

**IMPLICATIONS OF REACTIVITY OF PERMEABLE REACTIVE
BARRIER (PRB) FOR REMEDIATION OF MULTIPLE
CONTAMINANTS AND ITS LONG-TERM PERFORMANCE
EVALUATION**

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CONTAMINANTS AND ITS LONG-TERM PERFORMANCE
EVALUATION**

by

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Department of Civil Engineering

Submitted

in fulfilment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

to the



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I dedicate this dissertation to my mother

Anita Singh

CERTIFICATE

This is certified that the thesis entitled “**Implications of Reactivity of Permeable Reactive Barrier (PRB) for Remediation of Multiple Contaminants and Its Long-Term Performance Evaluation**” being submitted by **Mr Rahul Singh** to the **Indian Institute of Technology Delhi, India**, for the award of the **degree of Doctor of Philosophy** is a record of the original bonafide research work carried by him under our guidance and supervision. The thesis work, in our opinion, has reached the requisite standards fulfilling the requirement for the **Degree of Doctor of Philosophy**.

The material contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

The study aims to investigate the reactivity of permeable reactive barriers (PRBs) for the remediation of multiple contaminants using selected reactive materials and their respective production batches. PRBs are significant among all the established remediation technologies for the in-situ treatment of contaminated aquifers and groundwater. Various permeable reactive media are available for treating different organic and inorganic groundwater contaminants or even mixtures of them successfully in groundwater. Among them, zero-valent iron (ZVI), supplied by different brands worldwide, dominates reactive material applied to PRBs. However, many of those ZVI brands have predominantly been produced for entirely different industrial purposes, such as food and electronic industries but not explicitly for groundwater remediation. Therefore, ZVIs do not represent tailored reagents specifically regarding destroying or immobilizing pollutants in groundwater. Thus, their reactivity towards certain contaminants in groundwater may vary significantly in a wide range. Further, it defines that different reactivity can be encountered among certain single ZVI brands, which has already been known since the technology started in the 1990s. At the same time, different reactivity may also depend on different production batches of a particular ZVI brand, which has rarely been known and consequently not comprehensively addressed and resolved so far.

Therefore, the research implemented an extensive, long-term study to develop a semi-empirical test methodology for establishing improved quality assurance guidance regarding proper field-scale implementations of different ZVI brands in PRBs. In particular, focusing on different production batches of the same brand avoids potential major failures regarding field-scale applications. Extensive long-term column experiments were followed by short-term batch experiments covering kinetic analyses to investigate the impact of two technical ZVI brands. That is, Gotthart Maier and Sponge Iron, as well as their different production

batches from the same supplier, on the degradation efficacy regarding organic pollutants, i.e., polychloroethene in groundwater. Further, the study also investigated the possible amendments of ZVI to treat hexavalent chromium (Cr(VI)) in alkaline and hyperalkaline medium. Therefore, this study extended to analyze the reactivity improvement of micro-ZVI and nano-ZVI with copper (Cu) and nickel (Ni) catalyst precursors to enhance its Cr(VI) removal capacity of ZVIs in alkaline and hyperalkaline mediums. Furthermore, the research work also focused on the long-term performance evaluation of PRBs and the impact of essential factors that can significantly drive PRB performance in the long run, using numerical modeling to treat contaminants released from multiple sources.

The result of the study showed the reactivity difference in the ZVI brands and their respective production batches for the removal of PCE from groundwater. To encounter this reactivity difference during the field-scale application of PRB, a short-term effective batch experiment guidance is proposed for the right selection of the production batch of PRB reactive material just prior to its field emplacement. Further, the study also emphasizes the necessity of catalyst precursors with ZVI for the high Cr(VI) removal efficiency, especially in alkaline and hyperalkaline mediums. Metal catalyst precursors and ZVIs provide 100% removal efficacy for Cr(VI) removal within 5 mins in hyperalkaline medium. Therefore, a modification of ZVI brands with Ni and Cu catalyst precursors is highly recommended for Cr(VI) remediation sites in hyperalkaline medium.

Furthermore, the study also suggests the performance evaluation of multi-permeable reactive barrier systems through numerical modeling and its significance for the effective and efficient remediation of a contaminated site. However, the PRB's installation cost is very high for the treatment of aquifer and groundwater, irrespective of the target contaminant. However, its in-situ passive treatment of various contaminants, with high longevity and sustainability of 20 – 30 years at low maintenance cost, makes it the best remediation

technology available. However, multiple reactivity issues and a lack of long-term performance study before its field-scale emplacement raise various long-term performance issues. Our investigations prove that appropriate guidance for successful full-scale in situ remediation is required to always properly select the right production batch of the reactive materials. Therefore, with the unique development of quality assurance guidance and proper understanding of long-term performance evaluation for different contaminants with some efficient reactive material amendments, this study may most likely prevent stakeholders from potentially severe failure after setting up a field-scale PRB for groundwater remediation.

शोध प्रबंध का शीर्षक: कई प्रदूषकों के उपचार और इसके दीर्घकालिक प्रदर्शन मूल्यांकन के लिए पारगम्य प्रतिक्रियाशील बाधा (पीआरबी) की प्रतिक्रियाशीलता के प्रभाव

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सार

अध्ययन का उद्देश्य चयनित प्रतिक्रियाशील सामग्रियों और उनके संबंधित उत्पादन बैचों का उपयोग करके कई दूषित पदार्थों के उपचार के लिए पारगम्य प्रतिक्रियाशील बाधाओं की प्रतिक्रियाशीलता की जांच करना है। दूषित जलभृत और भूजल के इन-सीटू उपचार के लिए सभी स्थापित उपचारात्मक प्रौद्योगिकियों में पारगम्य प्रतिक्रियाशील बाधाएं महत्वपूर्ण हैं। विभिन्न पारगम्य प्रतिक्रियाशील मीडिया विभिन्न कार्बनिक और अकार्बनिक भूजल संदूषकों या यहां तक कि उनके मिश्रण को सफलतापूर्वक भूजल में उपचार के लिए उपलब्ध हैं। उनमें से, दुनिया भर के विभिन्न ब्रांडों द्वारा आपूर्ति किए जाने वाले शून्य-वैलेंट आयरन को पारगम्य प्रतिक्रियाशील बाधाओं पर लागू प्रतिक्रियाशील सामग्रियों पर हावी होते देखा जाता है। हालांकि, उन शून्य-वैलेंट आयरन ब्रांडों में से कई मुख्य रूप से पूरी तरह से अलग औद्योगिक उद्देश्यों के लिए उत्पादित किए गए हैं, जैसे कि खाद्य और इलेक्ट्रॉनिक उद्योग, लेकिन भूजल उपचार के लिए स्पष्ट रूप से नहीं। इसलिए, शून्य-वैलेंट आयरन लोहा विशेष रूप से भूजल में प्रदूषकों को नष्ट करने या स्थिर करने के संबंध में अनुरूप अभिकर्मकों का प्रतिनिधित्व नहीं करते हैं। इस प्रकार, भूजल में कुछ संदूषकों के प्रति उनकी प्रतिक्रियाशीलता एक विस्तृत श्रृंखला में

महत्वपूर्ण रूप से भिन्न हो सकती है। इसके अलावा, यह परिभाषित करता है कि कुछ एकल शून्य-वैलेंट आयरन ब्रांडों के बीच अलग-अलग प्रतिक्रियाशीलता का सामना किया जा सकता है, जो पहले से ही 1990 के दशक में प्रौद्योगिकी शुरू होने के बाद से जाना जाता है। साथ ही, अलग-अलग प्रतिक्रियाशीलता एक विशेष शून्य-वैलेंट आयरन ब्रांड के विभिन्न उत्पादन बैचों पर भी निर्भर हो सकती है, जिसे शायद ही कभी जाना जाता है और परिणामस्वरूप अब तक व्यापक रूप से संबोधित और हल नहीं किया गया है।

इसलिए, अनुसंधान ने पारगम्य प्रतिक्रियाशील बाधाओं में विभिन्न शून्य-वैलेंट आयरन ब्रांडों के उचित क्षेत्र-स्तरीय कार्यान्वयन के संबंध में बेहतर गुणवत्ता आश्वासन मार्गदर्शन स्थापित करने के लिए एक अर्ध-अनुभवजन्य परीक्षण पद्धति विकसित करने के लिए एक व्यापक, दीर्घकालिक अध्ययन लागू किया। विशेष रूप से, एक ही ब्रांड के विभिन्न उत्पादन बैचों पर ध्यान केंद्रित करने से फील्ड-स्केल अनुप्रयोगों के संबंध में संभावित बड़ी विफलताओं से बचा जाता है। दो तकनीकी शून्य-वैलेंट आयरन ब्रांडों के प्रभाव की व्यापक जांच करने के लिए गतिज विश्लेषणों को कवर करने वाले अल्पकालिक बैच प्रयोगों के बाद व्यापक दीर्घकालिक स्तंभ प्रयोगों का पालन किया गया। यानी, गोथर्ट मायर और स्पंज आयरन के साथ-साथ एक ही आपूर्तिकर्ता से उनके अलग-अलग उत्पादन बैच, भूजल में कार्बनिक प्रदूषक, यानी पॉलीक्लोरोएथेन के बारे में गिरावट की प्रभावकारिता पर। इसके अलावा, अध्ययन ने हेक्सावैलेंट क्रोमियम को क्षारीय और हाइपरकेलेलाइन माध्यम में इलाज के लिए शून्य-वैलेंट आयरन के संभावित संशोधनों की भी जांच की। इसलिए, इस अध्ययन का विस्तार माइक्रो जीरो-वैलेंट

आयरन और नैनो जीरो-वैलेंट आयरन के कॉपर और निकेल उत्प्रेरक अग्रदूतों के साथ प्रतिक्रियात्मक सुधार का विश्लेषण करने के लिए किया गया ताकि क्षारीय और हाइपरकेलाइन माध्यमों में शून्य-वैलेंट आयरन की हेक्सावैलेंट क्रोमियम हटाने की क्षमता को बढ़ाया जा सके। इसके अलावा, अनुसंधान कार्य पारगम्य प्रतिक्रियाशील बाधाओं के दीर्घकालिक प्रदर्शन मूल्यांकन और आवश्यक कारकों के प्रभाव पर भी ध्यान केंद्रित करता है जो लंबे समय में पारगम्य प्रतिक्रियाशील बाधा प्रदर्शन को महत्वपूर्ण रूप से चला सकते हैं, जो कई से जारी दूषित पदार्थों के उपचार के लिए संख्यात्मक मॉडलिंग का उपयोग करते हैं। स्रोत।

अध्ययन के परिणाम ने भूजल से पीसीई को हटाने के लिए जीरो-वैलेंट आयरन ब्रांडों और उनके संबंधित उत्पादन बैचों में प्रतिक्रियात्मक अंतर दिखाया। इसके अलावा, अध्ययन उच्च हेक्सावैलेंट क्रोमियम हटाने की दक्षता के लिए उत्प्रेरक अग्रदूतों और शून्य-वैलेंट आयरन की आवश्यकता पर भी जोर देता है, विशेष रूप से क्षारीय और हाइपरकेलाइन माध्यमों में। इसके अलावा, अध्ययन संख्यात्मक मॉडलिंग के माध्यम से बहु-पारगम्य प्रतिक्रियाशील बाधा प्रणालियों के प्रदर्शन मूल्यांकन और दूषित साइट के प्रभावी और कुशल उपचार के लिए इसके महत्व का भी सुझाव देता है। हालांकि, लक्ष्य संदूषक के बावजूद, जलभृत और भूजल के उपचार के लिए पारगम्य प्रतिक्रियाशील अवरोध की स्थापना लागत बहुत अधिक है। हालांकि, विभिन्न संदूषकों का इन-सीटू निष्क्रिय उपचार, उच्च दीर्घायु और कम रखरखाव लागत पर 20-30 वर्षों की स्थिरता के साथ, इसे सर्वोत्तम उपचारात्मक तकनीक उपलब्ध कराता है। हालांकि, कई

प्रतिक्रियाशीलता के मुद्दे और इसके क्षेत्र पैमाने पर प्रतिस्थापन से पहले दीर्घकालिक प्रदर्शन अध्ययन की कमी विभिन्न दीर्घकालिक प्रदर्शन मुद्दों को उठाती है। हमारी जांच साबित करती है कि प्रतिक्रियाशील सामग्रियों के सही उत्पादन बैच का हमेशा सही ढंग से चयन करने के लिए स्वस्थानी उपचार में सफल पूर्ण पैमाने के लिए उपयुक्त मार्गदर्शन की आवश्यकता होती है। इसलिए, गुणवत्ता आश्वासन मार्गदर्शन के अद्वितीय विकास और कुछ कुशल प्रतिक्रियाशील सामग्री संशोधनों के साथ विभिन्न प्रदूषकों के लिए दीर्घकालिक प्रदर्शन मूल्यांकन की उचित समझ के साथ, यह अध्ययन हितधारकों को एक क्षेत्र-पैमाने भूजल उपचार के लिए प्रतिक्रियाशील बाधा पर पारगम्य स्थापित करने के बाद संभावित गंभीर विफलता का सामना करने से रोक सकता है।

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LIST OF ABBREVIATIONS

AC	Activated Carbon
AWC	Activated Wood Charcoal
BET	Brunauer–Emmett–Teller
bgl	Below Ground Level
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
CF	Chloroform
CHCs	Chlorinated Hydrocarbons
COPR	Chromium Ore Processing Residue
CRB	Continuous Reactive Barrier
CT	Tetrachloromethane
cVOC	Chlorinated Volatile Organic Compounds
DCE	Dichloroethene
DNAPL	Dense Non-aqueous Phase Liquid
EC	Electrical Conductivity
EC-PRB	Efficiently Controlled Permeable Reactive Barrier
F&G	Funnel-and-Gate
FID	Flame Ionization Detector
GAC	Granular Activated Carbon
GC	Gas Chromatography
GM	Gotthart Maier
GmbH	Gesellschaft mit beschränkter Haftung
ICP	Inductively Coupled Plasma
ISV	In-situ Vessels
min	Minute
mg	Milligram
mL	Milliliter
µm	Micrometer
MODFLOW	Modular Three-Dimensional Finite-Difference Groundwater Flow Model
MT3DMS	Modular Three-dimensional Multispecies Transport Model for Simulation
MZVI	Micro Zero Valent Iron
nm	Nanometer
NOM	Natural Organic Matter

NZVI	Nano Zero Valent Iron
PAHs	Polycyclic Aromatic Hydrocarbons
P&T	Pump-and-Treat
PCE	Perchloroethene
PRB	Permeable Reactive Barrier
PTZ	Pre-treatment Zones
R&D	Research and Development
RPM	Revolutions Per Minute
RUBIN	Reaktionswände und -barrieren im Netzwerkverbund
TCA	Trichloroethane
TCE	Trichloroethene
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
VC	Vinyl chloride
VMOD	Visual MODFLOW
ZVI	Zero Valent Iron

LIST OF SYMBOLS

As	Arsenic
C	Concentration Well
°C	Degree Celsius
Cd	Cadmium
Cl ⁻	Chloride
Cr	Chromium
Cr(VI)	Hexavalent Chromium
Cu	Copper
Fe	Iron
Fe ²⁺	Ferrous Iron
H ₂	Hydrogen
K	Hydraulic conductivity
k _{obs}	Rate Constant
kPa	kilopascal
Mn	Manganese
N ₂	Nitrogen
NO ₃ ⁻	Nitrate
Ni	Nickel
P	Pumping Well
Pb	Lead
Sr	Strontium
U	Uranium