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Review

Unlocking the Potential of Microbially Induced Calcium Carbonate Precipitation (MICP) for Hydrological Applications: A Review of Opportunities, Challenges, and Environmental Considerations

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Abstract: Microbially induced calcium carbonate precipitation (MICP) is an innovative biocementation technique that facilitates the formation of calcium carbonate within a pore network. Initially gaining prominence in the field of geotechnical engineering, MICP has attracted significant attention since its inception (the last three decades) and expanded its reach across various engineering disciplines. Examples include rock mechanics, geology and the oil and gas industry fields through the generation of rock-like specimens, and plugging of fractures, in civil and architectural engineering and material science for concrete repair, protection, and for self-healing of building materials, and in environmental engineering for the study of biomimetic materials. In response to this burgeoning interest, the current paper aims to present a comprehensive review of the main biochemical mechanisms underlying MICP (bacterial ureolytic activity, reactions duration and settling times, and chemical solution properties), their direct relevance to altering hydraulic and mechanical properties, both at the microscale and macroscale responses, and the precipitation mechanisms, particularly in relation to water resources and hydrology applications. Four main categories of relevant applications are identified, namely, the groundwater and soil remediation, the applications related to the generation of a low hydraulic conductivity barrier, those related to gaining cohesion, and the applications related to fluid flow studies in artificially generated porous media. Moreover, this comprehensive review not only aims to identify the existing applications of MICP within hydrological fields but also strives to propose novel and promising applications that can further expand its utility in this domain. Along with the investigation of the potential of MICP to revolutionize water resources and hydrology, it is imperative to delve deeper into its environmental implications to ensure sustainable and ecologically responsible implementation.

Keywords: MICP; biocementation; hydraulic conductivity; porosity; strength; water resources; contaminant hydrology

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1. Introduction

Microbially induced carbonate precipitation (MICP) refers to a natural biochemical phenomenon wherein micro-organisms stimulate the formation of calcium carbonate precipitation. Microbes trigger the formation of carbonate precipitation through various metabolic pathways, including photosynthesis, ureolysis, ammonification, denitrification, sulfate reduction, anaerobic sulfide oxidation, and methane oxidation. These pathways involve mechanisms that raise pH levels and increase the presence of dissolved inorganic carbon (DIC) [1]. Biocementation techniques having MICP as the underlying biochemical mechanism responsible for calcium carbonate generation are widely employed to achieve various outcomes with the main aim usually being the solidification of sand. The precipitating calcium carbonate forms the bonding material between particles. The key metabolic pathway is the one of urea hydrolysis, which is used in most relevant studies. The process involves three distinct stages: (i) introduction of bacteria into the medium, followed by (ii) the injection of a cementation solution containing urea and a calcium source, which (iii) results in the precipitation of the cementing agent that binds the sand particles, leading to an increase in both strength and stiffness [2,3].

It is described by two chemical equations, the first of which (see chemical Equation (1)) involves the hydrolysis of urea, which is a slow and irreversible reaction influenced by pH and various environmental conditions. The reaction results in the release of ammonium ions (NH^{4+}) and carbonate ions ($CO_3{}^{2-}$) in the form of inorganic carbon. The presence of ammonium ions leads to a rise of the pH of the solution due to their basic nature. The elevated pH creates an environment conducive to calcium carbonate precipitation. The carbonate ions, on the other hand, are essential for MICP. Urea hydrolysis, therefore, is considered one of the most effective reactions for MICP since it increases the alkalinity and concentration of dissolved inorganic carbon in the solution, as explained before. Then, as a result of the pH elevation, the carbonate ions react with the available calcium ions in the environment (see chemical Equation (2)), leading to precipitation at particle contacts. The reaction is enhanced within the alkaline environment and in the presence of inorganic carbon, and it occurs when the solution becomes supersaturated. Supersaturation can be achieved by introducing ionic salts that act as reactant sources, such as Na_2CO_3 and $CaCl_2$ [4].

$$CO(NH_2)_2 \rightarrow 2NH_4{}^{+} + CO_3{}^{2} \tag{1}$$

$$CaCl_2 + CO_3{}^{2-} \rightarrow CaCO_3 + 2Cl^{-} \tag{2}$$

Figure 1 serves as a comprehensive visual representation that intricately illustrates the step-by-step progression of the MICP process. Beginning with the introduction of bacteria into the medium, enzymatic action takes place whereby urea is hydrolyzed by the micro-organisms. This enzymatic activity yields ammonium ions (which, in turn, elevates pH) and carbonate ions as products. Positively charged calcium ions are attracted to the negatively charged bacterial walls, leading to the precipitation of calcium carbonate ($CaCO_3$) in solid form due to the alkaline environment and supersaturation around the cells. This precipitate formation is facilitated by the alkaline environment brought about by the elevated pH and the saturation of calcium and carbonate ions. Once the desired amount of calcite is achieved, the nutrition is halted, causing bacteria to die. As depicted in the MicroCT image in Figure 1, rock-like materials are generated which preserve to a great extent their pore network, and the calcium carbonate is found within this pore network or on and around the grains.

The carbonate precipitation involves several processes, including nucleation, transformation, and crystal growth. The reaction can produce different forms of calcium carbonate, including transformable (calcium carbonate forms that can undergo changes in their crystalline structure over time), unstable (forms that are not thermodynamically favored and can, eventually, transform into more stable structures), and stable forms (which represent the thermodynamically favoured, enduring configurations of calcium carbonate), depending on the specific conditions of the reaction (e.g., rhomboidal or amorphous calcite, vaterite, etc.). The specific form of calcium carbonate produced through MICP can impact the physical properties of the solidified material. For instance, some forms might have greater hardness or compressive strength than others. Also, stable forms of calcium carbonate are less prone to further transformations over time, making them more enduring and resistant to changes in environmental conditions while unstable forms are likely to undergo phase transformations, which could affect the stability and longevity of the solidified material.

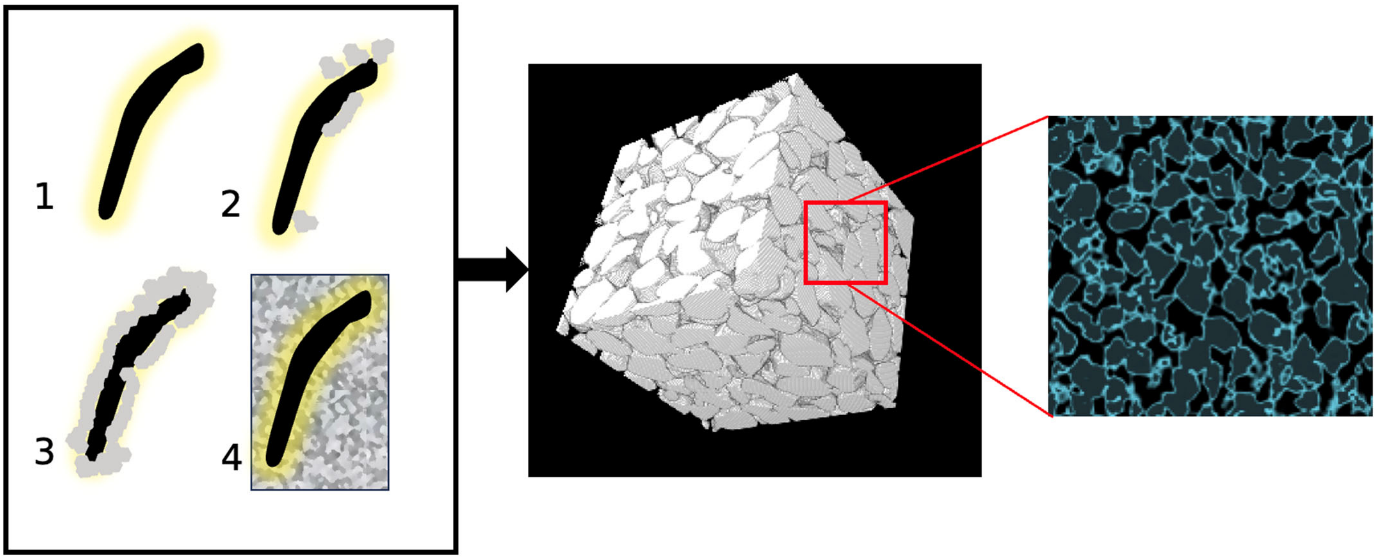

Figure 1. The biologically induced calcite process in sand [5]. 1. Bacteria hydrolyse urea to raise the pH of the system. 2–3. Cations are attracted to bacteria due to their negative-charged wall. The alkaline environment formed and the supersaturation around the cells results in the calcium carbonate precipitation into solid form. 4. Cement nucleates around bacterial cells within the pore space of the granular network. An example of a MicroCT image is shown with cementation highlighted in blue.

According to Rahman et al. [6], the method finds its routes in the work by Gollapudi et al. [7] back in 1995 aiming at controlling leaching of groundwater contaminants. Then, in 1999, Stocks-Fisher et al. [8] assessed the properties of the carbonate crystals resulting from MICP. In 2004, Whiffin [9] proposed the method for soil improvement and, then, the method received great interest in the field of geotechnical engineering involving even the upscaling of the process [10]. Initially employed for purposes like stabilizing soil against sliding, preventing liquefaction (prohibiting the onset of fluidized behaviour of cohesionless soil during dynamic loading), and erosion (prevention of movement, and transportation of soil particles by various external forces), microbially induced carbonate precipitation (MICP) has been extensively studied and applied in various fields imitating sedimentation processes and resembling natural geological formations with pore-filling carbonate cements [11,12]. Its applications include strengthening of soils to improve their mechanical properties with applications in tunneling to avoid wall collapsing and cave-ins during excavation, foundation engineering, self-healing of cracks in concrete and rocks restoring the structural integrity, and to reinforce methane hydrate layers beneath the deep-ocean floor during the depressurization process when producing methane gas, reducing the risk of destabilization during gas extraction [13–19]. In recent times, MICP has also found new applications in areas related to ocean and marine engineering like providing erosion resistance against wave actions, preventing corrosion in marine environments, and contributing to the construction of ocean islands and reefs, showcasing its adaptability and potential in addressing a range of challenges unique to aquatic environments [20–22].

MICP could find many applications in the fields of water resources and, specifically, for hydrologic applications. Several of these applications, such as groundwater and soil decontamination, have already been suggested in existing literature. These could be classified based on the various underlying MICP mechanisms and the fundamental target for each application, as shown in Figure 2. The classification includes four groups: (i) groundwater and soil remediation, (ii) generation of a low hydraulic conductivity barrier for inhibiting fluid transport, (iii) gaining cohesion to inhibit particles movement along with fluids, and (iv) for generation of porous media of controlled mechanical and hydraulic properties that could be used in fluid flow studies. The first application involves MICP pathways for remediation while the second and third applications are based on the hydraulic and mechanical properties alteration via MICP. Finally, the fourth application is routed on the combination of hydraulic and mechanical properties alteration.

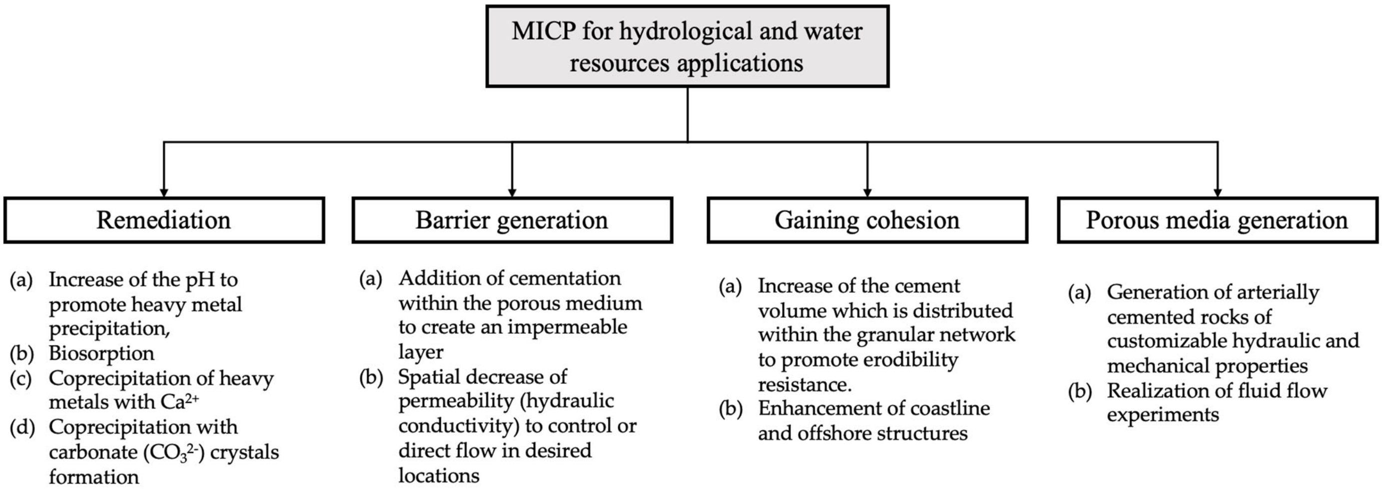

Figure 2. The MICP underlying mechanisms and the fundamental target for each application.

In this review, a comprehensive examination of the diverse applications of MICP in the fields of hydrology and water resources is presented. The objectives of this work are: (i) the identification of the relevant MICP mechanisms that play a potentially important role in hydrologic applications, (ii) the presentation of studies that have been utilizing MICP for such applications, (iii) the presentation of studies that have been utilizing MICP for applications that share fundamentals with those relevant to this study, (iv) the proposal of new MICP applications in hydrology and water resources fields that are near realization, and (v) the investigation of various potential environmental impacts.

The structure of this paper is as follows: first, the underlying mechanisms are given in Section 2 (bioremediation via MICP) and Section 3 (mechanical and hydraulic properties alteration) which are fundamental principles of the processes related to the presented applications. Then, in Section 4, the various applications are shown based on the classification made in Figure 2. A review is made on already proven cases, while opportunities for further research and new areas are investigated. The review highlights areas where further research is needed, discusses the challenges encountered, and outlines potential future directions for utilizing MICP in various applications. Finally, in Section 5, a summary of the challenges that could be experienced when moving forward, and the environmental issues are presented.

2. Bioremediation via MICP

Bioremediation through MICP stands as a significant and promising approach in tackling environmental contamination challenges since it mimics natural processes, it is versatile as it can be applied to a wide range of contaminated environments, including soil and groundwater, it has minimum environmental footprint, and is less costly and energy-intensive compared to other remediation techniques (e.g., chemical precipitation, adsorption, ion exchange, and membrane separation). This section reviews the biocementation pathways of MICP which are the underlying principles behind it. That is, MICP can be used to solidify and immobilize contaminants, particularly toxic metals, through various precipitating mechanisms. It offers an effective means to transform hazardous pollutants into stable, less mobile forms, thus preventing their migration and potential harm to the environment and human health.

The main mechanism that relates to this group of applications (Figure 2—remediation) is the solidification of contaminants. This can be succeeded via the increase in the pH (typically achieved by the release of ammonia ions) to promote (i) heavy metal precipitation, (ii) biosorption, and either (iii) coprecipitation of heavy metals with Ca^{2+} or (iv) copre cip itation with carbonate (CO_3^{2-}) crystals formation [23]. The four pathways might coexist. For example, Jiang et al. [24] suggested that Pb immobilization involves abiotic and biotic precipitation, as well as biosorption. The coexistence of various combinations of pathways has been reported in other studies also [25–27].

The toxic metal mineralization through MICP relies on ureolytic bacteria secreting urease to break down urea and the products are NH_3 and CO_2 (chemical Equation (3)). Following this, these substances reach a state of equilibrium within the solution, resulting in the creation of bicarbonate, ammonium, and hydroxide compounds (see Equations (4) and (5)) leading to an increase in both the alkalinity and carbonate levels. Finally, the formation of calcite is induced, with bacterial cells acting as the nuclei in an environment with high Ca^{2+} concentrations. In the presence of adequately active divalent cations, the carbonate has the potential to undergo precipitation from the solution and, therefore, toxic metals are mineralized by coprecipitation with carbonate (CO_3^{2-}) crystals, as shown in chem ical Equation (6) [28]. The letter M in chemical Equation (6) denotes heavy metals (HMs).

$$(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2 \tag{3}$$

$$2NH_3 + 2H_2O \rightarrow 2NH_4^+ + 2OH^- \tag{4}$$

$$CO_2 + 2OH^- \rightarrow HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \tag{5}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\ (\downarrow) + M\ (HMs) \rightarrow MCO_3\ (\downarrow) \tag{6}$$

$$xM^{2+} + (1-x)Ca^{2+} + CO_3^{2-} \rightarrow Ca_{(1-x)}M_xCO_3\ (s) \tag{7}$$

Throughout MICP and in the case of calcium sites substitution, heavy metals containing divalent ions like Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+}, Co^{2+}, Fe^{2+}, and Ni^{2+} replace Ca^{2+} ions, leading to the formation of heavy metal carbonates [28–32]. This transformation effectively changes these heavy metals from a bioavailable state to a non-bioavailable form, rendering them less accessible to living organisms [31]. The effectiveness of ureolytically active bacteria used in MICP process in removing heavy metals is attributed to the similarity in their divalent ion formation with calcium (Ca^{2+}), as well as the considerable surface area and abundance of negative ions on the cell surface.

The literature contains many MICP studies with successful outcomes in terms of immobilizing heavy metals via urea hydrolysis, including the listed heavy metals but also extent to other than divalent metals or radionuclides such as Cr^{6+}, As^{3+}, and ^{90}Sr which can be precipitated to form their own insoluble carbonate minerals via the same route (see chemical Equation (6)) [27,33,34]. Alternatively, they have the potential to undergo coprecip itation with calcium carbonate (as depicted in chemical Equation (7)), provided that calcifying micro-organisms can survive in environments containing toxic metals. Those heavy metal ions that possess ion radii similar to that of Ca^{2+} (approximately 1.0 Å) have the capability to integrate into the crystal lattice of $CaCO_3$ (adsorption in the intercellular spaces of $CaCO_3$—biosorption) [35]. This integration can occur through processes like isomorphic substitution, where the metal ions replace calcium ions, or by penetrating the interstice or defect of crystal. Subsequently, these heavy metals undergo a transformation from soluble ions into forms that are not soluble, effectively preventing their re-release into the environment.

As stated previously, there are several examples of the success of contaminants removal demonstrating the applicability of the fundamentals of the method. For example, 95% removal of Cr and Pb was reported in farmland soil via the use of urease-producing fungi in just 12 days [33] and a 90% removal of multiple heavy metals (nickel, lead, copper, cobalt, zinc, and cadmium) in aqueous solution was achieved in the study by Li et al. [36]. The removal efficiencies reported for lead and chromium by He et al. [27] were as high as 86% and 76.8%, respectively, when the initial metal concentration was 25 mg/L. The use of native ureolytic bacteria for ^{90}Sr in groundwater was also proven successful [37] with a removal rate of 59% when *S. pasteurii* was used in two-dimensional porous media reactors [38], while the use of mixed extracted ureolytic bacteria from mining sites was proven to be 83% successful [25]. In a study by Chen et al. [39], *S. pasteurii* was employed for the remediation of soil contaminated with Pb. The findings indicated a substantial reduction of 76.34% in the leaching of heavy metals from the soil subsequent to the remediation process. Mwandira et al. [40] reached 100% removal of high concentrations of Pb^{2+} via MICP. Peng et al. [29] successfully removed 99.50% of Cd within 7 days. Using indigenous bacterial, the biostimulation technique employed to enhance the MICP rates for copper immobilization resulted in notable decrease in the exchangeable soluble copper fraction in the soil, dropping from an initial level of 45.54 mg/kg to 1.55 mg/kg [41].

The success of the method depends on several factors. In most of the published studies, it is quantified as the efficiency of removing heavy metals expressed as a percentage of removal. One inhibiting factor is the bacterial toxicity which is a critical factor for contaminant removal [42,43]. The toxicity due to the presence of heavy metals is known to typically inhibit microbial activity, which, in turn, slows the bioremediation procedure, resulting in lower efficiency. Qiao et al. [43] studied the toxicity effects of these heavy metals to bacteria used in MICP, reporting that those effects, from most to least toxic, were cadmium, zinc, nickel, and copper. The bacterial strains, their population and urease activity, the calcium source and concentration of chemicals, the pH and initial concentration of the contaminant, and the type of the contaminant are some of the factors that need to be taken into account when designing such a remediation scheme [24,29,43,44]. Such factors interact with one another but also interact with the soil properties [43,44] and, therefore, to this point, laboratory experiments are required to simulate field conditions before applying the process in the field. For example, MICP was proven not suitable for very fine-grained soils (<100 µm), such as mine tailings [45]. Bacterial strains capable of establishing an alkaline nature through metabolism and, subsequently, achieving it are key to the process. At the same time, there is a clear link between the precipitation of carbonate and the extent of urea hydrolysis, controlled by the bacterial urease enzyme. Urease catalyzes the conversion of urea into products at a rate significantly higher than the spontaneous decomposition rate [35]. As a result, the bacterial population and levels of urease activity play an important role in bioremediation. It is important to allow enough time for reactions to occur, but, also, the treatment cycles should not last long as the urease activity is known to decline with time [46]. In addition, there is an interplay between reaction times and treatment duration as the two should be compatible. Bacterial strains should be also carefully selected based on the information known about the contaminant (type and concentration) due to its toxicity effects on micro-organisms, while in cases where the pH indicates acidic environment, it should be regulated so that it remains alkaline. The calcium source and the chemicals' concentration clearly depend on the characteristics and nature of the contaminant.

Other challenges related to the application of MICP for remediation include the identification of the appropriate MICP recipe (mainly, urea mass) and the recovery of ammonium to improve the economic and environmental benefits [47]. In comparison to alternative methods, the remediation process involving MICP is linked to elevated expenses due to the costs of reactant materials and the uneven effects observed in large-scale fields. Additionally, there may be environmental implications associated with MICP, as it has the potential to disrupt ecological balance and might not adapt effectively to intricate environmental conditions [48]. On a practical level, the long-term performance of heavy metal removal has not been assessed up to this point and there is no picture on a complete and comprehensive life-cycle assessment [49].

MICP offers a significant advantage over conventional methods due to its ability to withstand redox-insensitive conditions, ensuring that heavy metal carbonates remain non-toxic, insoluble, and inaccessible, giving long-term stability. According to Gadd [50], MICP can overcome some limitations associated with biosorption. Heavy metals that have been precipitated are integrated into mineral crystals, rendering them stable in geological terms. Zhao et al. [49] demonstrated the stability of Pb-MICP precipitates under continuous acid degradation. Moreover, MICP provides a low-cost and eco-friendly method for heavy metal remediation through bioimmobilization [40]. In terms of solidifying heavy metal-contaminated soils, MICP contributes to better strength improvement while maintaining better hydraulic conductivity and higher durability, and it rarely damages the original soil structure during grouting, making it more environmentally friendly compared to other agglutinate binders [23,48].

One common problem for MICP applications is usually upscaling. However, in this direction there are multiple field experiments in the literature proving its viability and applicability to real environmental conditions and industrial use. Few of these studies include the work by Fujita et al. [37] applied at the Hanford 100-N Area in Washington.

3. Mechanical and Hydraulic Properties Alteration

The addition of cementation within the pore network and on the surface of the grains results in strength enhancement and hydraulic conductivity alteration. In most hydrological applications, the hydraulic conductivity is the main property that controls any design. This section presents the two properties that change when applying an MICP injection scheme with a focus on hydraulic conductivity which is most relevant to the examined applications. The analysis focuses on both the macro- and micro-scales since both the amount of cementation and its microstructure characteristics control the response and behaviour of the resulting products.

The properties of the treated products are influenced by the characteristics of the base material (particle roughness, shape, size, and width of particle size distribution) as well as the distribution and structure of the cement within the medium (including the amount, crystal shape, size, and calcite location) [51–55]. Additionally, the cement properties are also governed by various other factors related to the MICP procedure and external/environmental factors, such as the number of injections, chemical concentration in each injection, retention time between injections, infiltration (or injection) rate, and bacterial density/activity, temperature, pH, and presence of oxygen [10,52,56]. Consequently, the mechanical properties may vary from one study to another, depending on the selection of biochemical parameters and the specific experimental protocol. To accurately assess the effects of each parameter, whether biological or related to the grains, it is essential to isolate other influences and follow a consistent procedure.

Both the strength enhancement and the hydraulic conductivity heavily depend on the microstructure. Three distinct and ideal types of grain/cement structures have been identified [57], as shown in Figure 3. These are:

(i) contact-cementing, in which the carbonate crystals precipitate on and around the contacts between the grains (see schematic in Figure 3a);
(ii) grain coating, in which cement forms a uniform film around the grains (see schematic in Figure 3b); and
(iii) matrix-supporting, in which the precipitate is identified within the granular network (see schematic in Figure 3c).

The distribution of the cement around the grains depends on the grain characteristics but also on the choice of MICP formulation and other environmental conditions. The resulting mechanical and hydraulic properties presented in the next subsections will be linked to the microstructure, frequently referring to Figure 3.

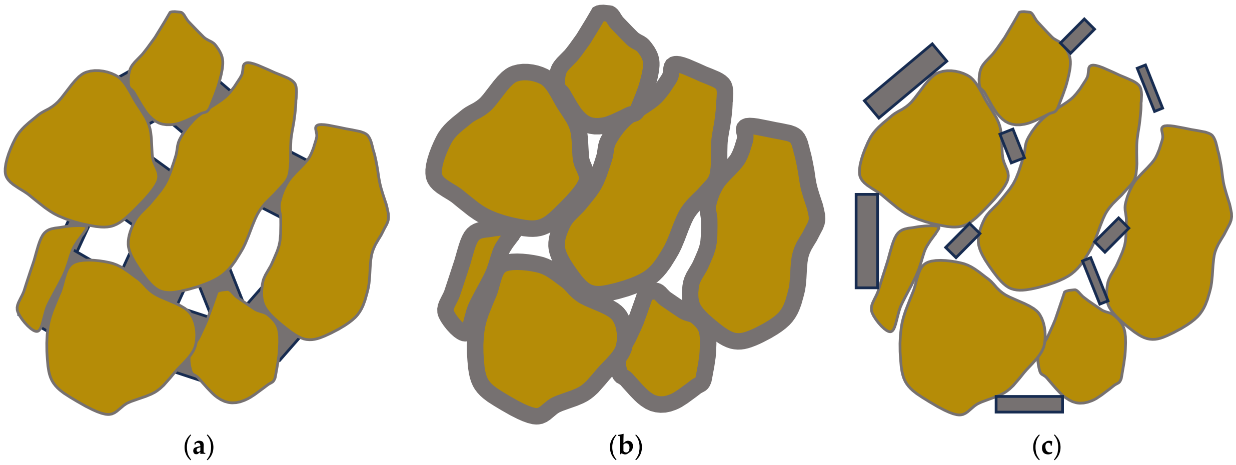
(**a**) (**b**) (**c**)

Figure 3. The three idealized of grain/cement structures: (**a**) contact-cementing, (**b**) grain coating, and (**c**) matrix-supporting.

3.1. Strength Enchancement

In the existing literature, the most common method used to evaluate the strength of biocemented sands is the unconfined compressive strength (UCS), although other measurements, such as the small strain shear stiffness, G_{max}, tangent modulus [14,57,58], friction angle, cohesion derived from triaxial compressional tests [59–61], and even tensile strength [62,63], have been evaluated.

Starting from the biochemical factors, the literature suggests that the bacterial strain selected, the population and the urease activity, the type of calcium source, the concentration of chemicals, and the treatment duration and frequency of injections, but also the injecting method, affect the precipitating carbonate crystals in terms of size, type, and distribution within the pore network which, in turn, affect the resulting microstructure and, therefore, strength enhancement, as shown in Figure 3.

Previous research by Cheng et al. [53] indicates that lower urease activity can enhance particle bonding and increase unconfined compressive strength (UCS) due to slower formation of carbonate and more effective particle bridging (see Figure 3a). The findings of this study were strengthened by the study of Konstantinou et al. [46], in which a protocol was proposed on the basis of selecting bacteria with reduced urease activity as part of a low-concentration cementation solution during the MICP procedure which leads to balanced and slower reactions, thereby promoting consistent, reproducible outcomes and, eventually, leading to more efficient and better strength enhancement. However, Whiffin [9] reported significant variability in enzyme levels, suggesting that consistent urease production cannot be guaranteed even under conducive growth conditions. This variability of enzymatic activity could be either resolved by using bacteria strains of lower variability or native micro-organism isolates which could also minimize any environmental impacts or by following proposed methods to generate bacterial populations with the desired urease activity [46]. The authors [46] linked the differences in behaviour with the microscale in which it was observed that when the urease activity was higher, the carbonate crystals formed were of comparable size, exhibiting a cubic shape and uniform distribution on the grain surface. With decreasing urease activity, the crystals grew larger and tended to form clusters, appearing to be more efficient in creating bridges between the particles. These observations were particularly noticeable in higher bacterial populations and explain the better strength enhancement obtained. Various bacterial types have been also used, demonstrating the success of the procedure with almost any ureaseorganisms [19,38,53,64–67].

The bacterial population does also have effects on the size and structure of the carbonate distribution. Wang et al. [68–70] used a microfluidic chip to observe the various biochemical MICP parameters in response to the carbonate precipitation. An example of a microfluidic chip experiment is shown in Figure 4. The injection process of bacterial and chemical solutions, distribution of bacteria, precipitation, calcium carbonate crystal growth process, and its spatial distribution were studied. The findings indicate that a higher bacterial density results in a higher precipitation rate of $CaCO_3$, with more crystals but with a smaller average crystal volume [71]. This finding indicates that a medium range of optical densities leads to more efficient bonding of particles and, thus, higher strength.

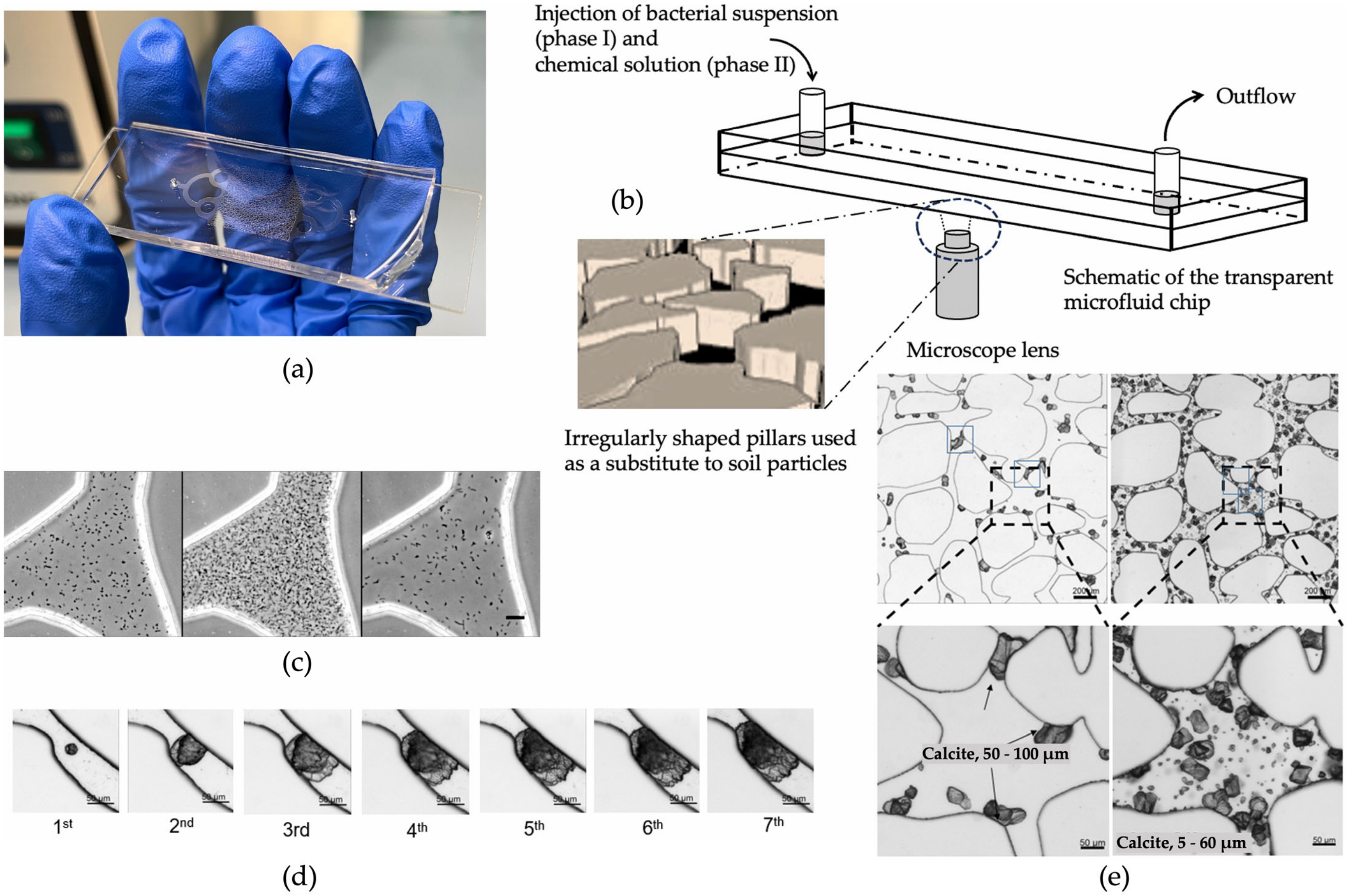

Figure 4. Schematic diagram of a MICP microfluidic example experiment [70]: (**a**) microfluidic chip; (**b**) schematic diagram of the injection process; (**c**) distribution of bacteria after injection, precipitation for 18 h, and injection of cementation solution; (**d**) calcium carbonate crystal growth process; (**e**) cementation of calcium carbonate in pores and throats.

The amounts of chemicals are also important parameters for these investigations. Al Qabany and Soga [51] demonstrated that reducing the chemical concentration level increases the unconfined compressive strength of biotreated specimens. In a relevant study at the grain scale level [72], the extent of the strength enhancement of the MICP-treated specimens was linked to the differences in crystal sizes and numbers and their growth dynamics. The authors identified that, regardless of the concentration of cementation, decreasing the normalized input rate (treatment frequency and duration) of the cementation solution resulted in a substantial increase in UCS. A further reduction in the normalized input rate led to a slight increase in UCS values. Poisson's ratio in MICP-treated sands was found to decrease with increasing calcium chloride concentration, indicating less lateral deformation and volume change at the same axial strain compared to lower concentrations [57].

The second group of factors is environmental factors. These could include factors such as the pH, the presence of oxygen, the salinity level, the saturation, the environmental temperature, the presence of competitive micro-organisms, applied stresses, etc. These, of course, have effects on both the gaining of cohesion but also on the hydraulic conductivity reduction. In the study by Cheng et al. [53], the unconfined compressive strength (UCS) was measured for various degrees of saturation. The authors found that lower degrees of saturation resulted in strength enhancement during the MICP procedure, likely due to more effective cementation at particle contacts (see Figure 3a). Triaxial testing revealed that the initial tangent Young's modulus (E_i) of MICP-treated sands was controlled by the $CaCO_3$ content and was less sensitive to an increase in effective confining pressure compared to untreated specimens [57]. Other studies also showed similar trends in friction angle and cohesion as a function of cementation level [59–61]. The durability of MICP-treated samples in freeze–thaw (FT) cycle tests was found to vary depending on the particle size distribution, with well-graded sands exhibiting improved resistance to FT cycles [53]. Additionally, conducting the MICP procedure at higher temperatures enhances the strength of the resulting samples [53,73,74]. However, at low or very high temperatures the bacterial growth was found to be lower, which has effects on crystal growth, as seen in the microfluidic experiments by Wang et al. [73] (see Figure 4). Such dynamics affect the resulting strength enhancement [75].

The third group of factors that affect the alteration of properties is granular network properties. The strength of cemented materials relies on the number of contact points and the position of the cement within the porous medium. A greater number of particles in a given volume leads to more contact points, distributing stresses evenly within the granular matrix and reducing stress on each particle. According to Konstantinou et al. [76], who systematically studied those effects, when cement is present at these contact points, it acts as a bonding agent, holding the particles together. The strength of these bonds depends on the amount of cementation around the contact points (effective cementation) which is shown in the ideal case in Figure 3a. In cases where there is no cementation, the contact points between particles become weak points. Large particles increase the likelihood of carbonate crystals forming on their surfaces, providing less effective cementation, resulting in a significant portion of the cementation not contributing much to strength improvement. While more contact points allow for more effective cementation, an excessive number of contact points requires a larger amount of cementation overall to enhance strength, as any uncemented contact points create preferential paths of failure under compression. Additionally, cementation may become random as the flow during treatment diverts from densely packed areas to those with less cementation. Very coarse sands with a larger average particle diameter had fewer particles but more surface area, making them less suitable for effective cementation, leading to consistently lower strength at any given cementation level (Figure 3b). On the other hand, very fine sands offered more contact points, making them better candidates for effective cementation, but their strength was still lower compared to fine sands [76,77]. If there are many contact points to be cemented, some might be left without cementation support, creating weak points susceptible to failure unless a substantial amount of cementation is provided. Fine-to-coarse sands strike a balance, providing the highest strength because of the combination of the absolute number of contact points and the ratio of contact points to surface grain area. An increase in the uniformity coefficient generates more contact points and reduces pore sizes, resulting in lower fluid flow during the treatment process. Therefore, mixtures with larger particles and a wide particle size distribution (PSD) achieved better strength enhancement since large particles offer fewer contact points, but the wider PSD reduces the chances of cementation depositing on the particle surfaces [76]. In materials with similar uniformity coefficients but different grain sizes, higher cementation levels were necessary to attain the same strength, primarily because smaller grains increase the likelihood of cementation occurring between particles rather than on their surfaces [76]. Particle shapes also influence mechanical properties [78]. Sub-rounded, spherical particles provided the highest strength due to their numerous contact points, while angular particles lacked sufficient contact points. Angular particles had initial strength from interlocking before cementation, and, while cementation increased strength, the effect was limited (i.e., diminishing returns with increasing cementation) [76]. On the other hand, Xiao et al. [78] demonstrated that a better base material for MICP treatments in terms of strength is provided by less round particles in mixtures of round and angular glass beads.

Figure 5 presents unconfined compressive strength values with respect to cementation level based on the results of various studies [3,51,53,72,76,77,79–81]. The literature contains a large number of data on UCS, yet some studies have been chosen to demonstrate its correlation with cementation level. As seen in the graph, in which the y-axis is in a log scale, an exponential fit describes the correlations, showing that cementation level is a main contributing factor despite the fact that experimental conditions are different across the studies (grain characteristics, chemical concentrations, bacterial population, and urease activity, temperature, and saturation level). These conditions are reflected in the precipitation patterns at the microscale level.

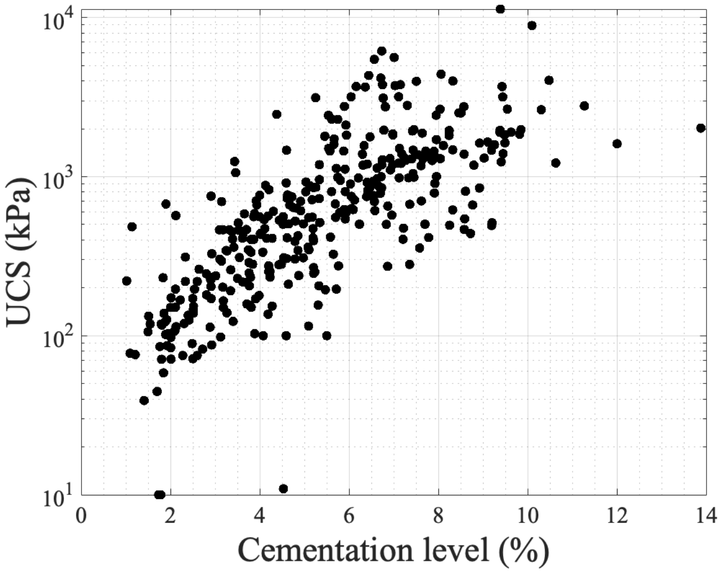

Figure 5. The experimental results of UCS with respect to cementation level as obtained in various studies.

3.2. Hydraulic Conductivity

Perhaps, the hydraulic conductivity is the property that is most understudied for MICP-treated porous media. This might be due to the very variable results and the fact that until this point most of studies focused on strength enhancement which is usually the main objective in geotechnical engineering studies. However, controlling the hydraulic conductivity in applications related to hydrology and water resources is of paramount importance. It is influenced by various factors related to the pore space, including its size, shape, and tortuosity (i.e., the Kozeny–Carman equation). As stated previously, the fate of calcium carbonate crystals within the granular medium depends on the biochemical MICP parameters and the environmental factors but also on the properties of the porous medium itself.

Previous research on MICP-treated sands has consistently shown that the hydraulic conductivity decreases significantly as the cementation level increases even up to 10 orders of magnitude. This reduction in hydraulic conductivity was reported in several studies [51,76,79,82–88]. However, there was an exception noted in the study by Whiffin et al. [3], where the measured hydraulic conductivity showed little change after treatment. This was supported by other studies suggesting that specimens with lower amounts of precipitated calcite experience a less significant reduction in relative hydraulic conductivity [89]. In the studies by Dawoud et al. [80,90,91], the hydraulic conductivity was shown to have an initial 'stable' phase at the very low cementation region in which there was almost no reduction in hydraulic conductivity. Song et al. [92] presented a typical or normalized reduction profile as shown in Figure 6. In the initial stage of low cementations (stage I), the decrease in hydraulic conductivity occurs at a gradual pace and is marginal. Subsequently, there is a rapid decline in hydraulic conductivity (stage II) at moderate cementation levels. Finally, at high cementations, hydraulic conductivity reaches a nearly constant level which is very low (stage III). Considering this diagram, the findings of the previous studies could be combined and interpreted given that in the study by Whiffin et al. [3], the cementation levels were closer to the lower cementation levels compared to the rest. The general sense, though, is based on a comparison between hydraulic conductivity and UCS for Portland cemented samples and MICP-treated samples, that there is a smaller trade-off between hydraulic conductivity and strength in the case of MICP, suggesting a relative ability of retaining soil hydraulic conductivity [79].

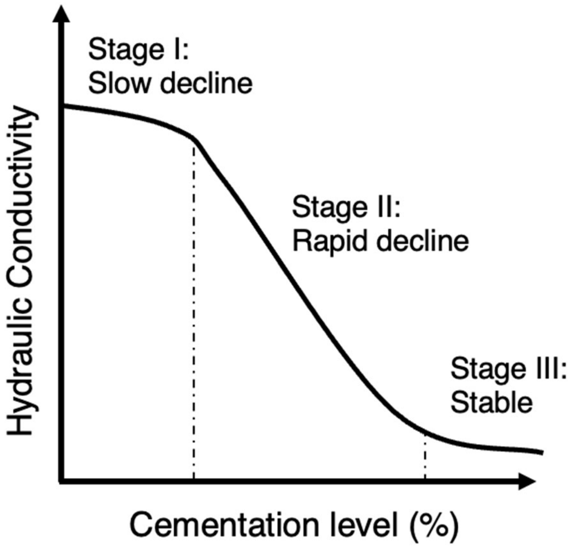

Figure 6. The typical reduction profile of hydraulic conductivity with respect to cementation level.

Beyond this general profile, which only presents a correlation with the overall volume of cement added, the resulting hydraulic conductivity could be explained to a great extent by evaluating the microscale response. This involves assessing properties such as carbonate crystal type, distribution, and size, which are routed on the three groups of factors mentioned earlier.

The level of urease activity employed during treatment had only a minor effect on hydraulic conductivity reduction in the study by Cheng et al. [53] and according to Choi et al. [93]. However, in the research by Konstantinou et al. [46], the higher the urease activity was, the more clogged the specimen was at the injection point, decreasing dramatically the flow rate in subsequent injections. The difference between the two studies might be attributed to the fact that in the second work, the range of urease activities was wider. Also, a lower hydraulic conductivity was measured for higher bacterial populations [94].

Al Qabany and Soga [51] reported that the high concentration cementation solution produced a quicker and greater reduction in the coefficient of hydraulic conductivity, suggesting that higher concentrations of calcium chloride and urea lead to larger calcite crystals and a more uniform distribution of precipitation when using lower concentrations. The larger crystals can cause early clogging, as observed in their study.

Similar findings were reported by other studies [91,95]. In the study by Duo et al. [95], the hydraulic conductivity gradually decreased as the concentration of the solidification solution increased, with a maximum reduction of approximately three orders of magnitude. The hydraulic conductivity coefficient reduction was particularly prominent up to a concentration of 1.5 mol/L, beyond which it remained constant despite having higher concentrations of chemicals. The authors linked this behaviour with the microstructure stating that during biocementation, calcium carbonate accumulated on the surface of the sand particles (see Figure 3b) and filled the gaps between them, leading to a gradual reduction in the volume of sand pores and, subsequently, a decrease in hydraulic conductivity.

According to the authors, these findings of absolute hydraulic conductivity values suggest that the MICP technique holds promise for seepage control in pond and landfill engineering projects in desert areas due to the low hydraulic conductivity obtained [95].

Dawoud et al. [91] classified the hydraulic conductivity reduction in three phases: during the initial stages of treatment hydraulic conductivity shows a slight decrease or remains relatively unchanged. At this point, a small amount of precipitated calcite adds stiffness to the soil without causing pore clogging. This phase can be represented by a linear relationship with a slight negative slope (in agreement with the profile in Figure 6). As the precipitation of calcite continues, a certain threshold is reached where the accumulated calcite starts to clog the pores, leading to a new steeper trend of decreasing hydraulic conductivity after each treatment. During this stage, the concentration of the chemical solutions used in the treatment significantly influences the soil's behavior and characteristics (again in agreement with Figure 6). The study noticed that using a 1M concentration for the urea–$CaCl_2$ solution resulted in an earlier transition to the clogging phase. Once clogging initiates, the distribution of MICP becomes more uncertain. Blocked flow paths cause new precipitates to accumulate near the injection point, resulting in less uniform treatment across the sample. This phenomenon is consistent with the findings of Qabany and Soga [51].

The calcium source is also another biochemical factor that has effects on hydraulic conductivity. In the study by Kadhim et al. [96], the incorporation of a cementation solution containing calcium chloride derived from eggshells had a substantial impact on hydraulic conductivity. However, the effect was more pronounced in the silica sand samples rather than the river sands as in the former higher hydraulic conductivity reduction was observed. In other studies, the use of calcium acetate caused the greatest hydraulic conductivity reduction followed by calcium chloride. A very low hydraulic conductivity reduction was observed with the use of calcium nitrate [97].

MICP process under lower saturation conditions is more favorable if the goal is to improve the mechanical properties while still maintaining relatively high residual hydraulic conductivity [79]; however, it was also reported that there is a general trend of decreasing hydraulic conductivity with the increase in produced calcite content ($CaCO_3$) irrespective of the degree of saturation at which the soil was treated [98]. The differences observed are likely due to the interaction effects (a variable is behaving differently at various levels of another variable) added from the choice of other biochemical parameters.

The relative density (RD) and injection volume in a single injection event (VIP—void injection percentage) were also studied showing a negative correlation with hydraulic conductivity [99]. That is, as the two factors increased, there was a corresponding decrease in hydraulic conductivity. This reduction in hydraulic conductivity was attributed to several reasons. With an increase in RD, the pore volume (PV) decreased, leading to the formation of smaller and less permeable pore throats. However, at very high RD some inconsistency was observed, likely due to the pore throats becoming smaller, increasing the likelihood of clogging and facilitating the creation of preferential flow paths during bacterial suspension and cementation fluid injection. Moreover, the decrease in hydraulic conductivity with increasing VIP was attributed to localized bacterial concentration near the injection point, which promoted more significant calcite precipitation in that specific region. This localized effect led to a reduction in hydraulic conductivity in the surrounding area [99].

One of the very few environmental factors studied for MICP in relation to the reduction of hydraulic conductivity was the use of seawater. The hydraulic conductivity coefficients of the samples treated with natural seawater-based biocementation were slightly higher compared to those treated with freshwater-based biocementation. This difference was attributed to a higher precipitation of carbonates in the freshwater columns than in the seawater columns. However, despite this disparity, using seawater-based biocementation instead of freshwater cementation did not have a significant impact on hydraulic conductivity [22]. Similarly, the ureolytic bacteria utilized by Cheng et al. [67] were acclimated to high-salinity conditions by employing a growth medium containing high concentrations of ammonium sulfate ($(NH_4)_2SO_4$) to help prevent significant osmotic effects when exposed to seawater. The use of seawater supplemented with urea, instead of a concentrated cementation solution, had no substantial impact on the hydraulic conductivity per carbonate formed. However, the same carbonate formation resulted in higher strength in the seawater cementation trials, which, consequently, allowed for greater hydraulic conductivity for a given level of strength [67].

In terms of injection strategy, the use of continuous flow technique resulted in a significant reduction in hydraulic conductivity compared to the stopped-flow technique. This was attributed to the higher likelihood of columns treated with continuous flow to experience plugging near the injection source [84]. Also, the presence of a stationary liquid during biocementation resulted in slightly higher hydraulic conductivity reduction [100].

The work by Konstantinou et al. [76,82] on the grain characteristics effects on hydraulic conductivity revealed valuable insights on this link. Hydraulic conductivity undergoes a significant decrease when cement is present at contact points, leading to a reduction in pore throat size. Materials with numerous particle-to-particle contacts prove challenging to decrease hydraulic conductivity, as many contacts require cementing. Such materials regulate flow through paths with larger pores and pore throats, which involve uncemented particle contacts.

As the grain size increases in a packed bed of solids, the hydraulic conductivity is expected to rise as well (see example MicroCT images in Figure 7a–c). For example, the Kozeny–Carman equation incorporates the squared average particle diameter in its empirical equation's numerator. This trend of reduced hydraulic conductivity with increased cementation was also observed in very fine to coarse sands during the study and is in agreement with other studies where a D_{10} increase, resulted in a smaller reduction in relative hydraulic conductivity [89].

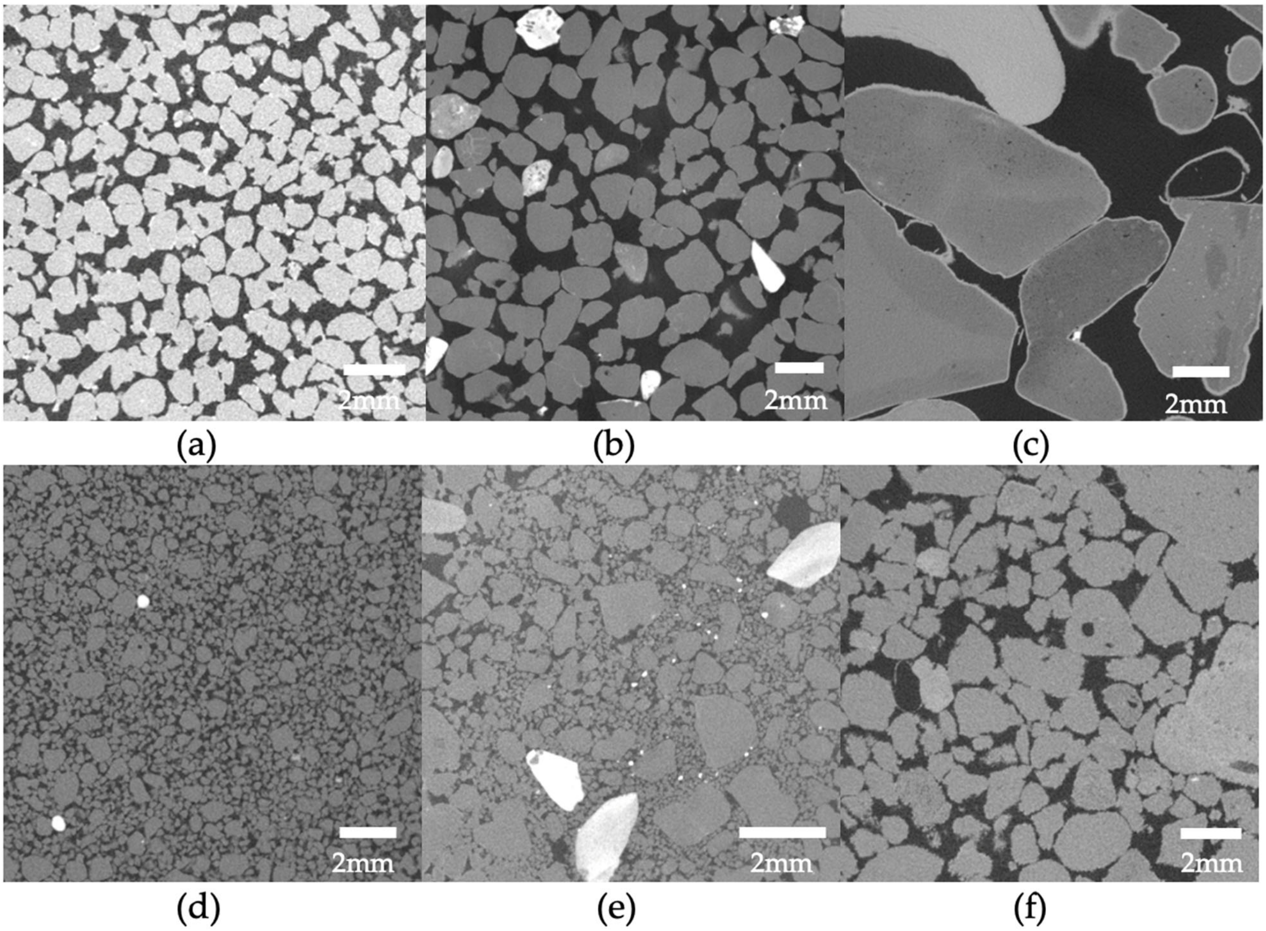

Figure 7. Example MicroCT images of biotreated sands by Konstantinou et al. [76]: (**a**–**c**) increasing grain size and (**d**–**f**) increasing grain size and width of particle size distribution.

However, very coarse sands and gravel did not follow the same pattern and displayed a less controlled reduction in hydraulic conductivity [76]. In very coarse materials, carbonate precipitation mainly occurs on the surface of particles rather than at contacts among them. As a result, the reduction in hydraulic conductivity is not expected to be significant. Nevertheless, the lower number of contact points leads to fewer flow path options, explaining the rapid decline of hydraulic conductivity in very coarse particles at lower cementation levels. When comparing gravel and very coarse sand (both deemed ineffective for MICP treatment), gravel exhibited a larger reduction in hydraulic conductivity due to the lower number of available flow paths. Gravel's erratic pore distribution and randomness, caused by its very large grains, provide for unpredictable fluid flow paths, resembling a system with small and few large pipes dominating the flow [76].

Hydraulic conductivity in relation to cementation is lower when the base material has a wider spread of particle size distribution (PSD) due to the narrower initial pore space distribution before cementation (see example MicroCT images in Figure 7d–f). The reduction in hydraulic conductivity with increasing carbonate content is also lower compared to more uniform sands, as there are too many narrow flow paths to be cemented (and, essentially, closed) when a higher number of contact points exists. This holds true for granular materials with wide PSD [76]. This was confirmed by other studies in which the hydraulic conductivity of cemented sand was found to be influenced also by its grain gradation in a similar manner. The reduction in the hydraulic conductivity coefficient during each MICP treatment cycle increased with higher values of the uniformity coefficient (C_u) and the curvature coefficient (C_c) [86].

On the other hand, the absolute value and reduction of hydraulic conductivity in two materials with similar uniformity coefficients but different grain sizes are the same, demonstrating that the dominant factor controlling flow is the spread of PSD [76]. Although the material with smaller grain sizes has more contact points, it provides more flow path options compared to the one with larger grain sizes. At the same time, the latter has a lower ratio of contact points over surface grain area, resulting in some of the cementation being consumed on the surface of the grains, leading to a lower rate of hydraulic conductivity reduction.

While particle sphericity is known to impede flow, according to the Kozeny–Carman equation, significant hydraulic conductivity differences were only observed in the case of angular sand in the study by Konstantinou et al. [76]. However, the reduction trend with respect to cementation levels was similar for angular sand, fine and coarse glass beads, and fine and very coarse subrounded sand, indicating that grain size is the dominant factor in these cases. The flow paths are affected, to some extent, by grain shapes, but the addition of cementation causes proportional hydraulic conductivity reduction in spheres, sub-rounded, and angular sands. In the study by Song et al. [101], though, the non-spherical particles (crushed Ottawa sand) experienced the highest drop in hydraulic conductivity compared to the spherical particles despite having a lower calcium carbonate content showing a specific trend: the angular grains exhibited the highest hydraulic conductivity reduction, followed by the near-spherical particles, with the spherical particles showing the least reduction [101].

To investigate how pore-scale $CaCO_3$ distributions affect the hydraulic conductivity of MICP-treated sands, the researchers used the Panda–Lake model [102]. This model incorporated three reduction factors: the porosity reduction factor, tortuosity reduction factor, and specific surface area reduction factor. Additionally, the Kozeny–Carman model was used to estimate hydraulic conductivity reduction with $CaCO_3$ content, considering only the reduction of porosity [103]. By comparing the calculated hydraulic conductivity using the Panda–Lake and Kozeny–Carman models with the measured hydraulic conductivity reported in existing literature, the researchers developed an analytical model that can reasonably predict the hydraulic conductivity of MICP-treated sands for different $CaCO_3$ contents and types of sands [103].

Lin et al. [103] performed an analysis on measured hydraulic conductivity values across various studies identifying that the grain coating (Figure 3b) Panda–Lake model provides reasonable fits to the data provided that the main mechanism is matrix-supporting. The Panda–Lake model takes into account, the shape, tortuosity, specific surface area (surface area of the grain/the volume of the grain), the statistical characteristics of the particle size distribution, the cement saturation of the pore space, the fraction of $CaCO_3$ volume to the total volume of solids, and the specific surface area of the $CaCO_3$ crystals. The matrix-supporting environment seen in Figure 3c shows smaller reduction of hydraulic conductivity with respect to cementation level. It follows, based on the findings of Lin et al. [103] and Konstantinou et al. [76], that the Kozeny–Carman equation would give better estimations of the reduction of hydraulic conductivity for the contact-cementing model.

Even though the findings are in good agreement, there is room for further research to examine the combinations of factors and their effects on the resulting hydraulic conductivity. Figure 8 presents the data concentrated from the available references that measured hydraulic conductivity [3,22,51,53,67,76,79,82–89,91–101,104–130]. The y-axis is in a log scale. Despite the fact that there is a trend in reduction similar to the profile presented in Figure 5, the results are scattered showing a weak correlation with the cementation level. This is because not only the volume of cementation is required to identify the reduction in hydraulic conductivity but also the carbonate crystal size and distribution is required. Also, the initial configuration of the granular network is required, and this is the reason the Panda–Lake model performs better compared to the Kozeny–Carman equation. The results also show that UCS has a higher correlation coefficient (0.55) (Figure 5) compared to hydraulic conductivity (with a value of 0.1) showing more dependence on cementation level and less dependence on the granular and cement configuration.

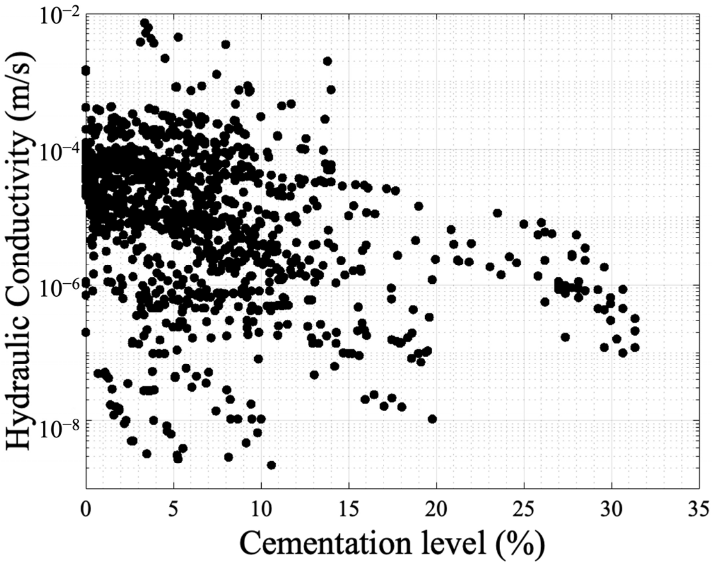

Figure 8. Experimental results of hydraulic conductivity with respect to cementation level as obtained in various studies.

4. Applications of MICP to the Fields of Hydrology and Water Resources

As stated earlier, the main property that needs to be controlled in hydrological and water resources applications is hydraulic conductivity while for erosion problems cohesion is the controlling factor. When it comes to addressing contamination issues and implementing successful remediation strategies, precipitation mechanisms play a critical role. Therefore, MICP could emerge as an innovative and effective technique as it could solve many different problems and applications related to water. This section presents the various MICP applications in these sectors that were studied. It also proposes other potential applications based on Figure 2 which classifies the applications according to their underlying mechanisms. The grouping and presentation of results are made based on Figure 2. First, the applications related to groundwater and soil remediation are presented followed by the applications related to hydraulic conductivity reduction and to gaining cohesion. Lastly, the applications related to the use of MICP-treated specimens as artificial materials are shown.

4.1. Groundwater and Soil Remediation

Groundwater and soil remediation or contaminant sequestration is defined as the process of cleaning and removing contaminants from groundwater aiming to restore its quality to make it safe for human consumption and to eventually protect the environment by conforming with the relevant regulations. The MICP technology is technically proven in terms of its fundamentals since there are many relevant studies as mentioned earlier (Figure 2—remediation and Section 2). Heavy metal precipitation via MICP could be succeeded via biosorption, coprecipitation of heavy metals with Ca^{2+}, or coprecipitation with carbonate ($CO_3{}^{2-}$) crystals formation [23]. By injecting suitable micro-organisms and substrates into contaminated areas, calcite precipitation occurs, which can immobilize or trap various pollutants and heavy metals, reducing their mobility and toxicity. Table 1 summarizes the relevant studies for various toxic metals that were studied and the environment in which these experiments have been conducted. The list is not exhaustive. As seen in the table, both soils and liquids have been tested as baseline environments for the specific MICP application while many heavy metals have been tested with successful outcomes (e.g., cadmium, copper, zinc, lead, arsenic, nickel, etc.). Therefore, MICP can be used for in situ groundwater and soil remediation.

Table 1. MICP applications for removal of contaminants.

Authors	Contaminant(s)	Type of Environment
[131]	Cd^{2+}	Liquid environment
[24]	Pb^{2+}	Liquid environment
[132]	Cr^{6+}, Cu^{2+}, Zn^{2+}	Contaminated soil (Changhua County in Taiwan)
[133]	Zn^{2+}, Ld^{2+}, Cd^{2+}	Liquid environment
[28]	Ni^{2+}, Cu^{2+}, Pb^{2+}, Co^{2+}, Zn^{2+}	Liquid environment
[134]	Ld^{2+}	Liquid environment
[135]	Cd^{2+}	Liquid environment
[25]	As^{3+}	Farmland soil
[136]	Cu^{2+}	Liquid environment
[137]	Cu^{2+}, Ld^{2+}, Cd^{2+}	Contaminated mine tailing soils
[45]	Cu^{2+}	Mine tailing soils (Greenfields copper mine project in Columbia)
[29]	Cd^{2+}	Soil and liquid environment
[43]	Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}	Soil
[47]	Ld^{2+}, Cd^{2+}	Pyrite mine sites synthetic landfill leachate
[38]	^{90}Sr	Two-dimensional porous media reactors

While the conceptual design in terms of biochemical reactions has been investigated extensively, the implementation schemes for MICP application in the field remains largely unexplored. A step forward is the integration of the MICP technique in many designs for groundwater remediation, which, in turn, depends on the type and extent of contamination. Specifically, there are opportunities for MICP to be incorporated in the following steps/designs that are traditionally used in groundwater remediation schemes:

(a) Pump-and-treat schemes: extraction of groundwater through a well, surface treatment to remove contaminants, and injection of treated water back to the aquifer;

(b) Permeable reactive barriers (PRBs) which are proffered in the presence of plumes: generation of subsurface walls which react when in contact with contaminants and, therefore, immobilize the contaminant by the processes described earlier (adsorption, precipitation, and microbial degradation);

(c) In situ bioremediation: direct injection of bacteria and chemicals via a well into the contaminated region;
(d) Remediation train: effective remediation often involves a combination of these techniques, known as a “remediation train”, to achieve the best results.

Each groundwater remediation design and application have their advantages and limitations, and the appropriate approach depends on site-specific conditions, the type and concentration of contaminants, hydrogeological factors, and regulatory considerations. The balance of reactions needs to be taken into account not only for the reaction rates of bacteria and chemicals but also in relation to whether uniform replacement of fluid is required in the pore space or fracturing is targeted to generate a conductive channel for better delivery of the reactants to the targeted locations. Another challenge in designing a remediation plan is the viability of MICP in terms of the various environmental conditions in groundwater (i.e., anoxic, anaerobic, aerobic conditions, pH levels, salinity, and bacterial competition). The selection of various biochemical parameters must be considered, such as the specific bacterial strain, its population and urease activity, the calcium source, the concentration of chemicals, the initial contaminant concentration, and the type of contaminant itself. These factors not only interact with one another but also influence the properties of the soil being treated and the environmental conditions in the field (salinity, existence of other bacterial strains leading to competition, etc.). For instance, the suitability of MICP has been demonstrated for various soils, but it is unsuitable for very fine-grained soils [45]. Also, bacterial strains capable of creating an alkaline environment (control of pH levels) through metabolic processes should be selected. The extent of urea hydrolysis, a reaction catalyzed by bacterial urease enzyme, is closely tied to the precipitation of carbonate. This emphasizes the importance of the bacterial population and its urease activity in the remediation process. Balancing reaction times and treatment duration is essential, considering that the urease activity tends to decrease over time [46]. When selecting bacterial strains, it is also vital to consider the type and concentration of the contaminant due to its potential toxicity to micro-organisms. In cases where the pH of the environment is acidic, careful regulation is necessary to maintain an alkaline pH for the MICP process. The choice of calcium source and chemical concentrations depends on the specific characteristics and nature of the contaminant being addressed. By accounting for these factors, a tailored MICP remediation strategy can be developed to effectively mitigate contamination in a given environment. To overcome these challenges, laboratory experiments in controlled and simulated environments need to be conducted first, to assess the viability and success of the process before its application in the field.

Beyond groundwater remediation and design, the carbonate precipitation process can also contribute to essentially any water quality improvement techniques by trapping and immobilizing suspended particles, organic matter, and some pollutants, leading to cleaner water. As seen in Table 1, many of the experiments have been conducted in liquid environments, while studies have been exploring few options in terms of surface waters. For example, studies have been conducted to assess the viability of MICP removing contaminants from wastewater [32].

4.2. Applications of MICP Related to Hydraulic Conductivity Reduction

The main mechanism in place for such application is the complete or near-complete reduction of hydraulic conductivity by clogging the pores of a granular network in order to prevent fluid flow (Figure 2—barrier). This is commonly referred as a ‘barrier’ in the literature and is applicable to cases such as leak sealing, generation of a contaminant barrier for landfills, and generation of a subsurface dam for seawater intrusion control, for groundwater flow control, for aquifer remediation, and managed aquifer recharge. Most of these studies are new ground in terms of investigation and assessment of their viability. However, the fundamentals of MICP have been investigated in the literature via other routes and there are some studies that measured the reduction of hydraulic conductivity of MICP-treated materials. Despite, though, the high variability of hydraulic conductivity that was observed in the various studies, a standard profile of the property with respect to cementation level has been derived, as shown in Figure 6. During the initial phase of low cementation (stage I), there is a gradual and minor decrease in hydraulic conductivity. Following this, a swift reduction in hydraulic conductivity is observed at moderate cementation levels (stage II). Ultimately, when high cementation levels are reached, hydraulic conductivity stabilizes at an extremely low and nearly constant level (stage III). This information can be used in designing the relevant applications which should be further investigated with laboratory testing. Table 2 presents the relevant studies that have been looking at the listed applications.

Table 2. MICP applications for hydraulic conductivity reduction.

References	Application
[138]	Sealing subsurface fractures in the near-wellbore environment.
[139]	Reduction of near-wellbore permeability to reduce CO_2-related corrosion and lower the risk of unwanted migration of CO_2 or other fluids.
[140]	Seal fluid pathways in subsurface ground, for example, to secure waste storage repositories/hydraulic barriers.
[141]	Generation of a landfill barrier to inhibit contaminant transport underground.
[142,143]	Construction of an aquaculture pond in sand and/or in arid desert.
[144]	Prevention of contaminant transport within the porous medium.
[113]	Seepage control in sand using bioslurry applicable to many infrastructure projects, such as reservoirs, earth dams, tunnels, and other underground constructions.
[15,16]	Seepage control to mitigate erosion in existing dams.
[112]	Permeability preservation for strength enhancement for fully permeable pavement.
[120]	Landfill control/groundwater contamination prevention.
[94]	Generation of an impermeable layer in the soil.
[92,104]	Natural fracture sealing/permeable rock sealing/plugging in high-permeability zones.
[145]	Drought mitigation by water evaporation suppression.
[146]	Irrigation channels and water reservoirs construction in sandy soil ground.

MICP can be employed to seal cracks and leaks in underground structures, such as tunnels, subsurface dams, and retaining walls (see relevant studies in Table 2). The precipitation of calcite within the cracks and voids can effectively reduce or stop water flow, preventing further damage.

In hydraulic and hydrologic engineering, MICP can be used for hydraulic conductivity reduction in porous media. For example, in construction projects involving dams, reservoirs, or underground structures, MICP can help reduce water seepage and leakage through the porous materials, increasing their water-holding capacity and integrity. Leakages in hydraulic-engineering water-retaining constructions or in natural impervious layers are major problems in constructional and environmental applications. Apart from subsurface fluid leakage, preserving water resources is also an important environmental consideration. In regions facing water scarcity, MICP can be utilized to enhance rainwater harvesting techniques. By promoting the formation of calcite in rainwater storage tanks or reservoirs, water losses due to seepage can be minimized, leading to increased water availability.

Another tested application is the contaminant barrier for landfills. Instead of precipitating the heavy metals, MICP can be employed as a barrier system in landfills to minimize the leaching of pollutants into the surrounding environment and block the transport of pollutants with the aim to contain them in a specific area. By inducing calcite precipitation in the landfill's soil liner, the barrier becomes more impermeable, reducing the risk of groundwater contamination.

There are also opportunities which have not been investigated previously and the MICP technology is not far from being proven. One such opportunity is the construction of a subsurface dam or cut-off wall for seawater intrusion control (SWI). Due to the overexploitation of the groundwater, the aquifer levels are lowered leading to seawater invading freshwater aquifers leading to huge environmental problems. A novel geochemical cutoff wall method was proposed in the literature with the use of chemicals without any bacterial reactions [147,148]. In a similar manner, MICP is an environmentally friendly technique that could be applied to generate a barrier for seawater intrusion control using even local bacterial strains. The fundamentals have already been studied and further work needs to be completed in order to optimize the design (effective clogging of the pores) with respect to the porous medium properties (grain size, shape, and width of particle size distribution).

MICP can be applied essentially for any groundwater flow control schemes. The ultimate difference between this application and the seawater control is the fact that, in the former case, controlled reduction of hydraulic conductivity is required at a spatial level. These are cases where groundwater flow needs to be managed to prevent excessive waterlogging or the migration of contaminants. By introducing carbonate-precipitating bacteria selectively, the hydraulic properties of the subsurface can be altered to create flow barriers or preferential flow pathways.

Another opportunity in the fields of hydrology and water resources where MICP could find an application is aquifer remediation. By stimulating carbonate precipitation and microbial activity, it may be possible to enhance natural attenuation processes, leading to the breakdown and immobilization of certain pollutants in groundwater. Similarly,

MICP could aid managed aquifer recharge (MAR). In managed aquifer recharge projects, where excess surface water is intentionally injected into aquifers for storage, MICP can play a role in creating a more suitable subsurface environment. The introduction of carbonate-precipitating bacteria can aid in the formation of hydraulic conductivity barriers or modify aquifer properties to improve water storage capacity and retention.

Some challenges associated with applying MICP to the mentioned applications include:

(i) The efficiency of the process could vary considerably in dynamic environments where water levels, wave action, and tidal fluctuations constantly change;

(ii) The metabolic activity of bacterial strains might be affected by variations in environmental conditions such as salinity, temperature, and nutrient availability, which can have an impact on the performance of MICP overall;

(iii) The mechanical and hydraulic properties of the precipitating carbonate and the porous medium could be affected by the mechanical stresses from wave action and other adverse environmental conditions;

(iv) The scaling-up challenge also is of great importance. The uniform distribution of bacteria, nutrients, and chemicals over larger areas, especially in heterogeneous coastal environments, may be difficult to achieve and monitor effectively.

4.3. Applications of MICP Related to Erosion Control (Gaining Cohesion)

Some applications in water resources and hydrology require the gaining of cohesion with the aim to avoid dislocation of particles preventing sediment runoff into water bodies (erosion control, see Figure 2). The literature contains few studies with this fundamental requirement and are presented in Table 3. The generation of artificial islands in distant seas with the deposition of sand within the sea is one such application [86], where the use of calcareous sand as a foundation filler is common due to its mechanical strength and wide availability. A key challenge in this application is to reduce permeability to store more fresh water on these islands. The study by Li and Chen [86] used a specialized device for MICP grouting and permeability testing. The authors measured permeability coefficients under varying grain gradations showing that as the curvature coefficient (C_c) and uniformity coefficient (C_u) increased, reductions in hydraulic conductivity and porosity were more pronounced. MICP could be also used to aid the process to prevent particle erosion due to wave action in coastal engineering. In a similar manner, MICP could be applied to stabilize soil in surface water environments [96,123]. Wang et al. [149], Sun et al. [150], and Liu et al. [151] found that MICP was efficient in protecting soil against rain erosion.

Table 3. MICP applications for erosion control (gaining cohesion).

References	Application
[86]	Artificial islands generation.
[96]	MICP for areas near river applications (different calcium sources).
[22,67]	Biocementation in seawater and marine environment.
[123]	Prevention of surface erosion.
[95,100,109]	Dust control and wind erosion control [1].
[149–151]	Rainfall-induced erosion control.
[152]	Erosion resistance of biocemented sandy slope subjected to wave actions.
[153–156]	Coastal line protection.

[1] This application is identical to resistance to rainfall erosion and surface runoff and, therefore, is relevant to this study.

The most studied application in this category is coastal protection on a fundamental level [153–156]. MICP has the potential to strengthen and protect coastal structures and shorelines from erosion caused by waves and tides. Originally applied in the coastal line, the technique can be extended to artificial structures, such as breakwaters or groins (breakwaters that are placed perpendicular to the coastal line), since the calcite formation can enhance the resilience of these structures against erosive forces. The higher are the acting forces, the higher should be the cementation deposition.

Kadhim and Zheng [96] have investigated the fundamentals of MICP in terms of the use of calcium source utilizing successfully egg-shell in replacement to calcium chloride with similar effectiveness, taking advantage of the environmental conditions in marine and water environments. In contrast to the commonly MICP technique parameters used in the literature, the study by Cheng et al. [67] introduced a novel method that relies solely on calcium ions found in seawater for calcite formation by introducing bacteria that can tolerate high salinity and possess urease activity into sandy soil. A mixture of urea and seawater was then flushed through the soil, triggering a urease reaction that released bacterial carbonate. This, in turn, caused the precipitation of carbonate salts like calcium carbonate and magnesium carbonate trihydrate. The measured UCS reached up to 300 kPa. Hydraulic conductivity remained at around 30% for all MICP-treated samples, indicating effective drainage. Liu et al. [151] studied how MICP-treated sandy slopes fare against rainfall-induced erosion by using two different concentrations of MICP treatment. In the case of 0.25 M calcium treatment, surface erosion occurred rapidly during rainfall-induced erosion testing. In contrast, the 0.5 M calcium MICP-treated slope remained intact after 24 h of rainfall exposure. Roughness testing showed that the surface of the 0.5 M Ca MICP-treated slope appeared smoother after 24 h of rainfall-induced erosion, while the 10% cement-treated slope became rougher.

Salifu et al. [157] demonstrated the effectiveness of MICP in mitigating sediment detachment on steep slopes, commonly prone to collapse during tidal events. Chek et al. [156] discovered that higher optical densities, higher quantities of bacteria relative to void volume, and higher bacteria quantities relative to urea led to lower erodibility and deeper crust formation. In a different study, Shahin et al. [155] conducted laboratory-scale flume experiments demonstrating the effectiveness of MICP in preventing coastal erosion. Kou et al. [152] also assessed erosion resistance in biocemented sandy slopes under wave action by conducting bench-scale flume erosion tests on MICP-treated and untreated sandy slopes under waves, considering different treatment cycles (0 to 4 cycles) and slope angles (10°, 20°, and 35°). Findings revealed a nonlinear link between erosion resistance and penetration strength. Microstructure analysis showed that MICP treatment created interlocking cementation among sand particles, contributing to improved erosion resistance. However, more experiments are required to establish the applicability of the MICP method for erosion in order to fill the rest of the gaps. For example, experiments need to be conducted under saline environments and with the presence of competitive micro-organisms.

The challenges experienced in this group of applications relate to the effectiveness of MICP treatment which was found to decrease on steeper dune slopes exposed to prolonged wave attack. The forces acting on such structures have seasonality (rainfall and wave action, i.e., cyclic nature), while also presenting extreme values, especially in the climate change era. In designing such structures with MICP fatigue, testing is required in order to assess the integrity and strength of the material in relation to the number of cycles. For the generation of breakwaters or groins, traditionally, experiments are conducted in the laboratories in which dimensional analysis is used to simulate the actual field conditions. Therefore, there are challenges in applying MICP within those experiments but also it is not clear whether dimensional analysis could be applied also for MICP.

Like the rest of the MICP designs, MICP faces the challenge of adapting to diverse environmental conditions. In this case, the dominant factors are salinity and the presence of local strains. Key factors for consideration include selecting the right bacterial strain, determining its population and urease activity, choosing the calcium source, and specifying chemical concentrations. However, the various studies presented previously overcame those limitations. Bacterial strains that adapt to high salinity conditions have been used and tested. Also, various calcium sources have been used, even calcium sources that are native to the environment (e.g., eggshell). Tailoring an MICP strategy based on these factors can effectively combat erosion control issues.

A potential application that is proven is the generation of rocks for divers to step on but to also study the marine life that develops in cavities. These could be easy to be developed as the MICP technology is mature enough for such application. Currently, rocks are 3D printed, and the method does not allow for porosity values to be high enough.

Another opportunity is the biocementation of backfilling material of pipes in water supply networks. Often, the soil surrounding these pipes expands or contracts due to temperature and rainfall seasonal variations. The surrounding soil is often a reason responsible for pipe breaks in water supply networks for which capital investment is required for maintenance purposes [158].

4.4. Applications of MICP Related to Studies Involving Artificially Generated Porous Media

The MICP method has been proposed as a potential manufacturing approach to create customizable porous media, offering advantages over coring, which can be expensive and may disrupt cementation [82]. This technique has demonstrated success in producing specimens with varying hydraulic conductivity, porosity, and strength by using different base materials with diverse grain shapes, sizes, and particle size distributions [76]. The specimens can come in any size and shape while they can be of limitless quantities and are almost readily available [82]. The MICP method to generate such artificial specimens has been proven effective in the literature and the specimens have been characterized mechanically under various cementation levels and MICP treatment protocols. Various tests have been conducted to assess these parameters, such as tensile strength, unconfined compressive strength, stiffness, and the failure envelope [61,62,78,116,159]. The MICP porous media act as weakly cemented porous media which are slightly stronger than cohesionless sand and weaker than consolidated sandstone [159]. Amongst the available cementation methods, MICP has the advantage of retaining hydraulic conductivity (relative to other competent methods).

In the literature, there are many fluid flow experiments in cohesionless sands, which have been used as the closest substitute of poorly consolidated and weakly cemented rocks [160–166]. Thus, biotreated specimens have broadened the horizons in terms of testing and conducting in fluid flow experiments for applications in energy, hydraulics, and hydrology (refer to Table 4 for references). Such weak materials have very high porosity and hydraulic conductivity which govern the fluid flow due to excessive infiltration within the specimen. Experiments have been conducted to identify the transition between infiltration and fracturing regimes.

Table 4. MICP applications related to artificially generated porous media.

References	Application
[10,72,153,159,167]	Generation of artificial rocks of controlled properties.
[14,61,76,78,82]	Assessment of artificial rock mechanical and hydraulic properties.
[168]	Numerical simulations of artificial rock properties and fluid flow numerical experiments.
[169]	Fluid flow experiments in porous media for hydrological applications.
[170,171]	Fluid flow experiments in porous media for reservoir engineering applications.

In the field of groundwater hydrology, the desired regime depends on the application (whether uniform replacement of fluids avoiding damage of the formation or fracture induction). The success of any injection scheme depends on the delivery system of the relevant compounds [162].

One such application is groundwater remediation. The compounds could include emulsified oils (various oils and oil-in-water emulsions) to treat non-aqueous phase liquids (NAPLs), aqueous colloidal silica suspensions with increasing viscosity over time, or foams used to desorb pollutants or direct them to recovery wells. Efforts have been made to enhance the transport properties of soluble agents by increasing their viscosity. In all these cases, it is crucial to control the injection velocity (flow rate) and flow characteristics to prevent grain displacement or fracturing [162].

Another application is the subsurface injection of liquid waste, where hydraulic fracturing needs to be avoided to prevent risks to water resources. Liquid radioactive solutions are often disposed of through injection, requiring controlled fracture of the porous medium.

The findings of such experimental designs could be applicable to fluid injection events such as managed aquifer recharge (MAR) and aquifer storage and recovery (ASR). In weak formations, the dislocation of grains could potentially clog the formation, and fracturing might not be the desired outcome.

A more fundamental approach could be followed with the use of such materials. Fluid transport within the porous medium depends on available pore space, but research also focuses on flows through fractures or fractured media, as fluids can migrate through fractures rather than the pore space. Experiments can be conducted to validate and study theoretical models such as the Darcy and non-Darcy flows, the Forcheimer flow, diffusion, transient flow equations, pseudo-steady-state flows, and viscous fingering. These equations are influenced by particle size effects and, more generally, the properties of the porous medium, which define porosity and hydraulic conductivity [162].

The challenges and implications associated with the use of artificially generated biocement ed specimens are all related to the uniformity of the specimens. Even at the macroscale, cementation levels might vary greatly across the height of the specimen [46]. A balance of slower MICP reactions (either lower urease activity, or lower concentration of chemical solution) could aid in the production of uniform MICP specimens [46,159]. However, the precipitation of carbonate remains highly non-uniform at the microscale level and, up to this point, there is no control on where the carbonate crystals land in the granular network (either surface of grains, on the contacts between particles, or in the pore space) with no ability to target a specific distribution pattern, as shown in Figure 3. The distribution of the cementation within the pore network might, however, be important in many hydrological studies.

5. Further Challenges and Environmental Considerations of the Application of MICP in Hydrological Applications

Beyond the challenges discussed for each type of application, the principal challenge addressed in the MICP technology is upscaling. Most of the studies present laboratory experiments which are conducted in a controlled environment, however, there are few studies which investigated the upscaling effects of MICP [10,172–175]. The upscaling of the process requires careful planning and other considerations, such as the amount of chemicals required, the bacterial viability in such harsh environments, the possibility of inhomogeneous cementation in the spatial scale, and also the time required for application and completion of the process. The issue of uniformity/heterogeneity is crucial and in field applications there are more issues related to the delivery and distribution of bacterial solutions and chemicals and ensuring that they reach even the remotest place. Managing and controlling reaction times, as well as maintaining optimal conditions for bacterial activity, become also more difficult at larger scales. Achieving consistent and desirable precipitation results across extensive areas requires careful planning and monitoring. The cost-effectiveness and availability of resources required for large-scale MICP should be added to list of challenges associated with upscaling. Higher quantities of bacteria, nutrients, and other chemicals are required, potentially increasing costs. Importantly, the proof of concept with preliminary experiments needs to be conducted as the underlying MICP mechanisms are so complex, rendering it difficult to draw conclusions from studies that are applicable to new field application. Therefore, first, experiments should be conducted under simulated environments by varying the input parameters to identify the optimum design before any upscaling.

Another consideration is the long-term stability. In some of the applications presented in this review, the long-term stability is proven (i.e., contaminant precipitation), while for other applications this remains a great challenge (i.e., applications related to adverse environmental conditions). While short-term success can be achieved in laboratory settings, long-term stability and performance in real-world scenarios are critical. Factors such as natural weathering, environmental changes, and biological activity can have an impact on the durability of MICP-treated materials over time.

The MICP designs need to be incorporated into current designs and technologies which might be challenging. For example, the injection of bacteria and chemical solutions needs to be incorporated into current technologies (i.e., pump-and-treat, in situ bioremediation via injection wells, precise generation of barriers at targeted locations, etc.). In addition, the long-term technical performance of the technology needs to be assessed *a priori*, accounting for maintenance measures. Continuous monitoring and maintenance are essential to ensure the ongoing success of MICP in dynamic environments. The need for frequent assessment and potential retreatment can increase the complexity and costs of implementing MICP on a larger scale. These are usually detailed in a life cycle assessment plan.

Beyond the relevant discussion in this review at various sections, a more holistic and integrated approach needs to be followed for the environmental dimension. Environmental considerations need to be assessed via the development of environmental impact assessments (EIA). Factors such as the alteration of the bacterial balance, the deposition of by-products (usually ammonia for MICP) need to be assessed. It is well-known that the by-products of MICP, such as ammonia deposition, can have an impact on water quality and aquatic ecosystems. High levels of ammonia can lead to eutrophication, oxygen depletion, and harm to aquatic organisms. Introducing non-native bacteria into the various ecosystems could have unintended ecological consequences, such as disruptions in nutrient cycles, or could result in reduced biodiversity. The potential for altering microbial communities and disrupting natural processes needs to be carefully considered. These consequences may not become apparent immediately, making long-term environmental monitoring crucial. On the other hand, ecosystems with high biodiversity and various microbial communities tend to be more resilient to environmental changes which could also pose restrictions on the application of MICP if it is not conducted with native bacterial strains.

The development of an EIA might help in the standardization of the MICP procedure and its implementation in a safe manner, while it could, eventually, contribute to the development of a regulatory framework through which MICP applications in the field would require regulatory approvals. This is particularly important in the field of water resources and hydrology, since any harm to groundwater is almost irreversible.

Zhang et al. [176] have assessed the role of MICP within the frame of sustainable development goals (SDG) published by the United Nations Department of Global Communications. The authors, among other links, establish some of the relationships between hydrological and water resources applications. The list is expanded based on the findings of this work and includes more links, as shown in Table 5.

Table 5. The role of MICP on advancing the United Nations sustainable development goals (SDGs).

Sustainable Development Goals	MICP Application
SDG 14: Life below water	Water pollution—heavy metals removal. Water pollution—seawater intrusion control.
SDG 15: Life on land	Solid waste disposal—contaminated soil remediation. Erosion—rainfall erosion control. Erosion—surface erosion control in water environments on land. Erosion—coastline erosion control. Sand stability—artificial lands generation.
SDG 6: Clean water and sanitation	Water resource conservation—leakage mitigation. Water resource conservation—construction of ponds for water collection. Drought mitigation—water evaporation suppression. Groundwater recharge—MAR control via MICP.
SDG 13: Climate action	Global warming control—carbon capture and storage. Global warming control—natural fracture sealing/permeable rock sealing/plugging high permeability zones.

6. Conclusions

MICP has the potential for numerous applications in water resources, particularly in hydrologic and water resources engineering. Existing literature has already suggested several applications, which can be categorized according to the underlying mechanisms and their intended purposes: groundwater remediation, creating low hydraulic conductivity barriers to impede contaminant transport, enhancing cohesion to prevent particle movement along with fluids, and generating porous media with controlled mechanical and hydraulic properties for fluid flow studies. These underlying mechanisms have been extensively studied and are proven for various applications that share the same fundamentals as many hydrologic applications, highlighting both the potential of MICP in these fields but also its readiness level.

This review provides a comprehensive examination of the diverse applications of MICP in the fields of hydrology and water resources, elaborating on the fundamental mechanisms underlying MICP, namely, bioremediation via MICP and the alteration of mechanical and hydraulic properties. These mechanisms are proven to be central in these fields. Proven cases have been discussed, while studies that have been utilizing MICP for applications that share fundamentals with those relevant to this work have been presented. This review also discusses the new MICP applications that are near realization and opportunities for further research, and presents new areas demonstrating the great potential of the technique. The review emphasizes areas that require additional investigation, discusses encountered challenges, and outlines potential future directions for utilizing MICP in different applications, including the challenges that may arise during advancement and the environmental concerns associated with MICP implementation.

The microbially induced carbonate precipitation (MICP) technology's applicability in a variety of hydrological applications holds great promise and could broaden the horizons covering a wide spectrum of environmentally friendly engineering technologies. Further research to fine-tune the parameters of the MICP processes to align with such applications requirements could reveal more applications, fully unlocking the potential of the method in this field.

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