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Fate And Transport Modeling of Hexavalent Chromium in Soil and Groundwater Near Chlorate Manufacturing Facilities

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Abstract*- Hexavalent chromium [Cr (VI)] poses a significant global environmental and public health threat due to its high toxicity, carcinogenicity, and mobility in aquatic and soil environments. Industrial activities, particularly sodium chlorate production facilities, are major anthropogenic sources of Cr(VI) release through operational inefficiencies and improper waste handling practices. Understanding the complex interplay of physical transport processes (advection, dispersion, diffusion) and intricate geochemical transformations (adsorption, reduction, oxidation, precipitation) is critical for predicting Cr(VI) behavior in subsurface environments. Reactive transport modeling (RTM) has emerged as an indispensable tool for simulating these coupled processes, providing a framework for assessing contamination risks and designing effective remediation strategies. This article reviews the fundamental properties of Cr(VI), its fate and transport mechanisms, specific contamination pathways from chlorate facilities, and the application of RTM, highlighting key challenges such as subsurface heterogeneity and the dynamic interconversion of chromium species. Future research directions emphasize improving understanding of Cr(III) re-oxidation, enhancing model calibration and validation, and developing adaptive management approaches for long-term site remediation.

***Indexed Terms*- Environmental Remediation, Geochemical Processes, Groundwater Modeling, Fate and Transport, Hexavalent Chromium, Soil Contamination**

I. INTRODUCTION

1.1 Global Significance of Cr(VI) Contamination

Hexavalent chromium (Cr(VI)) is a globally recognized carcinogen and environmental pollutant due to its toxicity, mobility, and persistence. Classified by the World Health Organization (WHO) and the International Agency for Research on Cancer (IARC) as a Group 1 carcinogen [1], Cr(VI) exposure has been linked to respiratory illnesses, cancer, organ failure, DNA damage, and neurotoxicity. At the cellular level, it induces oxidative stress and apoptosis, while in plants, it impairs growth and photosynthesis. Cr(VI) primarily originates from industrial effluents, including wastewater and improperly managed waste. Regulatory limits for Cr in drinking water are set at 50 µg/L (WHO) [1], 100 µg/L (US EPA) [2], and 50 µg/L in India [3]. A major regulatory concern is that existing standards often target total chromium, which includes the less harmful Cr(III), failing to fully address risks specific to Cr(VI). This highlights the need for more stringent, Cr(VI)-focused environmental standards.

1.2 Industrial Sources of Cr(VI): Focus on Chlorate Facilities

Industries such as chrome plating, leather tanning, and chemical manufacturing are major Cr(VI) sources. In chlorate production, Cr(VI) in the form of sodium dichromate, is intentionally added to the electrolyte to improve hydrogen evolution efficiency and prevent cathode corrosion[4]. While it's reduced to Cr(III) on cathode surfaces, waste containing this Cr(III) can re-oxidize back to Cr(VI) under specific environmental conditions (e.g., oxic, alkaline environments with manganese oxides)[5]. This makes even "contained" Cr(VI) use a long-term environmental risk. Effective mitigation requires not only containment during use but also an understanding of the geochemical conditions that may reverse Cr(VI) reduction in the subsurface.

II. PROPERTIES AND SPECIATION OF CR(VI) IN SOIL AND GROUNDWATER

II.1 *Chemical Characteristics and Environmental Toxicity of Cr(VI)*

Chromium primarily exists as Cr(III) and Cr(VI), with Cr(VI) being far more toxic, mobile, and bioavailable. It penetrates cells easily, mimicking essential anions, and causes oxidative stress, DNA damage, and apoptosis, making it a carcinogen and genotoxic agent[6]. In plants, Cr(VI) inhibits photosynthesis and growth. While Cr(III) is typically immobile and less harmful, it can be re-oxidized to Cr(VI) under certain environmental conditions—particularly in the presence of manganese oxides and oxidizing conditions—posing a latent risk. This redox interconversion highlights the importance of understanding subsurface geochemical conditions for long-term environmental risk management[7].

II.2 *Influence of pH and Redox Potential (Eh)*

The speciation and mobility of chromium are highly sensitive to pH and redox conditions. Cr(VI) forms soluble chromate and dichromate ions under alkaline (pH > 6) and oxidizing conditions (Eh > 0), enhancing its mobility. In contrast, Cr(III) generally precipitates as $Cr(OH)_3$ in neutral to slightly basic environments, limiting mobility[8]. However, under highly reducing or very alkaline conditions, Cr(III) can also form soluble complexes. Environmental changes—such as organic matter decomposition (which lowers Eh) or acid rain infiltration (which lowers pH)—can shift the Cr redox balance, potentially transforming immobile Cr(III) back into toxic, mobile Cr(VI). Therefore, effective risk assessment and remediation require dynamic modeling of how pH and Eh evolve over time in the subsurface.

Table 1 provides a summary of the key properties such as toxicity, mobility and common oxidation states along.

Table 1: Key Properties and Environmental Standards of Cr(VI)

Property/Parameter	Description/Value
Oxidation States	Predominantly Cr(III) and Cr(VI) in natural environment; Cr(VI) is thousands of times more cytostatic and carcinogenic than Cr(III).
Toxicity	Group 1 carcinogen (WHO, IARC); genotoxic, mutagenic; causes oxidative stress, DNA damage, organ dysfunction, various cancers (lung, skin, stomach, intestinal); neurotoxicant.
Mobility	Highly soluble and mobile in aquatic environments; exists as oxyanions (chromate, dichromate); readily leaches through soil to groundwater.

Table 2: Summary of Cr(VI) Speciation and Mobility under Varying pH and Eh Conditions

Chromium Species	pH Range	Eh Conditions	Mobility/State
Cr(VI) Species			
Chromate (CrO42-)	~6.0 to 14.0	Oxidizing (>0 V)	Highly soluble, mobile
Dichromate (Cr2O72-)	~2.0 to 6.0	Oxidizing (>0 V)	Highly soluble, mobile
Monovalent Chromate (HCrO4-)	Below ~6.0	Oxidizing (>0 V)	Highly soluble, mobile
Cr(III)			

Species			
$Cr(OH)_3$ (amorphous hydroxide)	~6.0 to 8.0	Variable	Insoluble, immobile (precipitate)
Cr^{3+}, $CrOH^{2+}$ (cations)	Below ~5.0	Low Eh	Soluble, mobile
$Cr(OH)_4^-$ (anion)	>12.0	Extreme Reducing (<0 V)	Soluble, mobile
General Speciation Control			
Cr(VI) predominance	>6.0	Oxidizing (>0 V)	Mobile
Cr(III) predominance	<6.0	Reducing	Immobile (precipitate)

III. FATE AND TRANSPORT MECHANISMS OF CR(VI) IN SUBSURFACE ENVIRONMENTS

III.1 *Physical Transport Processes: Advection, Dispersion, and Diffusion*

The subsurface migration of Cr(VI) is primarily governed by advection, diffusion, and hydrodynamic dispersion. Advection refers to the bulk movement of dissolved Cr(VI) along with flowing groundwater, influenced by hydraulic conductivity and aquifer properties. Diffusion enables solute movement from areas of high to low concentration, even in the absence of flow, while mechanical dispersion accounts for spreading due to velocity variations and porous media structure.

Figure 1 describes a conceptual chromium transport model.

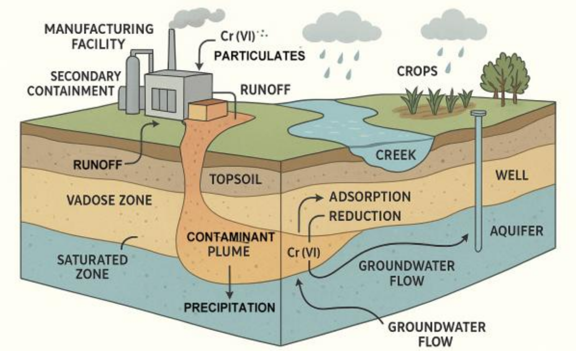

Figure 1: Conceptual Chromium Transport Model (Surface and Sub-surface)

A critical process is matrix diffusion, where Cr(VI) migrates from mobile zones (e.g., fractures) into immobile porewater regions within the rock matrix[10]. This prolongs residence time and enhances opportunities for geochemical reactions such as reduction by Fe(II) or organic matter. These slower interactions can significantly attenuate Cr(VI) plumes by converting the contaminant to Cr(III), which is more stable and less mobile. Hence, remediation strategies must consider both large-scale groundwater flow and microscale mass transfer to predict plume behavior and optimize attenuation.

III.2 *Geochemical Transformation Processes*

Beyond physical transport, the fate of Cr(VI) in the subsurface is critically determined by a series of geochemical transformation processes, primarily involving adsorption, reduction, and oxidation[11].

III.2.1 Adsorption and Desorption Mechanisms

Adsorption can temporarily immobilize Cr(VI) by binding it to positively charged mineral surfaces. This is influenced by pH, surface properties, and contaminant concentration. Natural adsorbents such as amorphous iron oxides, clay minerals, and organic matter play a major role. For example, studies show hematite and organobentonite exhibit high Cr(VI) adsorption capacity at acidic pH levels.

However, adsorption is reversible and pH-dependent. Higher pH typically reduces adsorption efficiency, which means fluctuations due to rainwater infiltration or industrial discharges can trigger desorption and remobilization. This makes long-term reliance on adsorption alone inadequate, emphasizing the need to pair it with permanent transformations such as reduction.

III.2.1 Reduction of Cr(VI) to Cr(III) (Abiotic and Biotic Pathways)

The reduction of highly toxic and mobile Cr(VI) to the less toxic and immobile Cr(III) is a cornerstone of Cr(VI) attenuation and remediation in subsurface environments. This transformation leads to the immobilization of chromium, typically as insoluble Cr(III) precipitates.

Abiotic reduction involves electron donors such as[9]:

- Organic Matter (OM): Humic substances with phenol/hydroxyl groups can reduce Cr(VI), especially under acidic conditions.
- Ferrous Iron (Fe(II)): Present in minerals (e.g., pyrite, magnetite) or added as nano zero-valent iron (nZVI), Fe(II) is highly effective in reducing Cr(VI) and forming co-precipitates with Fe(III).
- Sulfides: Reduced sulfur species also serve as efficient reductants.

Biotic reduction occurs via microbial metabolism:

- Some microbes, including *Bacillus paramycoides Cr6*, can enzymatically reduce Cr(VI) with high efficiency.
- Others contribute indirectly by generating Fe(II) or sulfides via dissimilatory reduction pathways.

The interaction between biotic and abiotic mechanisms is synergistic. Microbial processes regenerate reductants (like Fe(II)), sustain favorable redox conditions, and enhance Cr(VI) transformation, making integrated biogeochemical strategies more effective.

III.2.2 Oxidation of Cr(III) to Cr(VI)

While the reduction of Cr(VI) to Cr(III) is the desired outcome for remediation, the environmental fate of chromium is complicated by the potential for Cr(III) to re-oxidize back to the mobile and toxic Cr(VI)[10]. This re-oxidation poses a significant challenge for long-term remediation efforts.

- Manganese oxides (MnOx): Natural Mn(IV) oxides are the most potent oxidants of Cr(III), especially under acidic conditions (pH 3–5.5).
- Hydrogen peroxide (H_2O_2) and molecular oxygen (O_2): Less reactive but may contribute under specific conditions.
- Microbial activity: Can promote MnOx formation and indirectly facilitate Cr(III) oxidation.

This re-oxidation potential emphasizes the need for stable geochemical environments and possibly pH buffering or MnOx removal to avoid "rebound" effects where Cr(VI) levels rise after treatment.

III.2.3 Environmental Factors Influencing Cr(VI) Mobility and Reactivity

The mobility and reactivity of Cr(VI) in subsurface environments are controlled by a complex interplay of various environmental factors:

- pH and Eh (redox potential): These govern the speciation and stability of Cr(VI) vs. Cr(III).
- Organic matter: Acts as an electron donor and affects Cr(VI) mobility through complexation.
- Iron and manganese oxides: Central to redox transformations; Fe(II) promotes reduction while MnOx facilitates oxidation.
- Microbial activity: Drives both reduction and redox cycling; enhances the sustainability of abiotic processes.
- Soil properties: Texture, stratification, and the presence of reactive minerals and carbon content strongly influence adsorption and reactivity.

These factors create a redox buffering capacity that stabilizes or destabilizes chromium forms depending on environmental conditions. For example, if microbial activity is suppressed or organic matter is depleted, reductive capacity may fall, leading to re-oxidation and mobilization of Cr(VI). Conversely, robust microbial communities and stable pH/Eh conditions promote long-term Cr immobilization.

Advanced coupled biogeochemical models are necessary to simulate these complex feedbacks and accurately forecast chromium mobility and transformation in heterogeneous subsurface environments.

Table 3 provides an overview of the key Cr(VI) reduction and oxidation mechanisms and their influencing factors.

Table 3: Overview of Key Cr(VI) Reduction and Oxidation Mechanisms and Influencing Factors

Mechanism Type	Pathway/ Agent	Key Influencing Factors	Typical Reaction Rates/Conditions
Abiotic	Organic Matter (OM/DOM)	pH (faster at acidic pH), OM content & quality, redox potential	pH-dependent; loss of aromatic compounds & hydroxyl groups; 1.4x10^-8 to 1.5x10^-7 s^-1 (first-order)
	Ferrous Iron (Fe(II))	Fe(II) concentration, pH (faster at lower pH), presence of complexing ligands	Rapid (minutes); enhanced by Fe(II) proximity to surfaces; (CrxFe1-x)(OH)3(s) precipitation
	Sulfides (S(-II))	Sulfide concentration, redox potential	Rapid reduction by pyrite, AVS
Biotic	Microbial Activity	Microbial community structure, nutrient availability, electron donors/acceptors, Cr(VI) concentration	Direct enzymatic reduction; indirect via Fe(II) or sulfide generation; can be depressed by high Cr(VI)
Abiotic	Manganese Oxides (MnOx)	pH (optimal pH 3.0-4.0, inhibited >5.0-5.5), Mn(IV) content, Fe(II)aq presence	Primary natural oxidant; can be microbially mediated; Rate controlled by Cr(OH)3 solubility
	Hydrogen Peroxide (H2O2)	H2O2 concentration	Can oxidize Cr(III); potential secondary oxidant via Mn-oxides
	Oxygen (O2)	Kinetics	Direct oxidation by O2 is limited due to slow kinetics

IV. REACTIVE TRANSPORT MODELING OF CR(VI) IN SOIL AND GROUNDWATER

IV.1 *Principles and Common Approaches in Reactive Transport Modeling*

Reactive transport models (RTMs) are sophisticated computational tools that provide a process-based framework for simulating the intricate coupling of physical transport processes (advection, diffusion, dispersion) with a multitude of biogeochemical reactions in subsurface environments[12]. These models are designed to describe the complex interactions of competing processes across various spatial and temporal scales, making them critical for understanding and predicting contaminant behavior. RTMs integrate hydrological, geochemical, and biogeochemical processes, allowing for a comprehensive representation of contaminant fate. They serve as powerful platforms for synthesizing diverse experimental data, evaluating the relative importance of different processes, and identifying knowledge gaps that require further research.

A significant advancement in RTMs is their ability to account for "evolving porous media". This concept recognizes that biogeochemical reactions, such as mineral dissolution or precipitation and microbial growth (bioclogging), can dynamically alter the physical properties of the porous medium itself. For instance, mineral dissolution can increase porosity and permeability, while mineral precipitation (e.g., Cr(III) hydroxides, Fe(III) oxyhydroxides) can reduce porosity, potentially leading to clogging of flow pathways or the formation of impermeable layers. Conversely, microbial growth can also lead to bioclogging, reducing soil hydraulic properties. These changes in porosity, permeability, tortuosity, and reactive surface area create a dynamic feedback loop between flow, transport, and reaction.

The complexity introduced by evolving porous media extends significantly beyond traditional contaminant transport models that assume static physical properties. This dynamic feedback loop implies that long-term predictions of Cr(VI) fate, especially in remediation scenarios where substantial precipitation of Cr(III) and Fe(III) minerals occurs, require models capable of coupling geochemical reactions with changes in the hydraulic properties of the aquifer. For example, if remediation efforts lead to significant Cr(III) precipitation, the resulting decrease in porosity could alter groundwater flow paths, potentially bypassing treatment zones or creating new preferential flow channels. Therefore, accurately predicting the long-term performance and sustainability of remediation strategies necessitates RTMs that can simulate these coupled physical and chemical changes in the subsurface.

IV.2 *Widely Used Software and Models*

The field of reactive transport modeling for Cr(VI) contamination leverages several widely used software packages, often employed in a modular fashion to address different aspects of the problem:

- MODFLOW: This is a widely adopted groundwater flow modeling program, frequently integrated with Geographic Information Systems (GIS) for comprehensive groundwater resource management. It simulates the movement of water through porous media.
- PHREEQC: A powerful geochemical modeling software, PHREEQC is used to simulate chemical reactions, including speciation, adsorption, redox transformations, and precipitation/dissolution[13]. It forms the chemical engine for many coupled RTMs.
- PHT3D: This model is a reactive multicomponent transport code specifically designed to couple groundwater flow and solute transport (from MODFLOW/MT3DMS) with comprehensive geochemical reactions (from PHREEQC). An extended version, PHT3D-UZF, further extends these capabilities to variably-saturated zones, allowing for simulation in both saturated and unsaturated soil environments.
- MIN3P: This reactive transport model is utilized for simulating complex processes, including chromium isotope fractionation, which can provide insights into Cr(VI) reduction mechanisms and attenuation.
- HYDRUS-1D: This dynamics model has been shown to effectively simulate Cr(VI) migration in soil, particularly in one-dimensional systems like slag-soil profiles, providing insights into contaminant leaching and transport.
- Other Frameworks: The Numerical Environmental Multimedia Modeling System (NEMMS) extends to assessing heavy metal fate in landfill sites. Furthermore, advanced optimization techniques like Bayesian optimization (BO) are increasingly being applied for efficient and automatic model calibration, reducing the computational burden associated with complex RTMs.

The modular nature of reactive transport modeling software, exemplified by the coupling of MODFLOW for flow with PHREEQC for geochemistry, represents a significant strength in the field. This modularity allows environmental engineers to leverage specialized tools for different aspects of the problem (e.g., hydrology, geochemistry) and combine them into a comprehensive RTM. This flexibility enables the construction of models tailored to specific site conditions and contaminant processes. However, this modularity also introduces considerable challenges. Ensuring accurate and consistent data exchange between different software modules, managing potentially disparate numerical schemes, and handling the computational intensity associated with coupling complex physical and chemical processes can be demanding. For instance, the need to re-initialize chemical reactions for each cell at every time step in some coupled models can significantly add to the computational overhead. Therefore, while modularity enhances the capability and adaptability of RTMs, it simultaneously necessitates careful model setup, robust coupling algorithms, and significant computational resources to achieve accurate and efficient simulations.

IV.3 *Essential Input Parameters for Cr(VI) Transport Models*

Accurate reactive transport modeling of Cr(VI) in soil and groundwater necessitates a comprehensive set of input parameters that characterize the physical, chemical, and biological aspects of the subsurface system. These parameters can be broadly categorized as follows:

- Hydraulic and Transport Parameters: These define the movement of water and solutes through the porous medium. Key parameters include hydraulic conductivity, porosity, tortuosity, and recharge rate. Transport parameters also encompass advection and dispersion coefficients.
- Geochemical Parameters: These describe the chemical environment and the reactive species present:
- Cr Speciation: Initial concentrations of Cr(VI) and Cr(III), and their specific forms (e.g., chromate, dichromate, chromium hydroxide).
- Redox Conditions: The redox potential (Eh) and dissolved oxygen (DO) concentration, which dictate the overall oxidizing or reducing nature of the environment.
- pH: The solution pH and the buffering capacity of the soil/groundwater system, which profoundly influence Cr speciation, adsorption, and reaction rates.
- Reactive Species Concentrations: Concentrations of key electron donors and acceptors, including organic matter (OM/DOC), aqueous and mineral-bound Fe(II), manganese(II/IV) oxides, and sulfides.
- Mineralogy: The presence, type, and reactive surface area of various minerals, such as iron oxides, manganese oxides, and clay minerals, which participate in adsorption and redox reactions.
- Kinetic Parameters: Rate constants for adsorption/desorption, reduction, and oxidation reactions, which govern the speed of chemical transformations.
- Microbial Parameters: For bioreactive systems, parameters related to microbial community structure, activity, and nutrient requirements are essential.

The sheer volume and interconnectedness of these essential input parameters underscore a fundamental challenge in Cr(VI) reactive transport modeling: data scarcity and measurement error. Obtaining comprehensive field data for all these parameters, especially across heterogeneous subsurface environments, is often cost-prohibitive and technically challenging. This means that models will inherently operate with some degree of uncertainty due to incomplete or imprecise input data. This situation highlights that extensive site characterization, while crucial, is rarely perfect. Therefore, uncertainty analysis becomes a critical component of RTM, allowing modelers to understand the robustness of their predictions given the inherent limitations in input data. It also helps prioritize which parameters are most influential, guiding future data collection efforts to maximize the value of characterization campaigns.

IV.4 *Challenges and Uncertainties in Model Application*

Despite the advancements in reactive transport modeling, several significant challenges and uncertainties persist in their application to Cr(VI) contamination in soil and groundwater:

- Subsurface Heterogeneity: Natural subsurface environments are highly heterogeneous, with variations in hydraulic properties, mineralogy, and geochemistry across different scales. This heterogeneity significantly affects groundwater flow paths, contaminant distribution, and the spatial variability of reaction rates, leading to uneven distribution of contaminant removal and secondary mineral precipitation.
- Coupled Biogeochemical Processes: The complex interactions and feedback loops between hydrological, geochemical, and microbial processes are difficult to fully capture and

quantify in models. For example, high Cr(VI) concentrations can depress microbial activity, altering the system's reductive capacity. The dynamic cycling of Fe(II)/Fe(III) and Mn(II)/Mn(IV) and their interactions with organic matter and microbial activity create a highly complex redox environment that is challenging to represent accurately.

- Long-Term Stability of Remediation: Predicting the long-term stability of immobilized Cr(III) is a major challenge due to the potential for re-oxidation under changing environmental conditions. Furthermore, the formation of secondary minerals (e.g., Cr(III)/Fe(III) hydroxides) can lead to passivation of reactive surfaces or a decrease in porosity over time, affecting the long-term performance and efficiency of remediation barriers.
- Inherent Uncertainty: Models are simplifications of complex natural systems and inherently contain uncertainties stemming from conceptual model limitations, lack of accurate input information, and measurement errors.
- Computational Cost: The high number of numerical model evaluations required for comprehensive calibration and uncertainty analysis can lead to significant computing overhead, limiting the practical application of complex RTMs to large-scale or long-term problems.

The convergence of subsurface heterogeneity intricately coupled biogeochemical processes, and the challenge of predicting long-term stability creates a "predictive dilemma" for Cr(VI) modeling. While RTMs are effective for simulating short-term contaminant behavior and understanding process interactions, the dynamic and often unpredictable nature of subsurface conditions (e.g., fluctuating redox potentials, evolving microbial communities, changes in mineral precipitation affecting flow paths) makes high-confidence, long-term predictions extremely difficult. Small initial uncertainties in parameter values or conceptual models can propagate into significant errors over extended simulation periods. This implies that relying solely on a single, static long-term prediction from a model may be insufficient for effective environmental management. Instead, an adaptive management strategy, which incorporates continuous field monitoring, periodic model recalibration, and flexible remediation approaches that can respond to evolving site conditions, is often necessary for sustainable contaminant management.

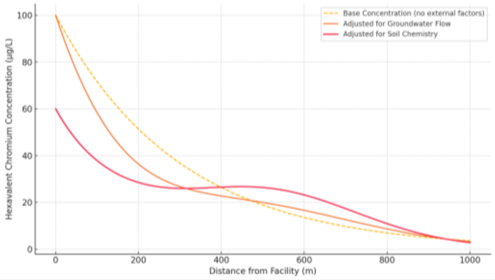

Figure 2: Typical Cr(VI) Concentration Profile Around Sodium Chlorate Manufacturing Facility

V.

V. FUTURE RESEARCH DIRECTIONS AND ADAPTIVE MANAGEMENT

V.1 *Improving Understanding of Cr(III) Re-oxidation*

A critical gap in the long-term management of Cr(VI) contamination is the incomplete understanding and prediction of Cr(III) re-oxidation to Cr(VI). While manganese oxides are recognized as the primary natural oxidants for Cr(III), the kinetics and extent of this reaction are highly dependent on environmental factors such as pH, the specific type and crystallinity of manganese oxides, and the presence of other reactive species like Fe(II). Future research should focus on:

- Detailed Kinetic Studies: Conduct more comprehensive laboratory and field studies to quantify Cr(III) oxidation rates under a wider range of environmentally relevant conditions, including varying pH (especially near neutral), redox fluctuations, and the presence of diverse organic and inorganic ligands that might complex Cr(III) or influence Mn-oxide reactivity.
- Role of Microbial Activity: Investigate the indirect role of microbial communities in mediating Cr(III) re-oxidation, particularly through their influence on manganese cycling and the formation of reactive biogenic manganese

oxides. This includes understanding how microbial metabolic pathways might either promote or inhibit Cr(III) oxidation.

- Impact of Secondary Minerals: Assess how the formation of secondary minerals (e.g., Cr(III) hydroxides, Fe(III) oxyhydroxides) influences the long-term stability of immobilized Cr(III) and its susceptibility to re-oxidation. This involves studying the passivation effects on reactive surfaces and the potential for Cr(III) to be incorporated into stable mineral structures that resist oxidation.
- Isotope Fractionation: Utilize chromium isotope fractionation as a tool to track Cr(III) re-oxidation in the field, providing a natural tracer for understanding the dominant processes and their spatial variability.

V.2 *Enhancing Model Calibration and Validation*

The predictive power of reactive transport models is directly linked to the accuracy of their input parameters and the robustness of their calibration and validation. Addressing the inherent uncertainties in subsurface systems requires:

- Advanced Characterization Techniques: Develop and apply high-resolution, non-invasive geophysical and geochemical techniques to better characterize subsurface heterogeneity and the spatial distribution of reactive minerals and microbial communities. This includes integrating data from multiple scales, from pore-scale imaging to field-scale surveys.
- Uncertainty Quantification and Sensitivity Analysis: Systematically incorporate uncertainty quantification and global sensitivity analysis into modeling workflows. This involves using probabilistic approaches (e.g., Monte Carlo simulations, Bayesian optimization) to explore the impact of uncertain input parameters on model predictions and identify the most influential parameters for targeted data collection.
- Long-Term Monitoring Data: Establish and maintain long-term monitoring programs at contaminated sites to collect data that can be used for robust model validation, particularly for assessing the long-term stability of remediation efforts and the potential for contaminant rebound. This data is crucial for refining conceptual models and improving predictive capabilities.
- Coupling of Models: Further develop coupled models that integrate different environmental compartments (e.g., vadose zone, saturated zone, surface water) and processes (e.g., hydrological, geochemical, biological, thermal) to provide a more holistic representation of contaminant fate and transport.

V.3 *Developing Adaptive Management Approaches*

Given the inherent complexities and uncertainties in subsurface environments, a static, one-time remediation plan is often insufficient for long-term contaminant management. Adaptive management, which involves continuous learning and adjustment, is crucial for Cr(VI) contamination:

- Flexible Remediation Strategies: Design remediation strategies that are flexible and can be adapted based on ongoing monitoring data and updated model predictions. This includes modular treatment systems that can be adjusted in response to changing plume dynamics or geochemical conditions.
- Real-Time Monitoring and Feedback: Implement real-time monitoring systems that provide immediate feedback on contaminant concentrations and key environmental parameters (e.g., pH, Eh, dissolved oxygen). This allows for rapid adjustments to remediation operations to optimize performance and prevent contaminant migration or rebound.
- Stakeholder Engagement: Foster strong collaboration between researchers, regulators, site managers, and local communities in the decision-making process. Adaptive management requires a shared understanding of uncertainties and a willingness to adjust strategies as new information becomes available.
- Cost-Benefit Analysis under Uncertainty: Develop robust cost-benefit analysis frameworks that explicitly account for uncertainties in contaminant behavior and remediation effectiveness. This helps in making informed decisions about resource allocation and long-term risk management.

By focusing on these future research directions and adopting adaptive management approaches, environmental engineers can significantly improve the effectiveness and sustainability of Cr(VI) contamination assessment and remediation efforts, particularly in complex settings like those near chlorate production facilities.

CONCLUSION

Hexavalent chromium (Cr(VI)) remains a significant environmental and public health concern, with industrial activities, especially chlorate production, being notable sources of contamination. Its high toxicity, mobility, and complex behavior in subsurface environments necessitate a comprehensive understanding of its fate and transport. This article has reviewed the fundamental properties of Cr(VI), highlighting its speciation dependence on pH and redox potential, and detailed the physical transport processes (advection, dispersion, diffusion) and crucial geochemical transformations (adsorption, reduction, oxidation). A key challenge identified is the dynamic interconversion between mobile Cr(VI) and less mobile Cr(III), particularly the re-oxidation of Cr(III) by manganese oxides, which can lead to contaminant rebound.

RTM has emerged as an indispensable tool for simulating these complex, coupled processes, integrating hydrological, geochemical, and biogeochemical interactions. While powerful, RTMs face challenges due to subsurface heterogeneity, the intricate nature of coupled processes, and the inherent uncertainties in input parameters. Despite these challenges, RTMs are vital for risk assessment and designing effective remediation strategies. Future research must prioritize improving the understanding of Cr(III) re-oxidation mechanisms, enhancing model calibration and validation through advanced characterization and uncertainty quantification, and developing adaptive management approaches that allow for flexible and responsive remediation strategies. By addressing these areas, there can be significant advancement towards more sustainable and effective management of Cr(VI) contaminated sites.

REFERENCES

[1] Guidelines for drinking-water quality, 2nd ed. Vol. 2. Health criteria and other supporting information. World Health Organization, Geneva, 1996.

[2] Chromium in Drinking Water, US EPA https://www.epa.gov/sdwa/chromium-drinking-water

[3] Drinking Water – Specification, Central Pollution Control Board, https://cpcb.nic.in/wqm/BIS_Drinking_Water_Specification.pdf

[4] Balázs Endrődi, Nina Simic, Mats Wildlock, Ann Cornell, A review of chromium(VI) use in chlorate electrolysis: Functions, challenges and suggested alternatives, Electrochimica Acta, Volume 234, 2017, Pages 108-122, ISSN 0013-4686, https://doi.org/10.1016/j.electacta.2017.02.150.

[5] Scott E. Fendorf and Robert J. Zasoski. Chromium(III) oxidation by manganese oxide (MnO2). Characterization. Environmental Science & Technology 1992 26 (1), 79-85 DOI: 10.1021/es00025a006

[6] WHO, Concise International Chemical Assessment Document 78 – Inorganic Chromium (VI) Compounds. International Programme on Chemical Safety, 2013.

[7] Bartlett. R. J., Kimble, J.M., Behavior of Chromium in Soils: II. Hexavalent Forms. Journal of Environmental Quality, 1976. https://doi.org/10.2134/jeq1976.00472425000500040010x

[8] Junnian Wu, Jing Zhang, Chaozheng Xiao, Focus on factors affecting pH, flow of Cr and transformation between Cr(VI) and Cr(III) in the soil with different electrolytes, Electrochimica Acta, Volume 211, 2016, Pages 652-662, ISSN 0013-4686, https://doi.org/10.1016/j.electacta.2016.06.048

[9] Aldmour, S. T. J. (2013). Abiotic reduction of Cr(VI) by humic acids: kinetics and removal mechanism (Doctoral dissertation, University of Leeds). https://etheses.whiterose.ac.uk/id/eprint/22801/

[10] Stanin, F. T. (2005). The transport and fate of chromium (VI) in the environment (pp. 165-214). CRC Press, Florida, USA.

[11] Jardine, P. M., Mehlhorn, T. L., Bailey, W. B., Brooks, S. C., Fendorf, S., Gentry, R. W., & Saiers, J. E. (2011). Geochemical processes governing the fate and transport of chromium (III) and chromium (VI) in soils. Vadose Zone Journal, 10(3), 1058-1070.

[12] Jamieson-Hanes, J. H., Amos, R. T., & Blowes, D. W. (2012). Reactive transport modeling of chromium isotope fractionation during Cr (VI) reduction. Environmental science & technology, 46(24), 13311-13316.

[13] David L. Parkhurst and C.A.J. Appelo, User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-Resources Investigation. Report99-4259.https://doi.org/10.3133/wri994259