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Date: JUN 26 2018  
 Refer To: N3B-18-0132

John Kieling, Bureau Chief  
 Hazardous Waste Bureau  
 New Mexico Environment Department  
 2905 Rodeo Park Drive East, Building 1  
 Santa Fe, NM 87505-6303

**Subject: Missing Appendix A to Attachment 9 of the Compendium of Technical Reports Conducted Under the Work Plan for Chromium Plume Center Characterization**

Dear Mr. Kieling:


Enclosed please find two hard copies of Appendix A to Attachment 9 of the Compendium of Technical Reports Conducted Under the Work Plan for Chromium Plume Center Characterization. Also enclosed are two replacement CDs with electronic files of the entire compendium. The compendium was originally submitted on March 28, 2018, by Los Alamos National Security, LLC, and Appendix A to Attachment 9 was inadvertently omitted.

If you have any questions, please contact Danny Katzman at (505) 309-1371 (danny.katzman@em-la.doe.gov) or Cheryl Rodriguez at (505) 665-5330 (cheryl.rodriguez@em.doe.gov).

Sincerely,

Sincerely,

  
 Joseph A. Legare  
 Program Manager  
 Environmental Remediation Program

  
 David S. Rhodes, Director  
 Office of Quality and Regulatory Compliance  
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JL/DR/DK/CR

- Enclosure(s):
1. Two hard copies of Appendix A to Attachment 9 of the Compendium of Technical Reports Conducted Under the Work Plan for Chromium Plume Center Characterization
  2. Two replacement CDs of the Compendium of Technical Reports Conducted Under the Work Plan for Chromium Plume Center Characterization (EP2018-0026)

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## **Appendix A**

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*CHROTRAN: A Massively Parallel Numerical Simulator  
for In Situ Biogeochemical Reduction  
of Heavy Metals in Heterogeneous Aquifers*

## A-1.0 INTRODUCTION

CHROTRAN (Chromium Transport Bio-Chemical Remediation Code) is a novel biogeochemical simulator capable of modeling the governing processes of in situ remediation of chromium, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and other contaminants in heterogeneous aquifers. CHROTRAN features full coupling between groundwater flow and reactive transport, allowing for three-dimensional simulation of the complex interactions of hydrology and biogeochemistry that occur during contaminant transport and remediation. CHROTRAN is based upon the existing PFLOTRAN code framework (Lichtner et al. 2017a, b), leveraging existing capabilities to model multi-component flow and reactive transport using highly parallelized computational solvers. CHROTRAN provides a framework for modeling biostimulation, biodegradation, abiotic degradation, growth inhibitors, and biocides, which can be used to evaluate remediation of chromium along with a variety of other contaminants. The CHROTRAN framework also considers specific processes related to chromium remediation by sodium dithionite, a strong chemical reductant with unique oxidation-reduction behavior. These key features allow CHROTRAN to simulate sophisticated, multiscale biogeochemical remediation processes and aid in the design of field pilot studies and long-term deployments at the Los Alamos National Laboratory (LANL) contamination sites.

CHROTRAN is open-source software that can be redistributed and/or modified under the terms of the GNU Lesser General Public License as published by the Free Software Foundation. The Fortran source code files for CHROTRAN, along with input files for the examples are freely available at <https://github.com/chrotran/release>. Additional information regarding CHROTRAN is available at <http://chrotran.lanl.gov>. Please refer to Hansen et al. (2017a) for a more detailed description of model development and implementation. CHROTRAN allows for simulations employing complex models with a large number of computational cells and unknown variables. Because of the abstraction of the model and its parametric flexibility, CHROTRAN can also be used to model the in situ remediation of groundwater contaminated with heavy metals besides chromium, along with a wide range of organic contaminants. These include but are not limited to explosives (e.g., RDX), hydrocarbons, chlorinated solvents, pesticides, and volatile organic compounds.

## A-2.0 USING CHROTRAN TO MODEL BIOCHEMICAL REMEDIATION

CHROTRAN biochemical remediation simulations account for spatial and temporal transients of (1) the heavy metal to be remediated, (2) introduced amendments (e.g., through well injection), and (3) biomass growth and decay. The introduced amendments can include (1) an electron donor (e.g., molasses), (2) a nontoxic conservative bio-inhibitor (e.g., ethanol), and (3) a biocide (e.g., dithionite). In addition, direct abiotic reduction by donor-metal interaction, as well as donor-driven biomass growth and bioreduction, are explicitly modeled in CHROTRAN. Other critical governing processes, such as donor sorption, bio-fouling and biomass death, are also modeled.

### A-2.0-1 Key Features

The following summarizes the key processes involved in CHROTRAN bioremediation simulations.

- **Direct abiotic reaction between introduced electron donor and contaminant:** Experimental results (Chen et al. 2015; Hansen et al. 2017b) have established a rapid direct redox reaction of hexavalent chromium [Cr(VI)] to trivalent chromium [Cr(III)] when molasses is used as an electron donor.

- **Indirect Monod kinetics:** CHROTRAN models Cr(VI) biotic degradation based upon Monod kinetics of microorganism growth (Monod 1949; Wang and Xiao 1995; Okeke 2008; Hansen et al. 2017b).
- **Biofouling/Bioclogging:** CHROTRAN adjusts flow parameters such as porosity and hydraulic conductivity to account for biomass growth. This feature can be used to represent buildup of biological material near the amendment injection wells, which interferes with amendment injection and may rapidly consume electron donors.
- **Biomass crowding:** CHROTRAN accounts for changes in the biomass growth if biomass becomes overly dense. This causes cell stress, which reduces the rate of further growth.
- **Amendment additives:** CHROTRAN simulates the impact of bio-inhibitors and biocides injected to control biomass density near the amendment injection wells. This helps the spread of injected electron donors farther from the well before they are consumed by microorganisms.
- **Multiple donor consumption pathways:** CHROTRAN accounts for different biogeochemical models of electron donor consumption.

#### A-2.0-2 Relevant Species

CHROTRAN bioremediation simulations model five species whose dynamics are governed by physical and biogeochemical aquifer processes:

- **Aqueous contaminant(s)** to be remediated.
- **Immobile and mobile electron donors**, with mass exchange between the two states.
- **Biomass**, a collection of microbial consortia and their associated extracellular material.
- **Biomass-growth inhibitor**, represented as a conservative species, whose increasing concentration decreases microbial growth.
- **Biocide**, which reacts directly with biomass and is consumed.

These species interact in the following manner:

- **Biomass growth:** the biomass growth reaction irreversibly consumes the donor to produce biomass. The process rate is linearly proportional to the biomass concentration and controlled by the contaminant concentration through Monod kinetics. Two inhibition effects are accounted for: (1) biomass crowding attenuates growth rate as the biomass concentration rises, (2) biomass growth rate is reduced as the concentration of nonlethal inhibitor increases.
- **Bioreduction:** removal of the contaminant by the biomass; the process rate is linearly proportional to the biomass concentration and controlled by the contaminant concentration through Monod kinetics. The contaminant reduction is not directly tied to any particular biological process.
- **Biocide reaction:** an interphase bimolecular reaction between the biocide and the biomass based on a second-order mass action rate law, with the added condition that the biomass concentration cannot fall below a specified minimum.
- **Biomass natural decay:** If left unstimulated (without electron donor), the biomass decays based on a first-order process and returns to its natural background level represented by a specified minimum biomass concentration.
- **Biomass respiration:** consumption of the electron donor by biomass for purposes of life maintenance, unrelated to growth.

- **Abiotic reduction:** an aqueous-phase reaction between the electron donor and the contaminant based on a second-order mass action rate law.
- **Mobile-immobile mass transfer:** a process with first-order kinetics representing sorptive retardation of the electron donor.

### A-3.0 USING CHROTRAN TO MODEL SODIUM DITHIONITE TREATMENT (GEOCHEMICAL REMEDIATION)

In situ geochemical remediation of aquifers contaminated with chromium involves the injection of a strong chemical reductant into sediments containing redox-sensitive elements. In the case of iron-bearing sediments, this results in the reduction of ferric iron [Fe(III)] to ferrous iron [Fe(II)], which binds to mineral surfaces and becomes a long-term, stationary source of reductant capable of transforming dissolved Cr(VI) to Cr(III). This process is referred to as in situ redox manipulation (ISRM). In the past, simple numerical models have been used by others (Amonette et al. 1994; Istok et al. 1999; Williams et al. 2000; Chilakapati et al. 2000) to help quantify certain steps of this process. However, a unified predictive model that combines all of the important steps that occur throughout the remediation process has not previously been developed. Such a model is critical to quantitatively evaluate remediation design strategies for field deployment. CHROTRAN is capable of modeling the entire process of ISRM using sodium dithionite from laboratory to field scale. Along with simulation of in situ reduction of Cr(VI), it is also capable of modeling other important processes that may influence remediation, such as mineral precipitation/dissolution, aqueous speciation, and pH.

#### A-3.0-1 Key Features

The following reactions are included to accurately model in situ remediation of Cr(VI) through the injection of a sodium dithionite amendment. These reactions are assumed to be kinetically limited, and rate laws were formulated after an extensive literature review (Morello et al. 1964; Creutz and Sutin 1974; Eary and Rai 1989; Rubio et al. 1992; Amonette et al. 1994; Buerge and Hug 1997, 1999; Istok et al. 1999; Williams et al. 2000; Chilakapati et al. 2000; Williams and Scherer 2001; Bond and Fendorf 2003).

- **Reduction of Fe(III) sediments by dithionite:** CHROTRAN accounts for Fe(III) and its reduction to Fe(II) by dithionite, which results in the formation of an ISRM zone (Istok et al. 1999; Williams et al. 2000).
- **Reduction of Cr(VI) by reduced iron sediments:** CHROTRAN models the reduction of and subsequent immobilization of Cr(VI) as it passes through the ISRM zone and reacts with Fe(II). This results in decreased Cr(VI) concentrations downstream of the ISRM zone but also decreases the concentration of Fe(II) within the ISRM zone.
- **Loss of dithionite through disproportionation:** Dissolved dithionite is known to be unstable and is prone to degradation through disproportionation reactions, which are accelerated in the presence of sediments (Amonette et al. 1994). This reaction is included in CHROTRAN and decreases the overall availability of dithionite, causing less reduction of Fe(III).
- **Loss of dithionite through reactions with oxygen:** In an aerobic aquifer, dissolved oxygen will also react with dithionite through redox reactions. This will also decrease the amount of injected dithionite available to reduce Fe(III) and is an important limiting factor of ISRM accounted for in CHROTRAN.
- **Oxidation of Fe(II) sediments by oxygen:** Surface-bound Fe(II) is capable of reducing other dissolved oxidants, which reduces the overall capacity of the ISRM zone to reduce Cr(VI). In an aerobic aquifer, dissolved oxygen will most likely be the dominant oxidant. The oxidation of Fe(II) sediments by dissolved oxygen is included in CHROTRAN.

### A-3.0-2 Relevant Species

CHROTRAN geochemical remediation simulations model the following species whose dynamics are governed by physical and geochemical aquifer processes:

- **Oxidants:** CHROTRAN accounts for dissolved oxygen, Cr(VI), and Fe(III). Oxygen and Cr(VI) exist in the aqueous phase and Fe(III) is represented in the solid phase as a mineral precipitate.
- **Injected reductant and its reaction products:** The injected reductant is sodium dithionite, which dissociates to sodium and dithionite. The reaction products of the different reactions involving dithionite are sulfate, sulfite, and thiosulfate.
- **Reduced species:** Dithionite reduces Fe(III) precipitates to Fe(II) bound to mineral surfaces. Surface-complexed Fe(II) is subsequently capable of reducing Cr(VI) to Cr(III) in the aqueous phase.
- **pH and pH buffers:** The degradation of dithionite is strongly pH dependent, as the kinetics of the reaction is greatly accelerated at high pH. CHROTRAN simulates pH changes that result from the redox reactions outlined above. In addition, the model accounts for injectant pH buffering (e.g., potassium bicarbonate, calcium carbonate).
- **Other aqueous species:** Equilibrium speciation is also included in CHROTRAN to estimate the concentrations of secondary aqueous species (e.g., OH<sup>-</sup>, CO<sub>3</sub><sup>-2</sup>, H<sub>2</sub>CO<sub>3</sub>(aq), HCrO<sub>4</sub><sup>-</sup>). These species influence the ionic strength, charge balance, and pH of the groundwater.
- **Mineral species and their dissolved constituents:** Both Cr(III) and Fe(III) are highly insoluble and readily precipitate in neutral to alkaline pH groundwater. For this reason, mineral precipitation is included in CHROTRAN to account for the fate of Cr(III) as chromium hydroxide and Fe(III) as ferric hydroxide. CHROTRAN considers the potential release of carbonates through the dissolution of minerals such as calcite, which will influence pH.

### A-4.0 REFERENCES

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