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Review of the Doctoral Dissertation titled

'Self Organization of Flow in Dissolving Rocks' by Rishabh Prakash Sharma, M.Sc.,

realised in the Faculty of Physics of the University of Warsaw
under the supervision of dr hab. Mariusz Białecki (Institute of Geophysics PAS)
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Pattern formation is ubiquitous in nature with links to physics, chemistry, biology, and computer science. While observed patterns may seem chaotic and random, they are influenced by a range of parameters (e.g. concentrations of chemical gradients, temperature, etc.), which, in turn, determine the interplay between the physical system and its environment. Understanding emerging patterns in physical systems is on its own right an important scientific area, since they are fundamentally intriguing, while control of their static and dynamic properties can directly be exploited in relevant applications. However, in view of the complexity of pattern-formation processes, due to the wide temporal and spatial scales involved, a multifaceted approach for their in-depth understanding is necessary, which can be based on mathematical modelling along theory and multiscale simulations as convenient scientific approaches to describe underlying instabilities that often dictate the formation of these patterns, as well as laboratory experiments in controlled environments. In this doctoral dissertation, both approaches are employed to describe *the self-organisation of flow in dissolving rocks*.

Chemical erosion leading to the so-called dissolution patterns are observed in various contexts, for example, in karst caves, dolines, sinkholes, kasrst funnels, and wormholes. In the case of such formations, it is known for the last decades that the interplay between reaction and transport as the reaction front advances along a flow direction creates complexities that arise from the occurrence of the so-called reaction–infiltration instabilities. In turn, this leads to the creation of fingers in a self-amplifying manner in phenomena appearing both at smaller (e.g. centimetre, redox fronts in siltstones) and larger (e.g. kilometre, uranium rolls) length scales. Not only are these instabilities important from a fundamental standpoint, but, also, they are relevant for applications as many engineering processes depend on them, such as CO_2 sequestration and reservoir stimulation. Here, wormholes are known representative examples of dissolution patterns and a main theme of the dissertation, which are based on the coupling of flow rate, reactive transport, and evolving geometry of the formed channels. Importantly, these have direct implications for the oil extraction industry, since they provide efficient stimulation of a reservoir through the formation of self-organized flows bypassing the rest of the medium. Moreover, for specific conditions, dominant wormholes appear, which minimise the amount of reactant required to increase permeability of the sample and thus are of particular interest for petroleum industry. Other applications relate to controlling contaminant migration or preventing CO_2 leakage during geological carbon sequestration. In these contexts, understanding the growth dynamics, shape, and morphology of the emerging patterns is crucial for improving the related engineering processes. Research in the area has underlined that shape and geometrical properties of the dissolution patterns rely on the flow through the system and the reactive rate of the reactive fluid, as well as system's parameters, such as its length and heterogeneity.

Despite progress, fully understanding such complexities has remained challenging, especially those concerning the role of rock heterogeneity and pore-scale mixing process, which are expected to affect the shape and growth dynamics of the patterns and are addressed in this doctoral dissertation. Lack of knowledge in this area were partly due to the fact that studies were often limited to visual observations of these processes, technological limitations regarding acquisition times, or limited data on the evolution of the dissolution patterns. While recent advances have provided further insights into the growth dynamics, more research to unveil the geometrical characteristics and role of inhomogeneities (e.g. vugs, packed regions) is required, for which one needs to consider a wide range of factors, such as micro-cracks, fractures, and voids. These can be the source of processes at micro- and macro-scales that are nonlinearly coupled and are crucial for understanding the growth and evolution of large-scale dissolution patterns. These aspects together with others discussed below have been specifically tackled in the doctoral dissertation.

The doctoral dissertation of Rishabh Prakash Sharma, M.Sc., deals with these complexities that are crucial for providing a coherent description of dissolution patterns, especially for wormholes. However, before delving into the details of how this is achieved and specific conclusions drawn in the dissertation, I would like to state that *this is an excellent thesis both in its scientific merits and presentation, which brings new knowledge in an important scientific area with direct implications for technological applications. The obtained results are of high quality and presented in a clear manner with proper credit given where and when due. The results were obtained in a rigorous manner and any limitations related to the methodologies have been clearly discussed. Moreover, appropriate research paths overcoming these challenges have been taken, when necessary, thus in specific cases leading to new methods that will also potentially impact other fields. These merits make this thesis a valuable scientific resource on the research topic of the dissertation and a robust basis for further scientific research in this direction.*

The dissertation is characterised by a clear and suitable structure and is organised in seven chapters. The first three of them provide introductory and background material relevant for the discussion of the results. Then, the subsequent three chapters present the research results of the dissertation, while the last chapter summarises the main conclusions and research achievements. Chapter 1 provides introduction into the topic of the dissertation, Chapter 2 discusses the physics of patterns and related theoretical concepts and experiments, while Chapter 3, the modelling of dissolution processes (i.e. related to the numerical framework employed in Chapter 6). Broadly, Chapter 4 contains results on pore-geometry changes of limestone due to natural dissolution, Chapter 5 is about the influence of rock characteristics and flow rates on the evolution of wormhole shape and geometry, while Chapter 6 focuses on the effect of micro-scale mixing process on large-scale dissolution patterns. The latter three chapters are based on the research articles mentioned on p. iii of the dissertation. Three of these articles have already been published in highly regarded in the field peer-reviewed journals, such as Geophys. Res. Lett., Chem. Geol., and Adv. Water Resour., while one article has been submitted to Geophys. Res. Lett. In two of these articles, Rishabh Prakash Sharma, M.Sc., is the first (two of the published articles) or second author (one published and one submitted). Their contribution has been clearly described in two of the publications appearing in Adv. Water Resour., 2023, and Geophys. Res. Lett., 2023, while in the article in Chem. Geol., 2022, Rishabh Prakash Sharma, M.Sc., is the first author. Chapter 5 contains a significant number of unpublished results obtained by the Author. This clearly indicates the dominant role of the Author in the execution of the research tasks related to the dissertation.

Chapters 1–3 take the reader from an introduction to the world of pattern formation (for the layman), providing a wealth of relevant examples in nature (also, those used by the author in their research), outlining the richness and possibilities of observed patterns, and introducing concepts relevant for the topic of the dissertation, to main physical concepts required to describe the patterns (e.g. reactive – infiltration instability, relevant dimensionless numbers, penetration length, dissolution patterns in experiments, permeability evolution in dissolving system, and others), and finally numerical models. The latter described in Chapter 3 refer to three categories of dissolution models, covering from micro to continuum scales, i.e. pore-scale, continuum-scale, and pore network models. The models have been adequately described and their advantages and disadvantages have been properly presented in the dissertation. Choosing network models in the research described in Chapter 6 has been adequately rationalised. In summary, Chapters 1 – 3 contain appropriate literature (appropriate literature is cited properly across the dissertation) in the area and all the necessary, background information required for the presentation of the dissertation results in the subsequent chapters. This has been done eloquently, succinctly, and accurately, which is an additional strength of this dissertation.

Chapter 4 presents original results that have been obtained within the frame of this research and have also been discussed in P. Sharma et al. Chem. Geol. 627, 121397 (2023). It deals with changes of pore geometry of collected limestone samples from karstified area (same host) during natural dissolution focusing on mechanisms, such as pore-enlarging, merging, or the combination of both. This is achieved by carrying out a comparative study of undissolved and karstified limestone taken as described in Fig. 4.1 of the doctoral dissertation, as well as a numerically eroded sample, which serves as a reference for homogeneous dissolution. Challenges in characterising these samples of high porosity, such as the irregular geometry of pores, have been overcome in the dissertation research by using geometrical and topological characteristics developed for bone research (e.g. by using the BoneJ plugin of ImageJ), which are properly introduced in Section 4.3. Moreover, analytical models have been employed and integrated with the data analysis of x-ray micro-tomography images, which have allowed for quantifying the pore-merging and inhomogeneous dissolution in the natural dissolution of the studied samples. Also, Lattice Boltzmann simulations have been carried out to estimate properties, such as permeability, tortuosity, and velocity distribution. The results presented in this chapter have been obtained by carefully following well-defined methodologies and protocols that allow for a fair comparison between the samples. This approach was crucial and has led to several important conclusions. Most importantly, one key mechanism of dissolution is merging of the pores with an increased thickness that can even be equal to the sum of thicknesses of the constituents in extreme cases. Moreover, a decrease in tortuosity of the flow paths and the increase of the fraction of the faster flow in the sample reflect a strong flow focusing of dissolution in larger pore spaces, which can be explained by the uniform channelling regime with the emergence of preferential pathways that link the regions of the highest local permeability. These and other conclusions are well supported by the data, which were carefully obtained and analysed.

Chapter 5 contains results that have been published in Cooper, Sharma, et al., Adv. Water Resour. 175, 104407 (2023). Here, experiments have been conducted on two different limestones (each from a different quarry, Pińczów and Wierzbica, and with a different porosity, Table 5.1) with a dominant role of the Author related to the image analysis. Hence, additional results based on a range of sophisticated image processing and analysis methods and properties (also, proposed methods, e.g. length wastefulness, which is a generalisation of the tortuosity for a branched structure) have been presented in the dissertation in comparison with the related publications, specifically methods to better identify evolving wormholes (also, in the form of skeletons and networks) and their analysis by using different (Python) codes and visualisation software. These together with their advantages and limitations have been described in detail in the dissertation and provide significant insights on the characteristics and time evolution of the wormholes in the samples. Explanations related to strategies and research decisions/aspects have been properly provided. Among many important results, the Author highlights the importance of tortuosity/length wastefulness as a metric for characterising (differentiating between) wormhole structures (e.g. Fig. 5.20), including post-experiment wormholes. Moreover, the Author has presented a novel data analysis for investigating dynamics of wormholes in dissolving limestone rocks to extract their shapes from tomography images. These have provided new insights into how rock structures and injection rates can affect the shape of the wormholes. An important conclusion from observing the tip propagation velocity is that regions with large structures (e.g. impermeable fossils) act as barriers to reactive flow, while it is numerically confirmed that the tip velocity increases once the wormhole penetrates such barriers. While the number of samples for carrying out the investigations is limited, the results of this research can be generalised to all Pińczów and Wierzbica samples, since the authors have taken all possible measures to remove bias, which is a strength of the research discussed in this dissertation.

Chapter 6 is based on Sharma et al., Geophys. Res. Lett. 50, e2023GL105183 (2023) and deals with the effect of mixing at pore intersections on large-scale dissolution patterns. This is an important aspect as it controls the transport of reactants at pore surfaces and the reactions induced by mixing processes. Here, the Author describes coarse-grained mixing rules to quantify the degree of mixing at intersections (pore network model, rhombic with four branch intersections that also takes into account heterogeneity), beyond traditional models (diffusion dominated) that consider a full mixing of reactant concentrations at pore-intersections, by additionally assuming streamline routing (advection dominated). This has been inspired by previous work by Kang et al. (Ref. [62] of the dissertation). Results in this chapter mainly provide a quantitative and qualitative comparison of dissolution patterns based on both types of mixing, as well as the effect of the interplay between mixing and network heterogeneity on the patterns and associated underlying mechanisms. From the point of view of applications, the breakthrough comparison is important for petroleum reservoir stimulation, since the amount of reactant required is an important parameter for breakthrough. The dissertation here draws several important conclusions. The mixing process at pore intersections is essential and affects the shape and propagation velocities of the formed dissolution channels in the unstable regime. When the reactant follows the streamline, the breakthrough time is reduced, which is more pronounced in the case of intermediate effective Damköhler (Da_{eff}) numbers (similar reactive and advective time scales). On the one hand, at lower Da_{eff} values, there is a uniform concentration or reactant and therefore the mixing rules do not matter. On the other hand, when is Da_{ef} higher than intermediate values, the wormhole tip focuses a very large flow and reactant concentration, which, combined with the short penetration length, reduces the mixing effect. As the initial heterogeneity of the pore space increases, the coupling between mixing rules and dissolution patterns is suppressed.

In summary, the research described in the dissertation concerns the investigation of dissolution patterns in porous rocks by using a combination of experimental (image-analysis), numerical, and theoretical methods unveiling the coupling between micro-scale processes and the macro-scale evolution of the formed patterns. It deals both with static and dynamic properties, as well as with both naturally karstified and experimentally altered environments. The dissertation has measurable outcomes and concrete achievements, which have been listed in Chapter 7. These clearly contribute to enhancing our understanding about the fundamental physics of reactive flow instabilities, pore-scale transport phenomena, and the formation of self-organised dissolution patterns. Beyond these fundamental aspects, the dissertation has direct implications for applications and specifically for geology and petroleum engineering, since it unravels the role of heterogeneities in wormholes. These also extend to similar systems with unstable growth for applications such as groundwater remediation and geological carbon storage. The research described in the dissertation has also provided us with methods for extracting and analysing dissolution pattern shapes, potentially impacting other research fields where these may be applicable.

The doctoral dissertation of Rishabh Prakash Sharma, M.Sc, has no specific weaknesses that would require further clarifications, other than inherent limitations of certain methods. To overcome these, the Author has taken appropriate steps by employing a range of different methods for realising the (numerical/simulation/physical) experiments and their analysis and has followed alternative pathways, while relevant discussion and context are provided in the dissertation wherever this was necessary. Finally, proper interpretation of the results has been provided in the dissertation. All these aspects taken together with the research impact of this dissertation briefly described above clearly point to its high-quality and that *this dissertation deserves distinction.*

Concluding, the doctoral dissertation of Mr Rishabh Prakash Sharma, M.Sc., meets the statutory and customary requirements for doctoral dissertations. I have no reservations to highly recommend that Rishabh Prakash Sharma, M.Sc., be admitted to the next stages of the doctoral process.

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