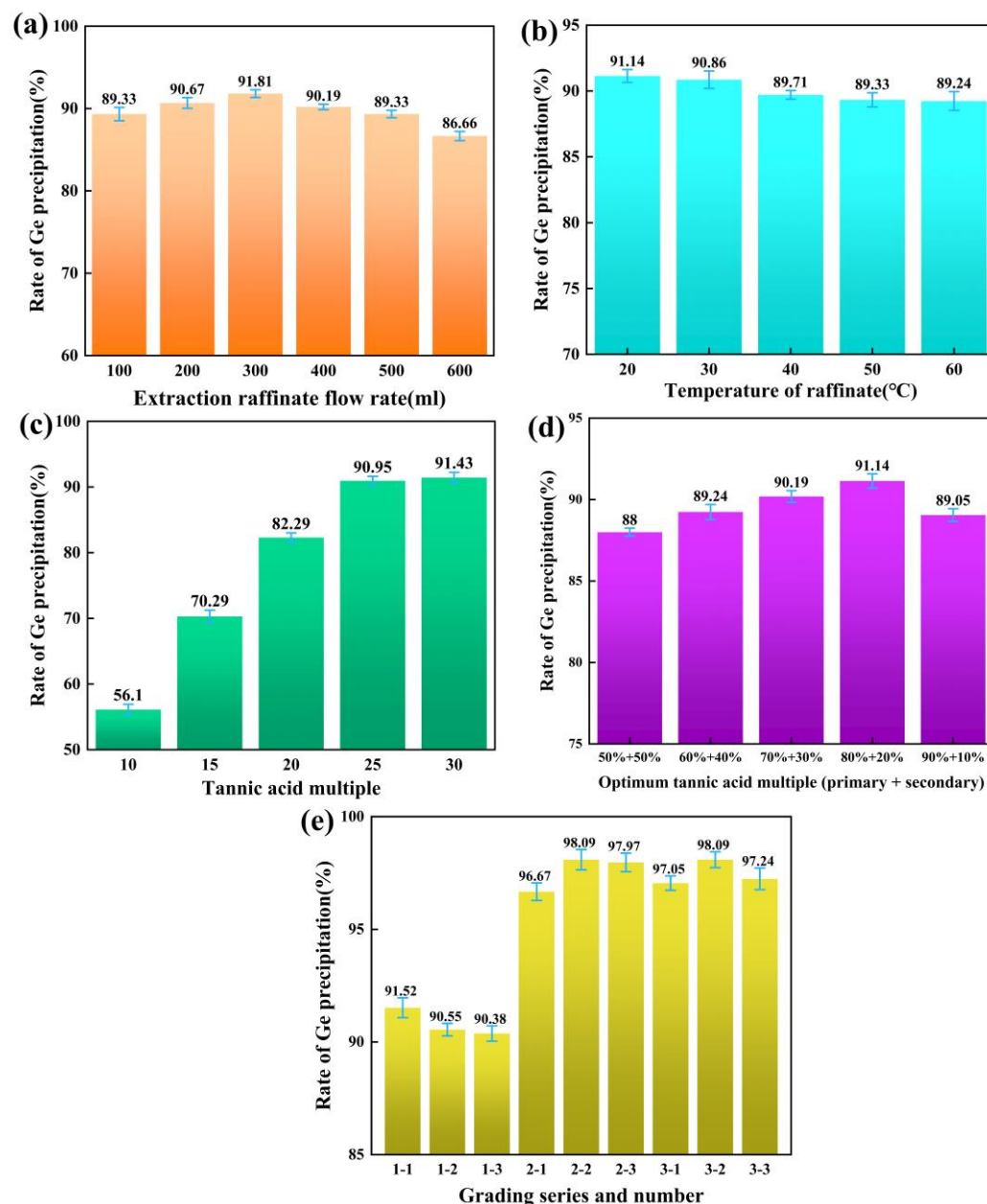


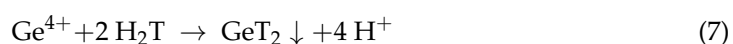
Figure 7. Effects of (a) raffinate flow rate, (b) temperature, (c) tannic acid dosage, (d) two-stage dosing ratio, and (e) channel structure on germanium precipitation efficiency. All data points represent the average of triplicate experiments, and error bars denote the standard deviation. Subplots (a–e) adopt orange-gradient, cyan-gradient, green-gradient, purple-gradient and yellow-gradient column fills, respectively, which correspond to germanium precipitation results under different experimental variables.

Compared with conventional stirred tank reactors, the serrated microchannel achieves effective flow field reorganization and millisecond-scale micromixing enhancement, which fundamentally optimizes the kinetic conditions of the tannin–germanium homogeneous precipitation reaction. To further clarify the technological advantages and essential differences in the present microchannel precipitation system, the mass transfer and intensification performance obtained in this work can be further contextualized and compared with the typical microchannel two-phase mass-transfer results reported by Li et al. [33]. Both studies rely on passive structure-induced chaotic mixing as the core intensification strategy, which is a well-established approach for microchannel reaction systems. Despite this shared fundamental mechanism, there are notable differences in application scenarios

and rate-limiting steps between the two works. The study by Li et al. [33] focused on a liquid–liquid two-phase extraction system in sinusoidal microchannels, where the overall volumetric mass-transfer coefficient is primarily governed by the specific interfacial area between the two phases. In contrast, the present work addresses a homogeneous complex precipitation system of germanium and tannic acid in a single serrated microchannel. The split-recombination flow and periodic vortex evolution induced by the serrated sidewalls enable efficient micromixing within milliseconds. Under these conditions, the precipitation process is dominated by homogeneous mixing kinetics rather than interphase mass transfer, which distinguishes the rate-control regime of this work from the two-phase extraction system.

3.4. Mechanism Elucidation

The essence of germanium precipitation with tannic acid lies in the coordination reaction between ortho-phenolic hydroxyl groups in the tannic acid molecular structure and Ge^{4+} in the strongly acidic system, which forms stable insoluble five-membered chelates to achieve selective precipitation of germanium. The complexation precipitation reaction between germanium (IV) and tannic acid can be expressed by the following balanced equation [5]. For simplicity, tannic acid—a macromolecular polyphenol compound with multiple adjacent phenolic hydroxyl active sites—is denoted as H_2T , where T represents the deprotonated tannin ligand.



In this reaction, Ge^{4+} in the sulfuric acid solution forms an insoluble chelate precipitate with the ortho-phenolic hydroxyl groups on tannic acid molecules, accompanied by the release of hydrogen ions. The millisecond-scale efficient mixing in the serrated microchannel ensures uniform contact between Ge^{4+} and tannic acid molecules, avoiding local reagent excess and reducing impurity co-precipitation.

The reaction mechanism is illustrated in Figure 8. The core intensification mechanism of tannic acid-mediated germanium precipitation in the microreactor is attributed to multi-dimensional process regulation: (1) Matching of mixing and reaction kinetics. The zigzag microchannel generates Dean vortices and pseudo-chaotic advection via periodic bends, shifting the characteristic mixing time from the quadratic scaling law of pure molecular diffusion to a logarithmic scaling law. Millisecond-scale, molecular-level homogeneous mixing can be realized under low-Reynolds-number laminar flow conditions ($\text{Re} < 400$). This ensures that the complexation reaction proceeds consistently within a uniform concentration field, fundamentally resolving the core contradiction between mixing lag and reaction progression. (2) Microscale mass-transfer intensification. Microscale channels feature an intrinsically extremely short mass-transfer distance and ultra-high specific surface area. Coupled with the dynamic interface renewal effect at the bends, the diffusion boundary layer can be effectively thinned, greatly enhancing the interphase mass-transfer rate and enabling the complexation reaction to proceed fully within a residence time of tens of milliseconds. (3) Selectivity regulation. The uniform concentration field gives full play to the thermodynamic stability advantage of tannic acid- Ge^{4+} chelates. Meanwhile, the precisely controllable residence time can restrict the progress of slower impurity complexation side reactions, effectively inhibiting impurity co-precipitation. On this basis, the staged dosing and two-stage serial processes regulate the concentration gradient: the first stage accomplishes rapid precipitation of high-concentration bulk germanium, and the second stage achieves deep capture of low-concentration residual germanium, further optimizing reagent utilization efficiency. Ultimately, a germanium precipitation efficiency

of approximately 98% can be achieved at a tannic acid dosage of 25 times, realizing deep recovery with high efficiency and low consumption [41,42].

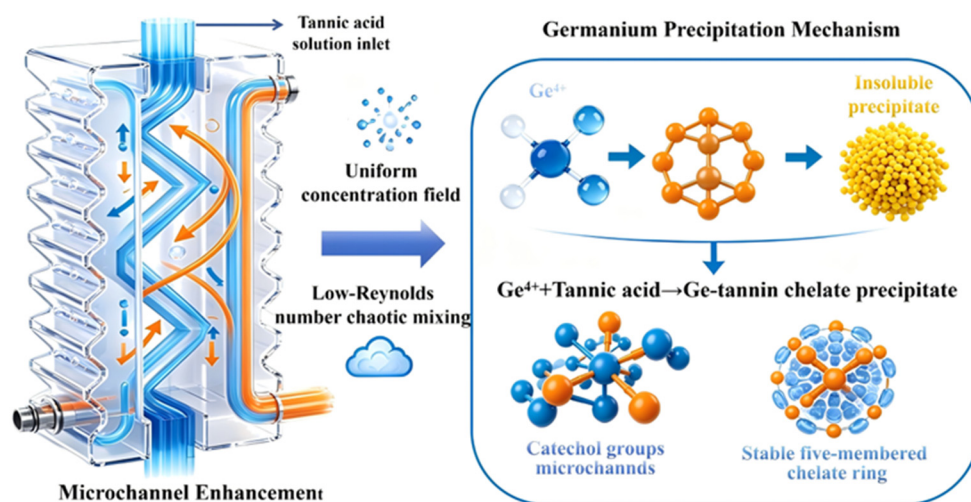


Figure 8. Reaction mechanism of germanium precipitation with tannic acid. Blue arrows represent the flow path of tannic-acid-containing solution; orange arrows denote the flow of germanium-containing solution. Blue spheres represent Ge^{4+} ions, and orange spheres represent tannic-acid-related structural fragments.

From the perspective of continuous separation methodology, the microchannel germanium precipitation process developed in this work follows the general framework of continuous microfluidic extraction and separation proposed by Wouters et al. [43]. Their systematic research confirmed that continuous-flow microreactors can achieve precise regulation of fluid contact and mass transfer through structural intensification, delivering higher separation selectivity, better product consistency and stronger operational stability than conventional batch stirred tanks. This work extends this microreactor intensification methodology from conventional liquid–liquid solvent extraction systems to homogeneous complex precipitation systems in hydrometallurgy. The high germanium precipitation efficiency and low iron coprecipitation achieved in the single serrated channel further verify that microscale mixing intensification has wide applicability in the separation and recovery of scattered metals, and also provide a reference for the continuous upgrading of similar batch precipitation processes in the metallurgical industry.

4. Conclusions

By combining numerical simulation with experimental validation, this work systematically investigates the mixing-intensification mechanism of zigzag microchannels, the scale-up design of a high-throughput microreactor, and the process-intensification characteristics of tannic acid-based germanium precipitation. In straight microchannels, the flow pattern sequentially undergoes three stages as inlet velocity increases: large-wavy flow, transitional flow, and stable parallel-laminar flow, where flow-pattern stability strongly correlates with the fluctuation characteristics of centerline velocity. By generating Dean vortices and pseudo-chaotic flow via periodic bends, zigzag microchannels deliver an order-of-magnitude enhancement in mixing efficiency under low-Reynolds-number laminar conditions ($\text{Re} < 400$). This shifts the characteristic mixing time from the quadratic scaling law dominated by pure molecular diffusion to a logarithmic scaling law. The 3D-printed high-throughput microreactor, developed based on the bidirectional symmetric superposition strategy, integrates 78 parallel zigzag channels, yielding total processing throughput two orders of magnitude higher than that of a single channel. A three-stage mixing mechanism

of “convective shearing-chaotic pre-mixing-microscale intensification” is established inside the reactor, enabling efficient and uniform mixing. Nevertheless, individual microchannel inlet velocities follow a “higher-in-the-center, lower-at-the-edges” distribution, and this non-uniformity becomes aggravated as the total flow velocity rises. The single-channel microreactor can significantly intensify the tannic acid-mediated germanium precipitation process. After parameter optimization, a single reactor achieves a germanium precipitation efficiency of 91.81% at a raffinate flow rate of 300 mL, ambient temperature, a 25-fold tannic acid dosage, and an 80%/20% two-stage dosing strategy. When adopting a two-stage serial configuration, precipitation efficiency can be elevated to approximately 98%, realizing deep germanium recovery from raffinate. The microreactor-based process substantially shortens reaction duration while improving reagent utilization efficiency and process selectivity. It offers a feasible technical solution for high-efficiency germanium recovery from zinc hydrometallurgical systems, and lays both theoretical and experimental foundations for the industrial deployment of microreactors in scattered-metal recovery.

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