Convective instability in homogeneous and porous media in the chlorite-tetrathionate system

Thesis of the PhD dissertation

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1   Introduction

The world surrounding us, either the artificial or the natural environment, is in constant motion. The flow of liquids belongs to these motions, like the drift of sea-water or the transportation of oil in a pipe. Hence it is absolutely important for science to precisely investigate the phenomena in which material is transported from one place to another. Diffusion due to concentration gradients, migration of ions in an electric field and convection in the presence of the gravity field of the Earth are the major transport processes in the absence of other external forces.

Convection driven by the density change between two miscible fluids is studied in my dissertation. An autocatalytic reaction is a very good choice for this type of experimental investigation because there is a narrow interface, the so-called chemical front, between the products and the reactants with a constant density difference which depends on temperature and concentration and influences the flow of the liquid.

Pouring a less dense fluid on the top of a more dense one in a vertical tube creates an interface that is hydrodynamically stable. Although when we switch the two liquids, the interface between them also can be stable if the tube is sufficiently narrow; the more dense fluid will descend and the other one will ascend inducing convection in a common situation if the tube sufficiently thick. The number of convection ring describing the phenomenon is increasing with the size of the gap. For a horizontally positioned vessel with a vertical interface between the liquids, the initial planar shape is hydrodynamically unstable for any height and a structure with a single convection roll may evolve for thin layers.

The chlorite-tetrathionate autocatalytic system with hydrogen ion being the autocatalyst was used to investigate the convection evolving from vertically initiated reaction fronts in horizontal vessels. The product solution has a greater density than the reactant under isothermal conditions. Since the reaction is strongly exothermic, the density of the solution decreases locally at the front if thermal effect is not eliminated by using proper thermostating.

Anne De Wit and her co-workers using two-dimensional calculations reported that the characteristic parameter of the profile – the mixing length – is proportional to the square of the liquid layer height, hence one purpose of the present work was to investigate experimentally the validity of this relation. The other aim was to describe the influence of thermal effects and the switching from homogeneous to porous medium on the shape of the front. Finally the three-dimensional flow field of the reaction front was also determined.

2 Experimental

The convective instability was investigated in the chlorite-tetrathionate system and the experiments were carried out in a Hele-Shaw reaction vessel which consists of two parallel Plexiglas plates with a spacer separating them as shown in Fig. 1. The size of the gap and hence the reaction volume, was varied by changing the thickness of the spacer from 1 to 5 mm. The reactant solution was poured into the gap with a pipette. The reaction was initiated with hydrogen ions created electrochemically by using platinum wires. The electrolysis was carried out for five seconds with 3 V potential difference. The same reaction vessel was used in the porous system where borosilicate beads were added with tweezers to create a monolayer close packed medium.
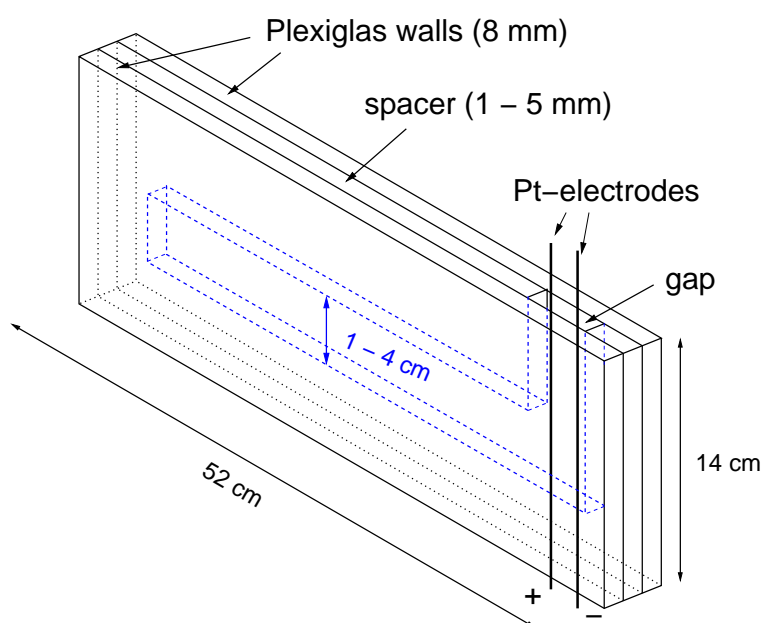

Figure 1: Sketch of the Hele-Shaw vessel.

Experiments at 3 °C were carried out in Hele-Shaw vessel as well: the entire setup was cooled down with a thermostate (Heto HMT 200). The solution was mixed at 3 °C temperature and injected into the pre-cooled cell.

A special experimental setup was constructed to explore the three-dimensional flow field in the chlorite-tetrathionate reaction as illustrated in Fig. 2. The essence of the technique is to place chemically inert particles with micron size and having the same density as the solution into the liquid so the particles will not sediment during the reaction but move along with the flow. The light scattered on the particles is visible hence the flow field can be reconstructed. A laser beam with 532 nm wavelength was used to ensure the sufficiently strong light (Roithner LaserTechnik - CW532-100). The beam was expanded to a sheet with two convex lenses. The

reaction vessel was placed on a table which was precisely positioned before the experiments, hence the light could penetrate into the liquid shining the appropriate layer in it.

Pictures were captured during the experiments with a suitable time resolution using a CCD camera (Sony DFW-X710 és Unibrain Fire-I620b) and were processed later.
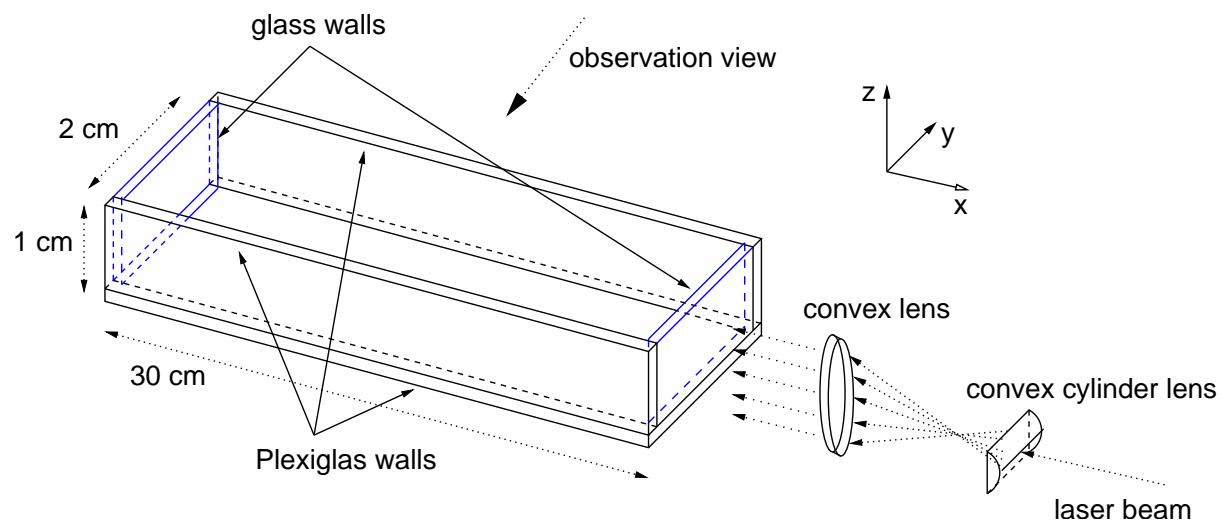

Figure 2: Experimental setup of the particle image velocimetry method.

3 Methods of the evaluation

An in-house software was used in the first step of the evaluation of the pictures which assigned gray scale values to the pixels on the basis of their brightness. We defined the front position as the inflection point of the first derivative of the gray scale value – space function. A low-pass Fourier filter was used in the case of porous system to eliminate the noise with low wavelength caused by scattering from the surface of the beads. The front velocity was calculated from the displacement of the front profile knowing the time resolution of the images.

The average front position was determined as the average of the positions perpendicular to the direction of propagation. The mixing length, defined as the standard deviation of the mean front position, was used to quantitatively describe the shape of the front. The average front profile was another important characteristic of the reaction front, which was calculated by subtracting the average front position from every front position – eliminating the shift of the position in time – and then averaging them in the direction parallel to the propagation.

To determine the three-dimensional flow field, the pictures of the experiments were divided into smaller interrogation windows and the spatial correlation function between these interrogation windows in subsequent images was calculated by using the Fourier-transforms of the gray scale field based on the following relation:

$$f(m,n) \circ g(m,n) \Leftrightarrow F(\xi,\eta)G^{\star}(\xi,\eta), \tag{1}$$

where g and f functions represent the digitized images in time t and $t+dt$, F is the Fourier-transform of f and $G^{\star}$ is the complex conjugate of the Fourier-transform of g. The maximum position of the correlation function determined the displacement associated with the motion in the selected interrogation window. The entire three-dimensional flow field was constructed by using these vectors, knowing the front velocity and the image of the reaction front.

4 New scientific results

I. *The thermal dilatation caused by the exothermicity of the reaction with thickness greater than 3 mm prevented the evolution of a constant shape after initiating a vertical reaction front in a horizontal vessel.* [1]

The density difference induced convection was investigated in the chlorite-tetrathionate autocatalytic reaction system where two different causes are responsible for the hydrodynamic motion. On the one hand the product solution has a greater density than the reactant because of compositional changes, on the other hand the reaction is highly exothermic, hence the density of the solution decreases locally with the increase of temperature. The density changes have opposite signs, therefor double convection is responsible for the evolution of the shape. The increase in temperature by using a liquid layer with 1 or 2 mm thickness is negligible and the solutal density determines the net density change as depicted in part (a) and (b) of Fig. 3. Using a 3 mm thick gap, the exothermicity of the reaction plays a dominant role: the products start to cool down and hence sink following the autocatalytic reaction, resulting in a row of convection rolls as seen in Fig. 3(c).
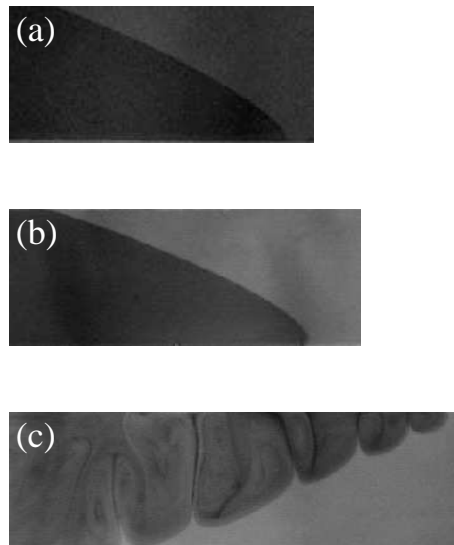

Figure 3: Front in systems with 1 mm (a), 2 mm (b), and 3 mm (c) thick and 4 cm high solution layers at room temperature. Concentrations in the reactant solution: $[K_2S_4O_6]_0 = 5.00$ mmol/L, $[NaClO_2]_0 = 20$ mmol/L, $[NaOH]_0 = 2.5$ mmol/L, and $[\text{congo red}]_0 = 0.057$ mmol/L. The darker color corresponds to the products and the brighter area represents the reactants.

II. *A reaction front with constant velocity and shape evolves in the 3 mm thick chlorite-tetrathionate solution layer after eliminating the thermal dilatation with thermostating the system at 3 °C.* [1]

The chlorite-tetrathionate reaction was carried out under the same experimental conditions like written above, except it was thermostated at 3 °C to verify the shape caused by the thermal effect, as seen in part (c) of Fig. 3. Regarding Fig. 4 , it is well visible that by eliminating the density decrease caused by the thermal dilatation with thermostating the system, the new fronts are in accordance with those expected for isothermal conditions. Although shapes are longer at 3 °C because of the density increase caused by cooling down.
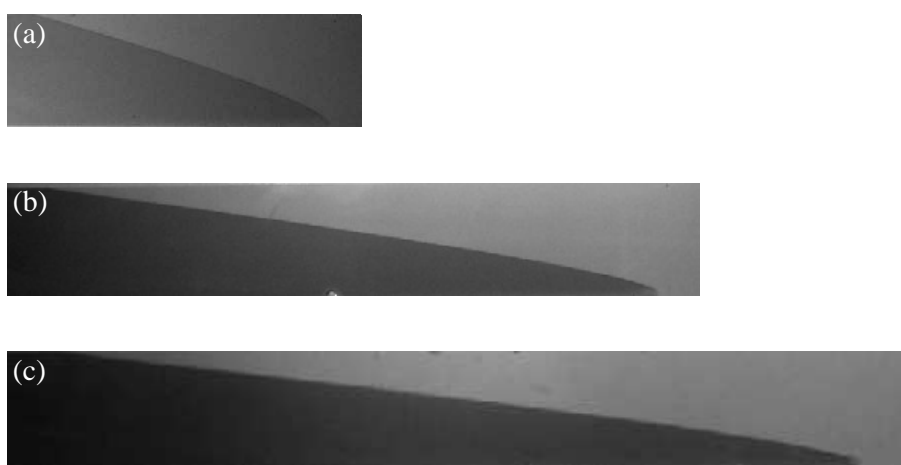

Figure 4: Front in systems with 1 mm (a), 2 mm (b), and 3 mm (c) thick and 4 cm high solution layers at 3 °C. Concentrations in the reactant solution: $[K_2S_4O_6]_0$ = 5.00 mmol/L, $[NaClO_2]_0$ = 20 mmol/L, $[NaOH]_0$ = 2.5 mmol/L and [congo red]$_0$ = 0.057 mmol/L. The darker color corresponds to the products and the brighter area represents the reactants.

III. *A scaling law exists between the mixing length and the vessel height in experiments carried out with different fluid thickness and concentrations using the chlorite-tetrathionate reaction system.* [1] [2]

Anne De Wit and her co-workers using two-dimensional calculations reported that the mixing length (L_m) – defined as the standard deviation of the average front position and used to qualitatively characterize the front – is proportional to the square of the liquid layer height (L_z). A large number of experiments were investigated under systematically modified conditions to verify the relationship between the two attributes. The experiments were carried out with three different initial concentration of potassium-tetrathionate ($[K_2S_4O_6]_0$= 3.75 mmol/L, 5.00 mmol/L, and 6.25 mmol/L), while keeping the ratio $[NaClO_2]_0/[K_2S_4O_6]_0$ = 4. A gap with 1, 2, and 3 mm thickness and 1.0, 1.5, 2.0, 2.5, 3.0, and 4.0 cm height was utilized. It was found that there exists a scaling law which significantly differs from the square function. An example corresponding to the system with composition $[K_2S_4O_6]_0$ = 5 mmol/L is depicted in Fig. 5.
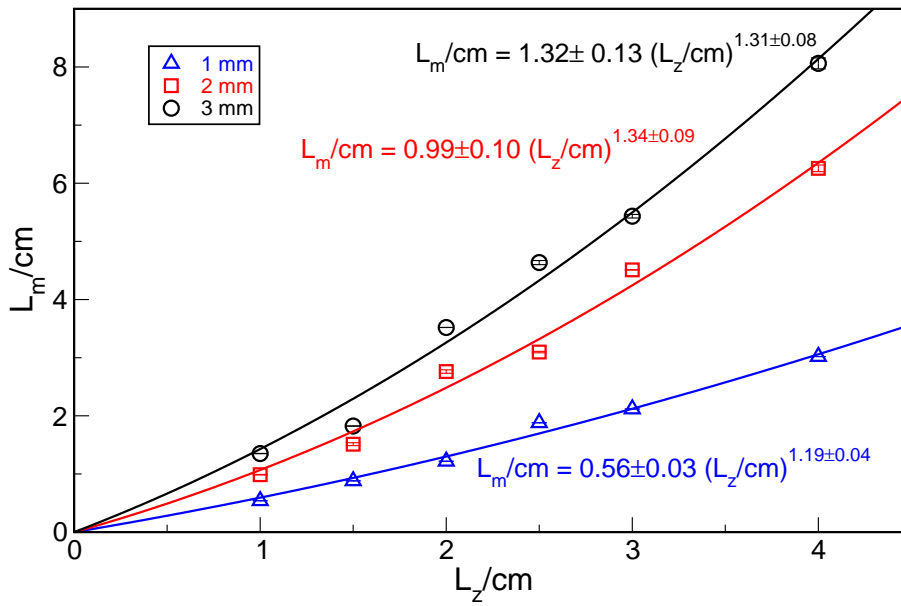

Figure 5: The mixing length as the function of the vessel height for various different thicknesses at 3 °C with $[K_2S_4O_6]_0$ = 5 mmol/L. Solid lines represent the results of the power function fitting.

IV. *A front with constant shape and velocity evolved in porous system around close-packed monolayers which was similar to that observed in homogeneous medium and a similar scaling law was also found.* [3]

The flow of fluids is influenced by porous medium hence the experiments were carried out with different sized borosilicate beads to investigate and characterize the influence of medium on the shape of the reaction. The observed fronts were shorter using porous setup than in the case of homogeneous system and this decrease in the mixing length was caused by the decrease of the effective reaction area. The effect is visible in Fig. 6 where shapes of experiments carried out with the same gap size, temperature and reactant concentration are depicted.
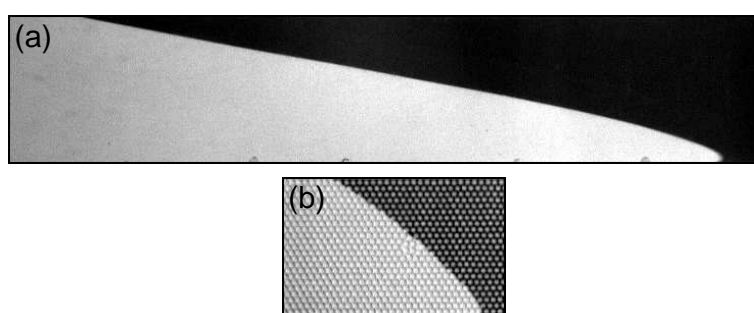

Figure 6: The comparison of the observed shapes in the case of homogeneous (a) and porous (b) media by using a spacer with 4 cm height and 2 mm thickness at 3 °C. Concentrations in the reactant solution: $[K_2S_4O_6]_0 = 5.00$ mmol/L, $[NaClO_2]_0 = 20$ mmol/L, $[NaOH]_0 = 2.5$ mmol/L, and $[$bromophenol blue$]_0 = 0.08$ mmol/L. The brighter color corresponds to the products and the darker area represents the reactants.

The influence of permeability on the shape and the velocity of the reaction front was investigated by using beads with different size. The width of the spacer was equal to the diameter of the bead in every experiment to ensure the close-packed arrangement. It was shown also experimentally and numerically that the porosity of the close-packed, monolayer, porous medium is independent of the bead size. The permeability (inverse of the resistance against the flow caused by the particles) was increased parallel with the bead size, hence the modification of this parameter changed the evolving structure. The exponents and the coefficients of the power function fitting in the case of the mixing length and the front velocity as the function of the vessel height were summarized in Table 1, while the curves belonging to the function of the mixing length were depicted in Fig. 7. The exponents of the functions corresponding to the mixing length are similar within experimental error but the coefficients increase with the bead size so the greater the permeability is, the longer the reaction front is.

Table 1: The coefficients (A) and the exponents (B) in the equation describing the mixing length as the function of vessel height ($L_m = AL_z^B$); the coefficients (C) and the exponents (D) in the equation describing the front velocity as the function of vessel height ($v = CL_z^D$) in experiments carried out with different bead size (d).

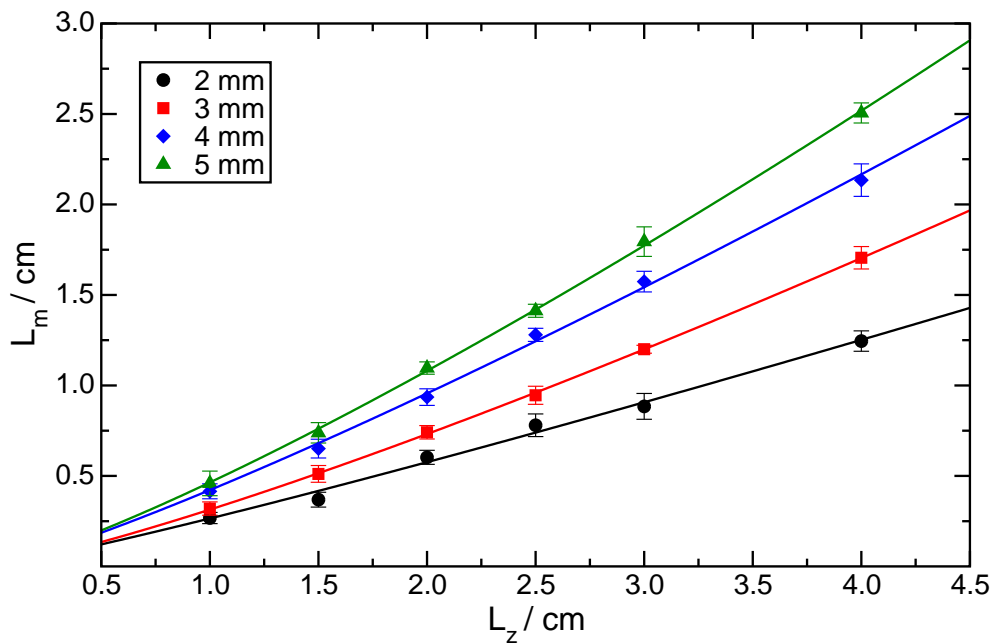| d (mm)	A	B	C	D
2	0.265 ± 0.018	1.12 ± 0.06	0.448 ± 0.007	0.124 ± 0.016
3	0.314 ± 0.005	1.22 ± 0.01	0.536 ± 0.018	0.202 ± 0.035
4	0.422 ± 0.016	1.18 ± 0.03	0.680 ± 0.010	0.203 ± 0.016
5	0.464 ± 0.009	1.22 ± 0.02	0.852 ± 0.034	0.355 ± 0.049

Figure 7: The mixing length as the function of vessel height in porous medium with different bead size at 3 °C. Solid lines represent the results of the power function fitting.

V. *A scaling law depending on the permeability exists between the mixing length and vessel height in heterogeneous media worked up in a gap with different thickness and height.* [3]

Experiments were carried out by using gaps with different size and the observed mixing length was investigated as the function of the permeability. The curves of the power functions fitted in the case of various spacer size could be summarized with the following equation

$$L_m/cm = (0.20 \pm 0.01)\,(L_z/cm)^{1.20 \pm 0.02}\,(K/10^{-9}m^2)^{0.30 \pm 0.02} \qquad (2)$$
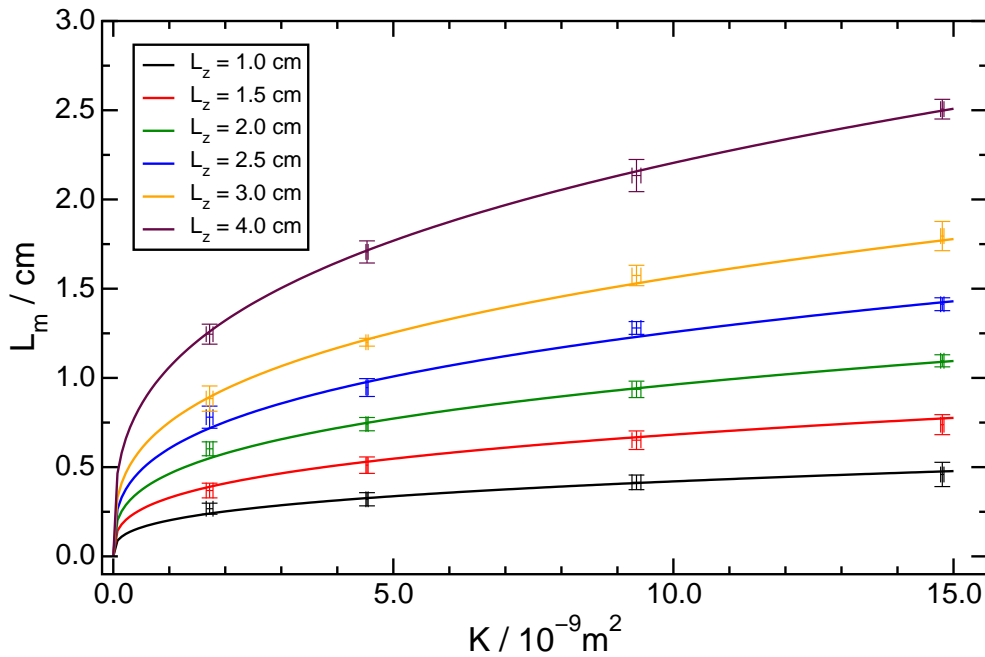
and those are illustrated in Fig. 8.

Figure 8: The mixing length (L_m) as the function of permeability (K) for various vessel heights. Solid lines were fitted with equation (2).

VI. *A strong upward flow evolves behind the tip of the front in a 20 mm thick chlorite-tetrathionate reactant solution which brakes up the structure in a direction perpendicular to the motion of the liquid.*

The solution was illuminated in different layers during the subsequent experiments and the vectors of the motion were placed in the appropriate position. The velocity, the top view of the front and the distance of the light sheet from the container wall were used to create the entire three-dimensional flow field of the reaction, as shown in Fig. 9. At the walls, the convection ring is very long and the downward flow is short and strong at the tip of the front, while the upward flow is much weaker and longer. Farther from the sides, the ring becomes shorter and stronger at the tip of the profile hence the medium moves upward strongly near behind the front. A second convection ring evolves in the middle of the convection area which rotates in the same direction as the first one and forms a V shaped cusp.
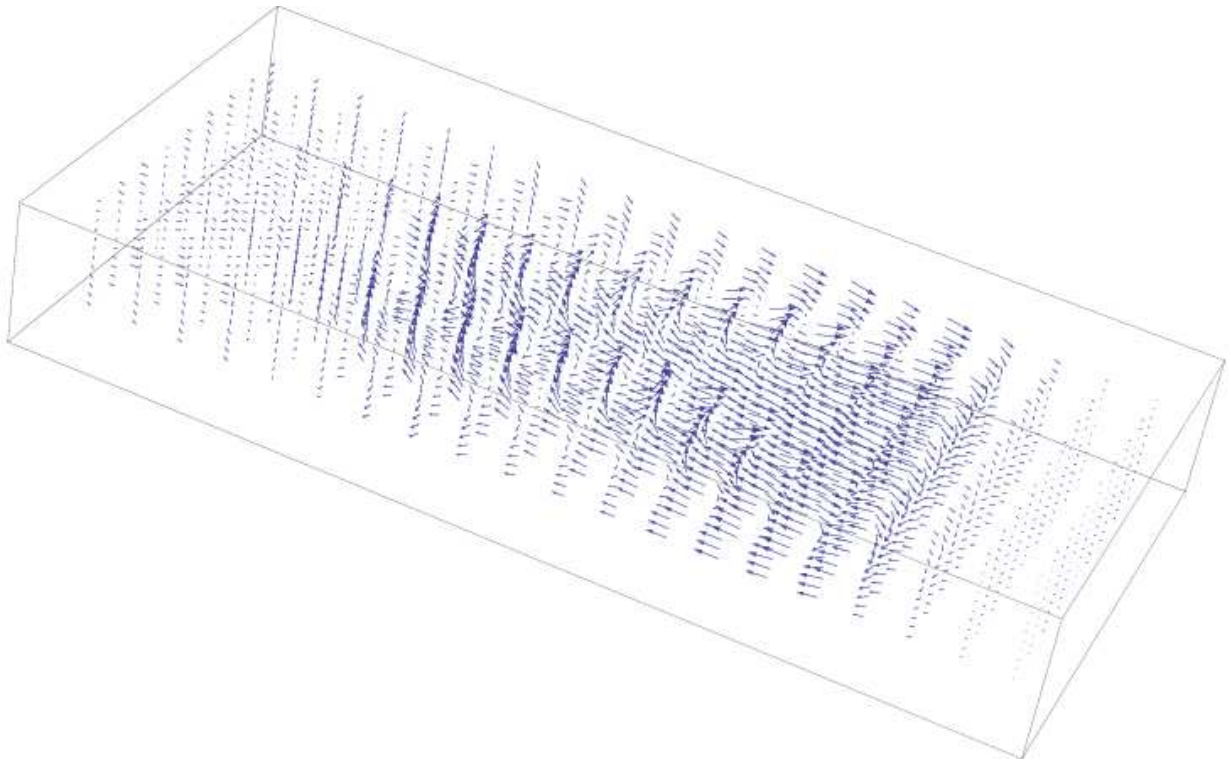

Figure 9: A three-dimensional flow field in the chlorite-tetrathionate reaction. The depicted structure is 6,3 mm high, 16 mm thick, and 41 mm long.

5 Publications related to the dissertation

1. Rongy, L; Schuszter, G; Sinkó, Z; Tóth, T; Horváth, D; Tóth, Á; De Wit, A,

   Influence of thermal effects on buoyancy-driven convection around autocatalytic chemical fronts propagating horizontally

   Chaos, **19**, 023110 (2009). (IF=1.795)

2. Schuszter, G; Tóth, T; Horváth, D; Tóth, Á,

   Convective instabilities in horizontally propagating vertical chemical fronts

   Physical Review E, **79**, 016216 (2009). (IF=2.400)

3. Schuszter, G; Horváth, D; Tóth, Á,

   Convective instabilities of chemical fronts in close-packed porous media

   Chemical Physics Letters, **546**, 63-66 (2012). (IF=2.337)

$\sum_{IF} =$ **6.532**

6 Lectures and poster presentations related to the dissertation

1. Tamara Tóth, Gábor Schuszter, Zita Sinkó, Dezső Horváth and Ágota Tóth

   Scaling law of stable single cells in density fingering of chemical fronts

   Gordon Research Conference on Oscillations and Dynamic Instabilities in Chemical Systems, Waterville, USA, 2008. (poster)

2. Gábor Schuszter, Dezső Horváth and Ágota Tóth

   A konvektív instabilitás vizsgálata pórusos közegben

   XXXIV. Kémiai Előadói Napok, 2011. (lecture in Hungarian)

3. Gábor Schuszter, Dezső Horváth and Ágota Tóth

   A konvektív instabilitás vizsgálata pórusos közegben

   MTA RKFMB, Gyöngyöstarján, 2011. (lecture in Hungarian)

4. Gábor Schuszter, Dezső Horváth, Ágota Tóth

   Convectice instability in horizontally propagating reaction fronts

   ESA Topical Team meeting on Chemo-hydrodynamic Patterns and Instabilities, Brussels, 2012. (lecture)

5. Gábor Schuszter, Dezső Horváth, Ágota Tóth

   Convectice instability in the three-dimensional chlorite tetrathionate system

   ESA Topical Team meeting on Chemo-hydrodynamic Patterns and Instabilities ülés, Brüsszel, 2013. (lecture)

6. Gábor Schuszter, Dezső Horváth, Ágota Tóth

   Convectice instability in the three-dimensional chlorite tetrathionate system

   Solvay workshop on Patterns and hydrodynamic instabilities in reactive systems, Brüsszel, 2013. (poster)

7. Gábor Schuszter, Éva Pópity-Tóth, Eszter Damásdi, Edit Pengő, Ágota Tóth and Dezső Horváth

   Háromdimenziós áramlási profil meghatározása a klorit-tetrationát autokatalitikus reakcióban

   XXXVI. Kémiai Előadói Napok, 2013. (lecture in Hungarian)

7 Publications not related to the dissertation

1. Rica, T; Schuszter, G; Horváth, D; Tóth, Á,

   Tuning density fingering by changing stoichiometry in the chlorite-tetrathionate reaction

   Chemical Physics Letters, **585**, 80-83 (2013). (IF=2.145)

8 Lectures not related to the dissertation

1. Gábor Schuszter and Noémi Laufer

   Oldószerpárolgás hatása szén nanocsőfilmek elektromos ellenállására

   XXXV. Kémiai Előadói Napok, 2012. (lecture in Hungarian)

2. Gábor Schuszter and Noémi Laufer

   Oldószerpárolgás hatása szén nanocsőfilmek elektromos ellenállására

   MTA RKFMB, Gyöngyöstarján, 2012. (lecture in Hungarian)

3. Eszter Tóth-Szeles, Tamás Bujdosó, Bíborka Bohner, Gábor Schuszter, Dezső Horváth and Ágota Tóth

   Horizontally growing precipitation patterns in flow-driven systems

   Chemical Gardens conference, Leiden, Netherland, 2012. (poster)

4. Eszter Tóth-Szeles, Tamás Bujdosó, Bíborka Bohner, Gábor Schuszter, Dezső Horváth and Ágota Tóth

   Horizontally growing precipitation patterns in flow-driven systems

   Gordon Research Conference on Oscillations and Dynamic Instabilities in Chemical Systems, Waterville, USA, 2012. (poster)

5. Eszter Tóth-Szeles, Tamás Bujdosó, Bíborka Bohner, Gábor Schuszter, Dezső Horváth and Ágota Tóth

   Horizontally growing precipitation patterns in flow-driven systems

   Emergence in Chemical Systems 3.0 conference, Anchorage, Alaska, 2013. (poster)

6. Szabolcs Muráth, Gábor Schuszter and Ágota Tóth

   Kezdő lépések a réteges kettős hidroxidok képződési mechanizmusának felderítésére

   XXXVI. Kémiai Előadói Napok, 2013. (lecture in Hungarian)