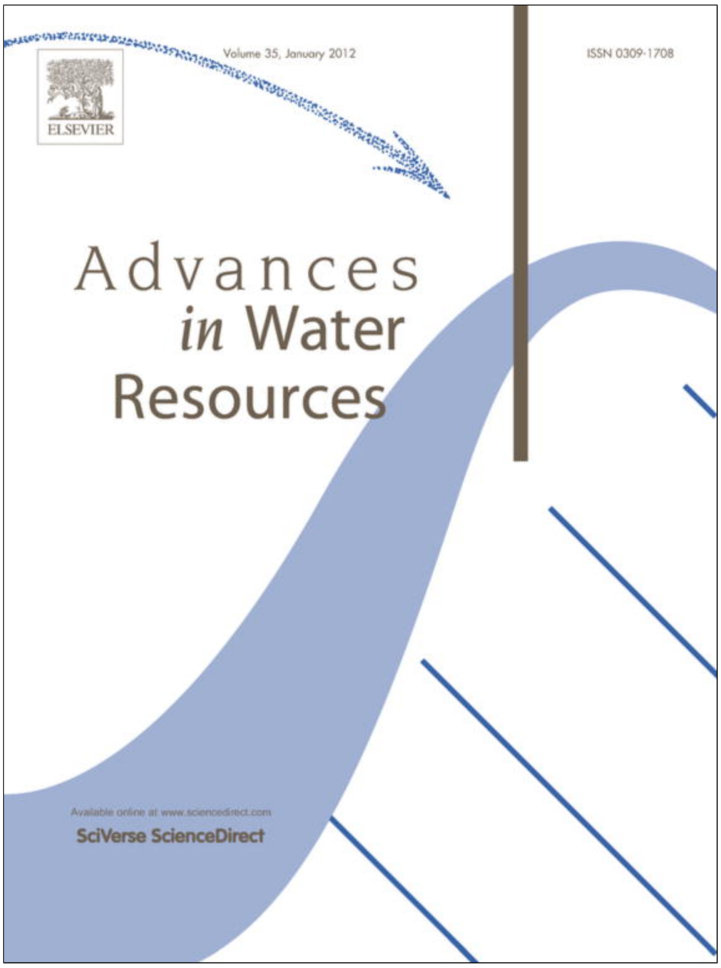
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A consistent compositional formulation for multiphase reactive transport where chemistry affects hydrodynamics

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ABSTRACT

Multiphase reactive transport formulations usually decouple flow (i.e., phase conservation) from reactive transport calculations (i.e., species conservation). Decoupling is not appropriate when reactions affect flow controlling variables (such as the partial pressure of gaseous components or the activity of water). We present a consistent compositional formulation that couples the conservation of all components. No explicit conservation of phases mass is required since they result from the conservation of all species in each phase. The formulation acknowledges that constant activity species do not affect speciation and can be eliminated, which reduces the number of unknowns. We discuss the formulation, the numerical solution, and the implementation into an object oriented code. The advantages of the formulation are illustrated by simulating the effect of mineral dehydration (including invariant points) on the hydrodynamic processes in an unsaturated column that reaches extremely dry conditions.

1. Introduction

The most common approach for solving reactive transport problems consists of decoupling the equations involved: first, the flow of fluid phases, and optionally energy transport; and, second, equations for conservation of components, including chemical reactions. Single phase (saturated and unsaturated) reactive transport codes uses this decoupled procedure [7,20,26,41]. The MIN3P code [24] couples gas flow and component conservation, but decouples the aqueous phase flow.

A similar approach is used by multiphase reactive transport codes, such as TOUGHREACT [45], CODEBRIGHT-RETRASO [35], MUFTE-UG [11] and PFLOTRAN [21]. Instead of mass balances of fluid phases, these codes adopt a compositional formulation that establishes the mass balance of the dominant components within each phase (e.g., water for the aqueous phase; dry air for the gas phase; dry CO_2 for the CO_2 phase). Phase mass balance results from the mass balance of the major components. The advantage and motivation of these formulation lies in the elimination of phase change terms, which is convenient since these terms are usually associated to heterogeneous equilibrium reactions that lack explicit expressions. Phase pressures and fluxes, and optionally temperature, are calculated in this first step. These are used as input for solving conservation equations of all chemical species.

This approach has been applied to a wide range of multiphase reactive transport problems. However it may be unsuitable when fluxes and mass balances of major components depend on chemical reactions. For example, when studying unsaturated tailings, oxygen is consumed by pyrite and Fe oxidation. It is clear that the effect of the oxygen consumption on gas flow cannot be evaluated considering only dominant components (nitrogen and vapor) in the gaseous phase. A consistent approach, besides including phase sink–source terms due to chemical reactions, should assure coherence between mass of the phase on one hand and the species on the other. The mass of all species belonging to a phase should be equal to the mass of that phase. All this aspects are difficult to represent by means of a decouple approach. Yet, none of the above codes consider them.

Soil salinization provides another example of dependency between phase fluxes and chemical reactions. The amount of liquid water in dry soils may be so small that both vapor and hydrated minerals become significant for the water balance. Wissmeier and Barry [43] addressed the effect of chemical sink–sources of water on liquid flow, for cases where transport is limited to unsaturated liquid phase. This may not suffice for cases, such as soil salinization, when gas transport is important or when water activity, which controls vapor pressure, is affected by capillary and salinity.

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