Theory of dissolution and precipitation waves—redux

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Abstract

We present a local equilibrium theory for the reactive transport of two salts that share an anion in an ideal solution. We revisit this classic problem using the theory of hyperbolic partial differential equations accounting for the volume of precipitates. We construct analytical solutions for the $2 \times 2$ system of conservation laws in the absence of hydrodynamic dispersion. The character of the system depends on the saturation of the salts, i.e., whether the fluid is saturated with both, either of the two or none of the salts. We provide a comprehensive analysis of the system and its solution. Each primitive variable, the amount of precipitate and the concentration of ions, remains constant along one class of waves that propagate in the system. The analysis of the system allows identification of seven bifurcations with respect to the intermediate state.

Keywords: reactive flow, dissolution and precipitation, nonlinear hyperbolic systems

1 Introduction

Precipitation and dissolution during flow in porous media play a major role in many different processes e.g., contaminant transport in aquifers,\textsuperscript{1,2} oil recovery processes,\textsuperscript{3–5} geothermal processes\textsuperscript{6,7} and concrete carbonation.\textsuperscript{8} Dissolution and precipitation can be induced by three distinct types of flow-induced reactions: mixing reactions between fluids of different composition,\textsuperscript{9} gradient reactions due to changes in temperature and pressure along the flow path,\textsuperscript{11} and frontal reactions driven by the invasion of a fluid with different composition and/or temperature.\textsuperscript{12–15} Here we are interested in the chromatographic patterns that arise during frontal dissolution-precipitation reactions.\textsuperscript{4} It should be noted that although the physical processes in chromatography are different than in dissolution and precipitation, the underlying mathematics is similar. It has been shown that the concept of multicomponent chromatography can be used in precipitation and dissolution problems.\textsuperscript{15}

Generally, a model for single-phase flow with dissolution and precipitation in porous media involves advective transport, hydrodynamic dispersion and molecular diffusion of components as well as chemical reactions between components.\textsuperscript{16,17} However, in large-scale problems the chromatographic pattern of frontal dissolution-precipitation reactions is independent of reaction kinetics and solute dispersion.\textsuperscript{18–21} The analysis presented below is therefore limited to systems in local chemical equilibrium and with negligible hydrodynamic dispersion. Other premises taken here are incompressibility of the medium and the fluid, immobility of precipitates and isothermal conditions. These assumptions allow for obtaining a model that falls in the class of hyperbolic partial differential equations (PDEs).\textsuperscript{15,22}

The assumption of local equilibrium introduces a discontinuity between two zones with different compositions. It is, therefore, necessary to study the evolution of the discontinuity in the initial condition. An initial-value problem with discontinuous initial states is known as \textit{Riemann Problem}. A very close concept related to the study of the evolution of discontinuities is “coherence”, initially developed for chromatography.\textsuperscript{23} Note that relaxing the local equilibrium assumption may impose a new structure for the solution. This has been studied for multiphase problems,\textsuperscript{24} where new shock structures emerge.

The coherence concept is able to demonstrate that an arbitrary initial variation may be unstable and hence it decomposes into several stable variations as it propagates through the system. These variations may travel at different speeds and new regions with constant state appear as a result.\textsuperscript{25} This is following
the method of characteristics (MOC) from which we obtain self-similar solutions for a Riemann Problem
with an initial single discontinuity at the origin.\textsuperscript{26} Self-similar solutions are characterised by a set of
waves or fronts that are separated by zones of constant composition. A wave is a composition variation
advancing through the porous medium in a transport problem.\textsuperscript{3,27–29} A phase space is usually con-
structed for analysis of the system that has the primary variables, e.g., the concentration of components,
as coordinates. In the context of hyperbolic equations, the phase space is often referred to as hodo-
graph space\textsuperscript{22} and as composition space in chromatography.\textsuperscript{18} In the composition space, waves obeying
the coherence condition translate to curves or “grids”. These grids define a map for the composition
space and are referred to as composition routes or composition paths. In the hyperbolic theory context,
composition routes are constructed using integral curves and Hugoniot loci and an additional entropy
condition.

Even relatively simple reactive transport problems display a surprisingly large number of behaviours
due to nonlinearity and coupling between the equations.\textsuperscript{30} The analysis in the hodograph plane allows
the graphical display of the entire set of solutions and hence gives an overview of the behaviour not
available with numerical solutions. For example, we show in the section Clogging waves that we can
determine if a reactive transport system can clog the pore space and identify the conditions when this
occurs.

Here, we present a local equilibrium theory for the reactive transport of two salts that share an ion
in an isothermal system with no gravity, capillary forces, mechanical or molecular diffusion. We consider
one-dimensional incompressible single-phase flow with three ionic components which can partition be-
tween the solid and fluid phases. The porous medium is also assumed to be incompressible. However, we
account for the volume of precipitates and hence, the porosity of the medium changes according to the
composition. The system is assumed to be ideal, i.e., the overall volume does not change as a chemical
reaction occurs.\textsuperscript{25} Therefore, the Darcy flux can be assumed constant.

This paper is structured as follows. In the section Model Equations, we constitute a material bal-
ance using “total concentration” that is based on the primitive variables concentration of ions and the
amount of precipitates. The resulting equations fall in the class of conservation laws. Therefore, in the
section Wave Analysis, the MOC is applied to analyse all the possible wave structures. In the section So-
lutions of the Riemann Problem, we use these waves to solve the Riemann Problem. Implications of the
theory for practical applications are highlighted in Section Implications. Conclusions are provided in the
section Conclusions.

2 Model Equations

We consider a one-dimensional reactive transport problem in a porous material $Q$. Two equilibrium
reactions are considered with ions $B$, $C$ and $S$ (e.g. $\text{Ba}^{2+}$, $\text{Ca}^{2+}$ and $\text{SO}_4^{2-}$) forming immobile $B$ and $C$
precipitate ($\text{BaSO}_4$ and $\text{CaSO}_4$) that reduce the pore-space:

\begin{align*}
\text{Ba}^{2+} (aq) + \text{SO}_4^{2-} (aq) &\leftrightarrow \text{BaSO}_4 (s), \quad k_B = n_B n_S, \quad (1a) \\
\text{Ca}^{2+} (aq) + \text{SO}_4^{2-} (aq) &\leftrightarrow \text{CaSO}_4 (s), \quad k_C = n_C n_S, \quad (1b)
\end{align*}

where $n_B$, $n_C$ and $n_S$ denote the molar concentration of ions $B$, $C$ and $S$ in the fluid per unit volume
(e.g., mol/litre). We consider an isothermal and isobaric system with equilibrium constants $k_B$ and
$k_C$. The molar densities $\omega_B$ and $\omega_C$ for precipitate $B$ and $C$, respectively, are always larger than the
concentration of ions in the fluid, i.e. $\omega_B > n_B$, $\omega_C > n_C$.

Volume conservation requires that all volume fractions sum up to one, i.e.,

\begin{equation}
\phi_F + \phi_B + \phi_C + \phi_Q = 1, \quad (2)
\end{equation}

where $\phi_j$ denotes the volume fraction of the fluid ($j = F$), $B$ precipitate ($j = B$), $C$ precipitate ($j = C$)
and the porous medium ($j = Q$). From the latter, we define the initial pore-space $\phi_P = 1 - \phi_Q$. The
resulting fluid/solid solution is assumed to be ideal, i.e., the overall volume of the solution does not change as chemical reactions occur.

We define the conservative variable or the total amount $N_j$ of ions $j$ per porous medium as

\begin{align*}
N_B &= \phi_F n_B + \phi_B \omega_B, \quad (3a) \\
N_C &= \phi_F n_C + \phi_C \omega_C, \quad (3b) \\
N_S &= \phi_F n_S + \phi_B \omega_B + \phi_C \omega_C, \quad (3c)
\end{align*}
Mass conservation requires that any variation of total amount of an ion \((N_j)\) within a volume is balanced by the net flux of that ion. We assume that the fluid and rock are incompressible and that precipitates are stationary. Hence, the flux of component \(j\) is given by the transport of the components in the fluid \(q^* n_j\). Therefore, the mass balance reads as

\[
\frac{\partial}{\partial t} \begin{pmatrix} N_B \\ N_C \\ N_S \end{pmatrix} + \frac{\partial}{\partial x} \begin{pmatrix} q^* n_B \\ q^* n_C \\ q^* n_S \end{pmatrix} = 0.
\]  

(4)

For the given assumptions, the Darcy velocity \(q^*\) is constant and using the dimensionless variables \(x = x^*/L\) for space and \(t = q^* t^*/L\) for time, where \(L\) is the length of medium, we obtain the dimensionless form of the equations

\[
\begin{align*}
\frac{\partial N_B}{\partial t} + \frac{\partial n_B}{\partial x} &= 0, \\
\frac{\partial N_C}{\partial t} + \frac{\partial n_C}{\partial x} &= 0, \\
\frac{\partial N_S}{\partial t} + \frac{\partial n_S}{\partial x} &= 0.
\end{align*}
\]

(5a) (5b) (5c)

Charge balance in an uncharged solution requires

\[n_B + n_C = n_S,\]

and hence \(N_B + N_C = N_S\). Therefore, Equation (5c) is linearly dependent to the other two and we only solve Equations (5a) and (5b).

Depending on the concentrations of ions in a fluid, we identify four distinct cases that are illustrated in Figure 1:

**BUCU:** Both ion concentrations are less than their respective saturation value \(\tilde{n}_B, \tilde{n}_C\) and the fluid is unsaturated with respect to both B and C.

**BSCU:** The fluid is saturated with salt B but is unsaturated with respect to C ions. Therefore, it may only contain B precipitate.

**BUCS:** This case is the reverse of **BSCU.** All the derivations referred to this case can be constructed by swapping B with C and vice versa. Therefore, unless specified differently, we discuss only **BSCU.** **BUCS** follows accordingly.

**BSCS:** The fluid is saturated with both salts, and the concentration of ions in the fluid is constant \((\hat{n}_B, \hat{n}_C)\). Any change in total concentration \(N_B, N_C\) changes the amount of precipitates.

Through the common ion effect, the saturation value depends on the presence of the other ions. The state variables are \(N_B\) and \(N_C\). Therefore, primitive variables, i.e., fluid concentrations \((n_B(N_B, N_C), n_C(N_B, N_C))\) and the volume fraction of precipitates \((\phi_B(N_B, N_C), \phi_C(N_B, N_C))\) are expressed in terms of \(N_B\) and \(N_C\). Their explicit form is given in the appendix.

We determine the saturated concentration \(\tilde{n}_B\) of B when there is no ion C by using the charge balance from Equation (6) to eliminate \(n_S\) in the chemical equilibrium Equation (1). We obtain

\[
\tilde{n}_B := \sqrt{k_B},
\]

(7a)

\[
\tilde{n}_C := \sqrt{k_C},
\]

(7b)

where \(\tilde{n}_B\) is the concentration of B in the fluid when it is saturated with B and no C is present. The concentrations \(\hat{n}_B, \hat{n}_C\) when the fluid is saturated with both salts are given by

\[
\hat{n}_B := \frac{\tilde{n}_B^2}{\sqrt{\tilde{n}_B^2 + \tilde{n}_C^2}},
\]

(8a)

\[
\hat{n}_C := \frac{\tilde{n}_C^2}{\sqrt{\tilde{n}_B^2 + \tilde{n}_C^2}}.
\]

(8b)
In order to obtain expressions for the curves that separate the four regions, we need to eliminate \( n_B \) and \( n_C \). Therefore, with \( \phi_B = 0 \) and solving Equation (3a) for \( n_B \) (and \( \phi_C = 0 \) and solving Equation (3b) for \( n_C \)) we obtain

\[
\begin{align*}
\phi_B &= \frac{N_B}{\phi_P - \phi_C}, \\
\phi_C &= \frac{N_C}{\phi_P - \phi_B}.
\end{align*}
\]

Using \( \phi_C = 0 \) and \( \phi_B = 0 \) in Equations (9a) and (9b) and replacing them in Equation (7a), we obtain a relation \( N_C(N_B) \) for the branch of the curve where \( C \) is unsaturated, \( B^{CU} \). Using \( \phi_B = 0 \) and \( n_B = \hat{n}_B \) in Equation (3a), we obtain an expression for \( \phi_C(N_B) \) which we insert in Equation (3b) with \( n_C = \hat{n}_C \) to obtain a relation \( N_C(N_B) \) for the branch of the curve where \( C \) is saturated, \( B^{CS} \).

\[
N_C(N_B) = \begin{cases} 
\phi_B \frac{n_B}{n_C} - N_B, & \text{for } C \text{ unsaturated}, \\
\frac{n_B - \phi_C}{n_B} N_B + \phi_P \omega_C, & \text{for } C \text{ saturated}.
\end{cases}
\]

Analogous to above, we can get the two other separating curves and obtain:

\[
N_B(N_C) = \begin{cases} 
\phi_C \frac{n_C}{n_B} - N_C, & \text{for } B \text{ unsaturated}, \\
\frac{n_C - \phi_B}{n_C} N_C + \phi_P \omega_B, & \text{for } B \text{ saturated}.
\end{cases}
\]

With the separating curves defined, we can identify the four regions as

\[
\begin{align*}
&BUCU = \{ (N_B, N_C) \mid N_B \leq C^{BU}(N_C), N_C \leq B^{CU}(N_B) \}, \\
&BSCU = \{ (N_B, N_C) \mid N_B \leq C^{BS}(N_C), N_C \geq B^{CU}(N_B) \}, \\
&BUCS = \{ (N_B, N_C) \mid N_B \geq C^{BU}(N_C), N_C \leq C^{CS}(N_B) \}, \\
&BSCS = \{ (N_B, N_C) \mid N_B \geq C^{BS}(N_C), N_C \geq C^{CS}(N_B) \}.
\end{align*}
\]

All regions lie within the triangular domain \( \{ N_B \geq 0, N_C \geq 0, N_B + \omega_B N_C < \omega_B \phi_P \} \). Figure 1 shows the hodograph plane with the separating curves Equations (10) and (11). For illustrative purposes, throughout this manuscript, we choose \( k_B = 1 \text{ mol}^2 \text{ m}^{-2}, k_C = 0.67 \text{ mol}^2 \text{ m}^{-2}, \omega_B = 3 \text{ mol, } \omega_C = 2 \text{ mol, } \phi_P = 0.4 \), unless stated otherwise. We denote the intersection of the curves from Equations (10) and (11) as \( N_t = \left( \begin{array}{c} \phi_B \hat{n}_B \\ \phi_C \hat{n}_C \end{array} \right) \) (Equation (8)); at this value, the fluid is saturated with both salts but there is no precipitate of either. The two points in the hodograph plane \( \left( \phi_B \omega_C \right) \) and \( \left( 0 \phi_C \omega_C \right) \) and the line connecting them are the union of limit points where \( \phi_P = \phi_B + \phi_C \), i.e., the porous medium is completely filled with precipitates. Therefore, the fractions in Equation (9) are definite since the denominator is always nonzero. Clearly, points above the line connecting the two corner points are unphysical because the corresponding volume of precipitates is larger than the pore space.

In this paper, we analyse the Riemann Problem associated with the system of equations (5). Therefore, we assume that at \( t = 0 \), two fluids with different compositions get in contact. In one dimension, this means that there is a point \( x_0 \) across which the concentration profile is discontinuous. Through a translation we can assume \( x_0 = 0 \) and therefore

\[
\mathbf{N}(x, 0) = \begin{cases} 
\mathbf{N}_l & x < 0, \\
\mathbf{N}_r & x > 0,
\end{cases}
\]

where \( \mathbf{N} \) is the composition vector \( \left( \begin{array}{c} N_B \\ N_C \end{array} \right) \) and the subscripts \( r \) and \( l \) refer to right fluid (downstream) and left fluid (upstream or injected fluid). Respectively. Throughout this text, we refer to a given fluid composition \( \mathbf{N} \) as state \( \mathbf{N}_l \). If a state is associated with a point in the hodograph plane, say \( \mathbf{N}_B \), the coordinates are labelled as \( N_B^l \) and \( N_B^r \). A similar notation is used for concentration of ions in the fluid and the amount of precipitates, i.e., \( \left( \phi_B^l \phi_C^l \right) \) and \( \left( \phi_B^r \phi_C^r \right) \).

### 3 Wave Analysis

This section presents the analysis of the possible waves for the system of Equations (5). For simplicity and illustration, we first treat the single reaction case where \( N_C = 0, n_C = 0, \phi_C = 0 \).
3.1 Single reaction

When ion C is not present, the fluid is either unsaturated with salt B \( (\phi_B = 0 \text{ and } N_B = \phi_P n_B = \phi_P \tilde{n}_B) \) or it is saturated and there is precipitate \( \phi_B \geq 0 \). The saturated fluid composition is \( n_B = 1/\sqrt{k_B} = \tilde{n}_B \) (c.f. Equation (1a)). Therefore, \( N_B = \phi_F \tilde{n}_B + \phi_B \omega_B = (\phi_P - \phi_B) \tilde{n}_B + \phi_B \omega_B \) and

\[
\phi_B(N_B) = \frac{N_B - \phi_P \tilde{n}_B}{\omega_B - \tilde{n}_B},
\]

(14)

where due to our assumption, \( \omega_B > \tilde{n}_B \), the above fraction is always well defined.

From Equation (5a), the resulting conservation equation is

\[
\frac{\partial N_B}{\partial t} + \frac{\partial}{\partial x} n_B(N_B) = 0.
\]

(15)

Its quasi-linear form reads

\[
\frac{\partial N_B}{\partial t} + \frac{dn_B}{dN_B} \frac{\partial N_B}{\partial x} = 0,
\]

(15a)

where

\[
\frac{dn_B}{dN_B} = \begin{cases} 0 & N_B > \phi_P \tilde{n}_B, \\ \frac{1}{\phi_P} & N_B < \phi_P \tilde{n}_B. \end{cases}
\]

(15b)

The flux function, \( n_B \) is not differentiable at \( N_B = \phi_P \tilde{n}_B \), and we need to use the integral form of mass conservation to seek the weak solution.\(^{31}\) In addition, since the flux function \( n_B \) is piece-wise linear and has a monotonic derivative (see Figure 2), the solution to the Riemann Problem is either a shock or a series of contact discontinuities.\(^{32,33}\) Contact discontinuities and shocks are elementary waves that transport a discontinuity and remain sharp in the absence of dispersion. We use the notation \( C \) for a contact discontinuity and \( S \) for a shock. In real systems, contact discontinuities smear out proportional to the square root of the travelled distance whereas shocks attain a constant shape that is continuous but does not dissipate further.\(^{15}\) Shock waves, like other waves, need to be mass conservative. The mass-conservation condition across the jump for a shock is referred to as the Rankine-Hugoniot condition. Here, in the scalar case, this means

\[
\bar{v} = \left[ \frac{n_B(N_B)}{N_B} \right],
\]

(16)

where \( \bar{v} \) is the velocity of the shock and \( [\cdot] \) represents the value of the jump across discontinuity.\(^{22}\)

In general, the solution to a single component transport problem is a wave connecting the left and right states. The notation

\[
N_l \xrightarrow{W} N_r
\]

can be used to represent the solution with \( W \) being either a shock, a contact discontinuity, or a compound wave consisting of two contact discontinuities. A compound wave appears when the single wave \( N_l \xrightarrow{W} N_r \) is not coherent and hence has to decompose into two coherent waves. In this case, since the two waves travel at different speeds, a constant intermediate state, \( i \), appears. Hence, the more descriptive notation

\[
N_l \xrightarrow{W} N_i \xrightarrow{W} N_r
\]

is used.

The single reaction case has 3 classes of solutions to the Riemann Problem. The solution can consist of

1) A contact discontinuity when \( \frac{dn_B}{dN_B} \bigg|_{N_B^l} = \frac{dn_B}{dN_B} \bigg|_{N_B^r} \) that travels with constant velocity \( \frac{dn_B}{dN_B} \bigg|_{N_B^i} \), i.e.,

\[
N_l \xrightarrow{i} N_r,
\]

2) Two contact discontinuities when \( \frac{dn_B}{dN_B} \bigg|_{N_B^l} < \frac{dn_B}{dN_B} \bigg|_{N_B^r} \): the first is stationary and the second one travels with velocity \( \frac{1}{\phi_P} \). In this case, a constant intermediate state appears between the two fronts, i.e., \( N_l \xrightarrow{i} N_i \xrightarrow{i} N_r \). The intermediate state \( N_i \) is the saturation concentration.

3) A shock wave when \( \frac{dn_B}{dN_B} \bigg|_{N_B^l} > \frac{dn_B}{dN_B} \bigg|_{N_B^r} \) that travels according to Rankine-Hugoniot condition, \( N_l \xrightarrow{\bar{v},S} N_r \).
Figure 2 provides an illustrative example for two Riemann Problems: a region of precipitate with total concentration $N_B^p$ is surrounded by unsaturated fluid with a total concentration $N_B^p$. Figure 2a shows the initial and a later profile of the total concentration. The first jump from $N_B^p$ to $N_B^q$ initially at $x_1$ belongs to the third category and is a shock. This shock travels to $x_2$ with a velocity equal to $\bar{v}$ and therefore $x_2 - x_1 = \bar{v}(t_2 - t_1)$. The second jump from $N_B^q$ to $N_B^p$ on $x_3$ belongs to the second category. In this case, the discontinuity propagates according to the derivative of the flux function. Since there is a discontinuity in the derivative, the solution wave is composed of two parts: the first part (from $N_B^q$ to $\phi p_B$) is stationary while the other part (from $\phi p_B$ to $N_B^p$) travels with fluid velocity $(1/\phi p)$. The discontinuity of the velocity at $N_B = \phi p_B$ is shown in Figure 2b. This point is the total concentration of the saturated fluid. Therefore, the front separating the saturated and the unsaturated fluid moves away to $x_4$ whereas the right bank stays at $x_3$ until the shock wave reaches it.

3.2 Two Reactions ($2 \times 2$ system)

The Riemann Problem for Equations (5a) and (5b) for the continuous case in quasi-linear form reads

$$\frac{\partial N}{\partial t} + \mathcal{J}(N) \frac{\partial N}{\partial x} = 0, \quad t > 0, \quad 1 > x > 0$$

(17a)

$$N(x, 0) = \begin{cases} N_l, & x < 0, \\ N_r, & x > 0, \end{cases}$$

(17b)

$$N(0, t) = N_l, \quad t > 0$$

(17c)

with $\mathcal{J}$ being the Jacobian matrix

$$\begin{pmatrix} \frac{\partial n_B}{\partial N_l} & \frac{\partial n_B}{\partial N_r} \\ \frac{\partial n_C}{\partial N_l} & \frac{\partial n_C}{\partial N_r} \end{pmatrix}.$$  

The functions $n_B$ and $n_C$ do not always have strong derivatives across the boundary curves (Equations (10) and (11)), because these functions take different forms in different regions that are continuous but not continuously differentiable (c.f. the appendix). Therefore, special care needs to be taken when the end points of a wave lie in different regions.

The initial concentration profile in a Riemann Problem is a discontinuity given in Equation (17b) that changes its shape as it propagates through the system. In a 2 × 2 system, this wave consists of two waves whose speeds depend on the eigenvalues of the Jacobian matrix $\mathcal{J}$. Therefore, for a strictly hyperbolic system, where the two eigenvalues are distinct and real, the solution is a superposition of a slow wave $W_l$ and a fast wave $W_2$. The two waves are concatenated through an intermediate state $N_i$. We use the following notation to denote the two waves and the intermediate point (solution for Equation (17))

$$N_l \rightarrow W_i \rightarrow N_i \rightarrow W_i \rightarrow N_r,$$

(18)

when both waves are simple.

The solution may also comprise compound waves, if either of the waves in Equation (18) is not coherent. Compound waves are typical shock-rarefactions such as those encountered in two-phase flow. However, the compound waves that arise in the solution of Equation (17) comprise only shocks and contact discontinuities. The compound wave has an additional constant state, similar to the intermediate state between the slow and fast waves. For the solution construction and representation, it is therefore helpful to represent it as an additional intermediate state and to adopt the following notation

$$N_l \rightarrow W_i \rightarrow N_{i1} \rightarrow W_{i2} \rightarrow N_r,$$

(19)

where the compound wave has been split into two simple and coherent waves and the constant states are labelled as $N_{i1}$ and $N_{i2}$. The compound wave along the slow path can be split similarly.

The composition paths are curves in the hodograph plane that follow the coherence condition. There are two classes of composition paths corresponding to each eigenvalue: integral curves ($I$) and Hugoniot loci ($H$). We obtain $N_i$ by calculating its coordinate in the hodograph plane through intersecting the composition paths corresponding to each wave.

Integral curves are the composition paths of elementary waves with smooth transition (rarefaction waves). A rarefaction wave widens with time even in the absence of diffusion. A $p$-rarefaction wave (associated with the eigenvalue $\lambda_p$) has the property $\lambda_p(N_l) < \lambda_p(N_r)$ and the $p$-integral curve ($I_p$) for an initial point $N$ is defined as

$$I_p(t, N) = N + \int_0^t r_p(N) \, dt,$$

(20)
where $r_p$ is the eigenvector for $\lambda_p$.\textsuperscript{22} If along an integral curve in Equation (20), the eigenvalue $\lambda_p$ remains constant, the resulting wave is a contact discontinuity, as is the case in the system we study.

The composition paths of shock waves are Hugoniot loci. As in the scalar case, a shock wave needs to satisfy Rankine-Hugoniot condition. The set of points that follow this condition for an arbitrary point $N$ are referred to as the Hugoniot locus

$$H(N) := \{N^*|n(N^*) - n(N) = \bar{v}(N^* - N)\},$$

(21)

where $n(N) = \left(\frac{n_B(N)}{n_C(N)}\right)$.\textsuperscript{22}

The solution to the system of algebraic nonlinear equations, given by Equation (21), is not necessarily unique and can have several branches, i.e., for a given $N$ and $N^*\bar{C}$ there may be more than one $N^*\bar{C}$ that honours Equation (21). However, only one solution is physical. One approach to obtain the correct and unique solution is to use the vanishing viscosity method.\textsuperscript{35} Accordingly, the unique solution to the original parabolic equation with diffusion approaches to that of its hyperbolic limit when the diffusion coefficient approaches zero.\textsuperscript{22} Under certain circumstances (strictly convex flux function), this can be translated to the condition for eigenvalues around a shock.\textsuperscript{36} In this manuscript, we use the Lax Entropy Condition to obtain the unique solution to Equation (21).

**Lax Entropy Condition.** A discontinuity that separates states $N_l$ and $N_r$ and propagates with velocity $\bar{v}$ satisfies Lax entropy condition if either of the inequalities below holds:

\[
\lambda_1(N_l) > \bar{v} > \lambda_1(N_r), \\
\lambda_2(N_l) > \bar{v} > \lambda_2(N_r).
\]

We enumerate the eigenvalues in ascending order, i.e., $\lambda_1 < \lambda_2$. Therefore, if the first inequality holds, the shock is a slow shock ($S_1$) and in the other case, it is referred to as a fast shock ($S_2$). For a shock wave we use the notation $N_l \xrightarrow{S_p} N_r$, $p = 1$ or 2. The Lax entropy condition ensures that a shock remains self-sharpening and therefore is stable.

### 3.2.1 Eigenvalue analysis and composition paths

The details of the calculation including the entries of the Jacobian matrix, eigenvalues, integral curves and Hugoniot loci are given in the appendix. In this subsection, we provide a summary of the mathematical character of the two classes of waves in the four different regions.

In the region $BUCU$, the eigenvalues are identical, $\lambda_1 = \lambda_2 \equiv 1/\phi_P$, and the system is diagonalisable. Therefore, every point is an umbilical point.\textsuperscript{37} In this case, the two linear transport equations can be decoupled. The solution to the system is also a contact discontinuity because the solution for each transport equation is a contact discontinuity. Also, every direction is an integral curve.

In the region $BSCU$, $\lambda_1 = 0$ and $\lambda_2 = \frac{1}{\phi_P - \phi_H}$, and so the system is strictly hyperbolic. Figure 3 illustrates the integral curves in regions $BSCU$ and $BUCS$. The slow integral curves $I_1$ are straight lines emerging from $(\omega_B\phi_P)$ and are depicted by dashed red lines in Figure 3. Along these lines, and therefore along the slow waves, the concentration of chemicals in the fluid is constant while the amount of precipitate changes. The fast integral curves $I_2$, on the other hand, are iso-porosity curves along which the concentration in the fluid changes according to Equation (1). The curves for $I_2$ are represented by solid blue lines.

The Jacobian matrix in region $BSCS$ is zero because the concentrations of the two ions in the fluid are constant as long as the fluid is saturated with both solid phases. Therefore, the flux function is constant and Equation (17) turns into a local ordinary differential equation for time. However, we shall look at it as a non-strictly hyperbolic system with both eigenvalues equal to zero. Hence, all precipitate variations (discontinuities in initial condition) remain stationary.

Figure 4a shows the slow Hugoniot locus $H_1$ for a point in $BUCU$. Any variation inside $BUCU$ is a contact discontinuity. This is equivalent to the transport of two tracers without any chemical reactions. However, if the right state belongs to another region, a shock develops, because $1/\phi_P = \lambda_1(N_r) > \lambda_1(N_l) = 0$. A shock develops as a result of the dissolution of a salt. In general, for a point in $BUCU$, there are three branches of $H_1$ curves in the other three regions: two lines emerging from the corner points in regions $BSCU$ and $BUCS$ and the line in $BSCS$ that passes through the point itself and $N_l$. A fast shock with the left state in $BUCU$ and the right state in $BSCU/BUCS$ is not admissible because it violates the Lax condition. Slow shocks are shown by dashed red straight lines.
For points in the region $BSCU$, $\mathcal{H}_4$ coincides with $\mathcal{I}_3$ because the latter are straight lines. A slow shock with the left state in $BSCU$ and right state in any other region violates the Lax condition. A fast shock with the left state in $BSCU$ is admissible if the right state lies in $BSCS$. Figure 4b illustrates fast shocks for four points in $BUCS$ and $BSCU$. The Hugoniot loci $\mathcal{H}_2$ with the left state in $BSCU$ coincide with $\mathcal{I}_2$ in the region $BSCU$ and are straight lines in the region $BSCS$. The slope of this line depends on the left state, (see Equation (23) in the section Clogging waves). The Hugoniot loci $\mathcal{H}_2$ in hodograph plane are depicted as blue lines.

Two regions $\alpha$ and $\beta$ in Figure 4 are highlighted in blue and green colour, respectively. These two regions are particularly interesting for us. A discontinuity with one of its end-points in any of these regions develops a non-coherent wave. The non-coherent wave then breaks into a compound wave. Presence of a compound wave in this system creates an additional constant state. The existence of regions $\alpha$ and $\beta$ depends on the curvature of the boundary curves (Equations (10) and (11)). These regions and their corresponding solution are discussed in the section Solution to Riemann Problem (Cases 11 to 16).

Figure 5 shows examples of solutions to the algebraic equation for $\mathcal{H}$ that are not physically admissible. In general, a shock with the left state in a region with more precipitate violates the entropy condition and is not admissible. In addition, for any point in $BSCU$, there is a detached branch of $\mathcal{H}$ in the region $BUCS$ (and for any point in $BUCS$ a detached branch in $BSCU$). Solutions on the detached $\mathcal{H}$ branch are not admissible either, because they violate the entropy condition.

In summary, we can divide all waves into three classes depending on the location of the left state; 
- **No precipitate** ($N_l \in BUCS$): Every direction is an integral curve in this region. For any point in this region, admissible shocks are $S_1$ with the right state in any other region. This class of shocks is represented by straight dashed red lines in Figure 4a.
- **One precipitate** ($N_l \in BUCS \cup BSCU$): There are two classes of integral curves in this region (Figure 3). In addition, admissible shocks have their right state in the region $BSCS$. Examples of fast shock waves are shown in Figure 4b.
- **Two precipitates** ($N_l \in BSCS$): Any variation in this region is stationary, and it corresponds to a change in the amount of precipitates. Therefore, no shock develops in this region.

The above 3 classes of composition paths are the only possible routes in the hodograph plane. Therefore, the solution of the Riemann Problem is a combination of waves that are defined by these composition paths. The analytical solution to the problem is constructed using these waves.

### 3.3 Clogging waves

In this section, we study the dissolution shock waves that reduce the porosity upon propagation. The mobile ions in the unsaturated upstream flow react with the dissolved ions from the salt and can re-precipitate in the form of another salt. This phenomenon occurs due to the presence of the co-ion effect, i.e., the shared ion between the two salts. If the re-precipitating salt has less density, it reduces the precipitation in the form of another salt. This phenomenon occurs due to the presence of the co-ion $\phi$ in this section. Recall from the section Eigenvalue analysis and composition paths and Figure 4, that $\mathcal{H}_2$ for a point $N_l = \left( \frac{N_l}{N_0}, \frac{N_l}{N_B} \right) \in BSCU$ is two parts. The first part coincides with $\mathcal{I}_2(N_l)$ inside $BSCU$ and the second part in $BSCS$ is the straight line

$$N_C = \frac{\hat{n}_C - n_B}{\hat{n}_B - n_B} (N_B - N_B) + N_B.$$

Therefore, the Hugoniot locus $\mathcal{H}$ for another point $N_l$, that is in $BSCU$ and on $\mathcal{I}_2(N_l)$, is different only on the second part. The second part of $\mathcal{H}(N_l)$, i.e., the staright line has a different slope. In fact, it can be shown that

$$\left( \frac{\partial}{\partial N_C} \right)_{\mathcal{H}_2} \left( \frac{\hat{n}_C - n_C}{\hat{n}_B - n_B} \right) < 0$$

in $BSCU$. Therefore, $\mathcal{H}_2$ for a point with $N_C = n_C = 0$ has the maximum slope $\frac{\hat{n}_C}{\hat{n}_B - n_B}$ in $BSCS$.

Analogous to this argument, the minimum slope converges to $-1 - \frac{\hat{n}_B^2}{\hat{n}_B^2}$ for a point that approaches the boundary curve $C^{BS}$ along $\mathcal{I}_2(N_l)$ (in $BSCU$). To calculate the minimum slope, l'Hospital's rule for multivariate functions is used with $(n_B, n_C) \rightarrow (\hat{n}_B, \hat{n}_C)$.39
Next, we look at the contours of porosity in the region $BSCS$. The iso-contours for porosity in this region are straight lines parallel to the hypotenuse of the domain with slope $-\omega_C/\omega_B$. Hence, if the second part of the Hugoniot locus $H$ has a slope more than the slope of iso-porosity lines, there is a decrease of porosity from the left state of a fast shock to the right state. Therefore, the necessary condition to avoid clogging is that the minimum slope of $H_2$ should be less than that of iso-porous lines, i.e.

$$-1 - \frac{n_B}{n_B} < -\frac{\omega_C}{\omega_B} \quad \Rightarrow \quad \frac{\omega_B}{\omega_C} \left(2 + \frac{1}{k_B/k_C}\right) > 1. \quad (24)$$

In other words, when a salt (C) with much higher density is more soluble, the other salt (B) starts to precipitate due to the co-ion effect. However, since the precipitating salt has lower density than the dissolving one, it will take more space and may eventually take the whole available pore space and clog the system.

Comparing the maximum slope of $H_2$ with iso-porosity lines, we obtain the sufficient condition to avoid clogging,

$$\frac{\hat{n}_C}{n_B - \hat{n}_B} < -\frac{\omega_C}{\omega_B} \quad \Rightarrow \quad \frac{\omega_B/\omega_C}{\sqrt{k_B/k_C+1} \sqrt{k_B/k_C}} > 1 \quad (25)$$

To illustrate this condition, we consider the system with $k_B = 0.5$, $k_C = 0.71$, $\omega_B = 1$, $\omega_C = 5$, $\phi_P = 0.4$, $N_r = (9/17)$. Figure 6 shows the corresponding hodograph plane. Here, we have $-\omega_C/\omega_B = -5$, whereas the maximum and minimum slopes are $-2.56$ and $-3.43$, respectively. We follow $H_2$ of a point as it approaches the boundary of the domain $(N_x + N_y)$ along two different trajectories $N_C = 0$ and $C^BS$. The resulting $H$-curves are shown as dashed (for trajectory $N_C = 0$) and solid (for trajectory $C^BS$) red lines in Figure 6, which divide $BSCS$ into three sections. Points in the upper part (e.g. $N_x = (9/20)$) cannot be the right state for any fast shock with the left state in $BSCU$. In the next section, we construct the solution to the Riemann Problem and explain why Equation (15) has no solution for this system with $N_r = (9/20)$. Extensions of the two red lines as $l_2$ in $BUCS$ divides the region $BUCS$ in three segments (Figure 6) and a similar argument applies here.

The presented wave analysis of Equation (17a) in this section allows us to provide an exact solution for the Riemann Problem Equation (17). We provide this exact solution in the next section.

### 4 Solutions of the Riemann Problem

In this section, we study the evolution of the discontinuity of the Riemann Problem (Equation (17)). There are 21 possible cases combining left and right states of the discontinuity from any of the four regions I to IV. Table 1 shows all of these cases and the corresponding locations of the left and right states. In this section, the 16 cases are considered, and the unique solution is provided for each case. The solution to cases 1-10 is straightforward, and we only briefly discuss them. Cases 10 to 16 are more involved and require a more extensive discussion. The value of the parameters, unless stated otherwise, are $k_B = 1\frac{mol}{m^2}$, $k_C = 0.67\frac{mol}{m^2}$, $\omega_B = 3\frac{mol}{m^2}$, $\omega_C = 2\frac{mol}{m^2}$, $\phi_P = 0.4$. All solutions have been confirmed using finite-volumes methods. The comparison is not shown here for the sake of brevity.

#### 4.1 Case 1 ($BSCS \rightarrow BSCS$)

When the left and right states are located in $BSCS$, then a saturated fluid is displaced by another saturated fluid. Hence, both eigenvalues are zero and the solution is a stationary wave.

#### 4.2 Case 2 ($BUCS \rightarrow BUCU$)

When both left and right states are located in $BUCS$, an unsaturated fluid is displaced by another unsaturated one. Both eigenvalues are identical (1/$\phi_P$), and the case corresponds to two tracer transport problems with the same velocity (1/$\phi_P$).

#### 4.3 Cases 3 and 4 ($BSCU \rightarrow BUCU$ and $BUCS \rightarrow BUCU$)

Case 3 describes the displacement of an unsaturated fluid by a saturated fluid emanating from a region containing precipitate of B. Figure 7 illustrates an example. Figure 7a shows that the intermediate point
\(N_i\) is found at the intersection of \(I_i(N_i)\) with the boundary \(B^{CU}\). \(N_i\) lies on the boundary \(B^{CU}\) because along the integral curve and across \(B^{CU}\) the eigenvalue has a discontinuity. The second wave \(N_i \xrightarrow{C_2} N_r\) is analogous to case 2 and propagates with velocity \(1/\phi_P\). Figure 7b illustrates these waves in the \(N - v\) plane (the profile of \(N\) after dimensionless time \(t = 1\)). Figure 7c illustrates the porosity profile for the solution. It shows the amount of precipitate \(\phi_B\) (blue), the sum \(\phi_B + \phi_C\) (dashed red) and \(\phi_P\) (yellow), such that the area between \(\phi_P\) and \(\phi_B + \phi_C\) represents the void space.

### 4.4 Case 5 and 6 (\(BSCS \rightarrow BSCU\) and \(BSCS \rightarrow BUCS\))

Case 5 models a situation where fluid flows from a region containing precipitates of both B and C into a region containing only precipitates of B. The solution is \(N_i \xrightarrow{C_1} N_i \xrightarrow{C_2} N_r\), with \(N_i\) being on the intersection of the boundary line \(B^{CS}\) and \(I_2(N_r)\). The fast eigenvalue is \(\lambda_2 = 0\) in \(BSCS\). In addition, it has a discontinuity that jumps to a nonzero value across the boundary line \(B^{CS}\). Hence, \(N_i\) lies on the boundary line \(B^{CS}\). The first wave is stationary in \(BSCS\) and does not follow any path.

### 4.5 Cases 7 (\(BSCU \rightarrow BSCU\)) and 8 (\(BUCU \rightarrow BUCS\))

Case 7 models fluid flow from a region containing precipitate B into a region containing precipitate B. Figure 8 illustrates an example for this case. The intermediate point \(N_i\) in Figure 8a is the intersection of \(I_i(N_i)\) with \(I_2(N_r)\). The solution is a stationary wave \(N_i \xrightarrow{C_1} N_i\) followed by a fast wave \(N_i \xrightarrow{C_2} N_r\). Figures 8b and 8c show the concentration and precipitate profiles, respectively. The amount of precipitates varies along the stationary wave \(C_1\) whereas the ion concentrations in the fluid \((n_B\) and \(n_C\)) vary along wave \(C_2\).

### 4.6 Case 9 (\(BSCS \rightarrow BUCU\))

Case 9 represents fluid flow from a region containing precipitates of both salts into a region without any precipitate. The wave through \(N_i\) is stationary because \(\lambda_1(N_i) = \lambda_2(N_i) = 0\). The transport wave through \(N_i\) has velocity \(1/\phi_P\). The two waves connect through point \(N_i\). A path in either of the regions \(BSCU\) and \(BUCS\) is not possible.

### 4.7 Case 10 (\(BUCU \rightarrow BSCS\))

Case 10 is the inverse of case 9, i.e., an unsaturated fluid from a region without any precipitate enters a region where precipitates of both B and C are present. Figure 10 illustrates an example for this case. As discussed in the section Two Reactions (2×2 system), the slow wave \(N_i \xrightarrow{W_1} N_i\) has to be a shock because a wave with the left state in \(BUCU\) and the right state in any other region is a shock wave. The fast wave \(N_i \xrightarrow{W_2} N_i\) has to be a shock as well because a wave with the right state in \(BSCS\) and the left state in any other region is a shock wave. The intermediate point in solution \(N_i \xrightarrow{S_1} N_i \xrightarrow{S_2} N_r\) can be either in \(BSCU\) or \(BUCS\) (\(N_{1B}\) and \(N_{1C}\) in Figure 10). I.e., either of the salts could dissolve faster. Note that also \(N_i\) is a possible intermediate point.

The sequence of dissolution depends on the solubility constants and the relative amount of precipitates and concentration of ions in the fluid for both left and right states. These criteria can be boiled down to a simple condition: If \(N_i\) lies below the extension of the line defined by \(N_r\) and \(N_i\), \(N_i\) is in \(BSCU\). Otherwise, it is in \(BUCS\). The line which connects \(N_r\) and \(N_i\) is in fact \(\mathcal{H}(N_r)\). Therefore, the solution is a slow shock \(S_1\) and the fast shock vanishes if \(N_i\) lies exactly on this line. The proofs are given in Lemmas 1 and 2 and Theorem 3 in the appendix. In summary, the solution is not stable if a slower shock is in front of a faster shock. The structure of the solution, i.e., the location of \(N_i\) changes so that this stability condition is satisfied because the speed of shocks depends on the location of all three points \(N_i\), \(N_i\) and \(N_r\). We refer to the line connecting \(N_r\) and \(N_i\) as the bifurcation line because the solution on the hodograph plane is discontinuous with respect to the location of the initial states relative to this line. However, the profile of the solution remains continuous with respect to the initial condition, because the velocities of the fronts are continuous functions of the composition (c.f. the appendix). In order to find \(N_{1B}\) (or \(N_{1C}\)) in the hodograph plane, the intersection of \(\mathcal{H}(N_i)\) with \(\mathcal{H}(N_r)\), is evaluated although the latter is not physically admissible. Generally, for any two points \(N_p\) and \(N_q\) if \(N_p \in \mathcal{H}(N_q)\) then \(N_q \in \mathcal{H}(N_p)\). Therefore, \(N_{1B}\) is the intersection \(\mathcal{H}(N_i)\) with \(\mathcal{H}(N_r)\) since \(N_{1B}\) belongs to \(\mathcal{H}(N_i)\) and \(N_r\) belongs to \(\mathcal{H}(N_i)\).
Figure 11a shows the concentration profiles of five Riemann Problems with identical $N_r$ and a $N_l$ with slightly differing $N_B$. The solution for each case in the hodograph (Figure 11b) has a completely different structure. Thus, the intermediate states are different. The velocity of the two fronts is slightly altered as a result of small changes of $N_l$.

Next, we consider a problem with the parameters and the initial condition as stated in the section Clogging waves. Here, point $N_l$ should be in $BSCU$ because $N_l$ lies on the right side of the bifurcation line $z$. However, we discussed in the section Clogging waves that $N_r$ cannot be the right state for a shock with the left state in $BSCU$. Therefore, this Riemann Problem has no solution. If, on the other hand, the right state $N'_r = (0.26, 0.20)$ as in Figure 12a, is in the middle section, the existence of a solution is determined by the location of $N_l$. Figure 12 illustrates the solution for this example with $N_l = (0.15)$. As depicted in Figure 12c, the void space in the transient region is lower than the initial void space in any other location. In fact, one can identify a prohibited region in $BUCU$ for which the solution has an unphysical intermediate state. This area is highlighted with yellow colour in Figure 10a and is bounded by two lines: The bifurcation line $z$ (cf. Figure 10) and the extension of $I_1$ of a set of limit points in $BSCU$. Physically speaking, completely fresh water cannot be used to dissolve both salts for such a system, because it leads to clogging, i.e., the porosity of the medium goes to zero (c.f. the section References sec:clog). Instead, an unsaturated fluid that contains a small amount of C should be used.

4.8 Cases 11 and 12 ($BUCU \rightarrow BSCU$ and $BUCU \rightarrow BUCS$)

An example for case 11, when an unsaturated fluid dissolves precipitate B, is depicted in Figure 13. The direct solution is $N_l \xrightarrow{S_1} N_i \xrightarrow{C_2} N_r$, where $N_i$ is the intersection of $H_1(N_l)$ and $I_2(N_r)$ in $BSCU$. This wave structure is not possible if $N_l$ belongs to region $\alpha$ in $BUCU$, because $H_1(N_l)$ and $I_2(N_r)$ cannot intersect in $BSCU$. In other words, the fast wave is not coherent. Figure 14 illustrates this case, with $N_l \xrightarrow{S_1} N_{i1} \xrightarrow{C_2} N_{i2} \xrightarrow{C_2} N_r$. Here, the second wave is compound wave of $S_2$ followed by $C_2$. $N_{i2}$ lies on the boundary $C^{B SU}$, because of the discontinuity of the second eigenvalue across this line.

There are two points to be highlighted:

1. In the second case, the first intermediate point is in $BUCS$, with C precipitates. Despite the fact that on neither side of the Riemann Problem C precipitates are present, a transient region forms with C precipitates. The region of precipitate C is forming after the dissolution of B because the concentration of C in the upstream fluid is relatively high and the added common ion S from the dissolution of salt B leads to precipitation of salt C.

2. The solution shows the compound wave structure only if $N_l$ lies in the region above the extension line. We prove in Theorem 4 that the compound wave structure is unstable if $N_l$ does not belong to $\alpha$ and the first structure is possible.

4.9 Case 13 ($BSCU \rightarrow BSCS$) and 14 ($BUCS \rightarrow BSCS$)

Cases 13 and 14 model flow from a region with one precipitate into a region where both precipitates are present. Case 13 with $N_l$ in $BSCU$ and $N_r$ in $BSCS$ is illustrated in Figures 15 and 16. In these figures, the solubility constants are altered from $k_B = 1.5 \text{mol}^2 \text{lit}^{-1}$, $k_C = 0.58 \text{mol}^2 \text{lit}^{-1}$ to $k_B = 1.5 \text{mol}^2 \text{lit}^{-1}$, $k_C = 2 \text{mol}^2 \text{lit}^{-1}$ for illustrative purposes. The structure of the solution depends on whether or not $N_r$ belongs to region $\beta$ (the green shaded region). When $N_r$ does not belong to region $\beta$, cf. Figure 15, $N_l$ is the intersection of $I_3(N_l)$ with $H(N_r)$ in $BSCU$ and therefore the solution is $N_l \xrightarrow{C_2} N_i \xrightarrow{S_1} N_r$. However, if $N_r$ lies in $\beta$, this structure is not possible, because no point on $I_3(N_l)$ can be connected to $N_r$ via $H_2(N_r)$ and the solution has a different structure. In this case, the slow wave is not coherent. Figure 16 shows an example for this case. The first wave is compound $N_l \xrightarrow{C_2} N_{i1} \xrightarrow{S_1} N_{i2}$. Its intermediate point $N_{i1}$ lies on the boundary $B^{CSU}$, where $\lambda_1$ is discontinuous. Its right state $N_{i2}$ lies in $BUCS$, where the second wave $S_2$ can follow to $N_r$.

In this case, a dissolution front initiates at $x = 0$. All the salts will eventually be dissolved by this wave because it is the slowest non-stationary wave. Using an argument similar to Theorem 4 of the appendix, it can be proved that this structure for the solution is only stable when $N_r$ lies in $\beta$. 

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4.10 Cases 15 (BSCU → BUCS) and 16 (BUCS → BSCU)

Case 15 describes the flow of a fluid from a region containing only B precipitate into a region containing only C precipitate. The first wave is a stationary wave $C_1$, because $\lambda_1(N_l) = 0$ and the last wave is $C_2$. The solution has two possible structures depending on the curvature of $B^{CU}$, i.e., whether the two non-coherent regions $\alpha$ and $\beta$ exist.

Figure 17 shows an example for the first case. Note that for illustrative purposes, we use the same parameter values as for Figure 16. The point $N_{l1}$ is the intersection of $B^{CU}$ with the integral curve $I_1(N_l)$ and $N_{l2}$ is the intersection of $H_1(N_{l1})$ with $I_2(N_r)$. The solution for this case is $N_l \xrightarrow{C_1} N_{l1} \xrightarrow{S_2} N_{l2} \xrightarrow{C_2} N_r$, i.e., the first wave is a compound wave starting from a stationary wave and followed by a $S_1$.

The above structure is unstable if the Hugoniot Locus $H_1$ of the intersection of the integral curve $I_1(N_l)$ with the separating curve $B^{CU}$ does not have a branch in $BUCS$. Then, the fast wave is a compound wave composed of a shock $S_2$ and a contact discontinuity $C_2$. Figure 18 illustrates an example for this case. Point $N_{l2}$ is the intersection of $B^{CS}$ with $I_2(N_r)$ and hence $N_{l1}$ is inside $BSCU$ and is the intersection of $H_1(N_l)$ with $H(N_{l2})$. The solution follows $N_l \xrightarrow{C_1} N_{l1} \xrightarrow{S_2} N_{l2} \xrightarrow{C_2} N_r$. The parameter values for Figure 18 are $k_B = 0.33 \frac{\text{mol}}{\text{m}^2 \text{lt}^2}$, $k_C = 1 \frac{\text{mol}}{\text{m}^2 \text{lt}^2}$, $\omega_B = 2 \frac{\text{mol}}{\text{lt}}$, $\omega_C = 3 \frac{\text{mol}}{\text{lt}}$. The two cases differ with respect to the existence of precipitates in the intermediate states.

5 Implications

In this section, we summarise and discuss the key findings of the section Solutions of the Riemann Problem from a chemical and physical perspective without the technical aspects of the construction of the solution. We make some interesting observations that can be used to design compositions in engineering applications.

In case 10 of the section Solutions of the Riemann Problem, we discussed two different solutions that occur when an unsaturated fluid enters a region with both precipitates (c.f. Figure 10a). The structure of the solution and therefore, the sequence of the dissolution of salts depends on the location of $N_l$ in the hodograph plane relative to the bifurcation line $z$. If an application prioritises the dissolution of one specific salt where both salts are present, the injection fluid composition can be designed with the help of bifurcation line $z$.

The priority is more important when the density difference between the two salts becomes more significant. Dissolution of a denser salt (for example CS) releases both ions in the fluid. The common ion (S) is now available to re-precipitate with the other mobile ion (B) and produce a less dense salt BS. Hence, the porosity of the medium reduces. If the relevant conditions hold (c.f. Equations (24) and (25)) the reduction is 100%, i.e., the system clogs itself. Figure 19 shows these two conditions in the space of $\omega_B/\omega_C$ vs $k_B/k_C$ as well as values for four pairs of minerals (BaSO$_4$, CaSO$_4$), (NaCl, KCl), (CaCO$_3$, CaSO$_4$), (LiF, LiCl). The pair (LiF, LiCl), does not satisfy either of conditions and therefore clogging is possible. Another example, why the sequence of dissolution may be important is to avoid such clogging by dissolving the less dense salt first.

Case 11 also shows a bifurcation in the behaviour on whether region $\alpha$ is present or not. The solution structure can have an intermediate precipitate of $C$ depending on the composition of $N_l$ (c.f. Figures 13a and 14a). If the unsaturated injection fluid is relatively rich in $C$ such that its corresponding point in the hodograph plane lies in the non-coherent region $\alpha$, an intermediate state with salt $C$ appears. The formation of salt $C$ effectively reduces the required pore volume of injection fluid if the main objective is only to dissolve salt $B$ but does not harm to precipitate salt $C$. That is, in dissolving salt $B$ we allow salt $C$ to precipitate and hence the lowest wave required to reach the producer is a fast shock.

When the region $\beta$ exists in the hodograph plane and contains the point corresponding to the initial fluid $N_r$, an intermediate point in the unsaturated zone appears. In other words, regardless of the amount of $B$ in the injection fluid, all the salts are dissolved (c.f. Figure 16a). However, if point $N_r$ is outside of region $\beta$, the injection of a fluid with a high concentration of $B$ does not completely dissolve salt $B$. Therefore, the transient region has precipitate of $B$.

6 Conclusions

This paper presents analytical solutions for reactive flow containing two precipitation and dissolution reactions with a shared ion in an ideal chemical solution. The presentation extends the theory of precip-
itation/dissolution waves developed by Helfferich\textsuperscript{15} to systems where changes of porosity are significant. The analysis of the structure of the solution provides a tool for identifying clogging and non-clogging situations. The mathematical solution is constructed using the method of characteristics from the theory of hyperbolic partial differential equations. The behaviour of the system is different depending on the presence of the two precipitates.

1. In the absence of precipitates, or when both precipitates exist, the system is non-strictly hyperbolic with identical eigenvalues.

2. When only one of the precipitates is present, eigenvalues are constant along integral curves, and the system is linearly degenerate.

3. Rarefaction waves do not form, and the solution is only composed of shocks and contact discontinuities.

4. Every shock wave completely dissolves at least one salt. A simple criterion is provided for the sequence of the dissolution of the salts.

5. Precipitation and partial dissolution of salts occur along stationary waves. Transport waves are not retarded and therefore travel with the fluid velocity.

6. In the solution to the general Riemann Problem, compound waves may form (shock + contact discontinuity). The compound waves form because the Jacobian matrix is not globally differentiable. The formation of compound waves depends on the parameters of the system and the initial composition. There are a total of 7 bifurcations with respect to the initial condition and system parameters for the general Riemann Problem.

7. Compound waves introduce new intermediate states. They can have a different amount of precipitates compared to the initial condition. An intermediate state with no precipitate appears when a region rich in two salts is flushed with a fluid that is saturated with only one salt (c.f. Figure 16). Conversely, intermediate states can form that have nearly no space for the fluid to flow (c.f. Figure 12).

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Secondary Variables and Derivatives

In this section, we derive explicit expressions for the secondary variables, \( n_B(N_B, N_C), n_C(N_B, N_C), \phi_B(N_B, N_C) \) and \( \phi_C(N_B, N_C) \), for each region. The expressions are given separately for each of the four regions in the hodograph plane.

In region \( BUCU \), \( \phi_B = \phi_C = 0 \) hold true and Equations (3a) and (3b) can be solved for \( n_B, n_C \):

\[
n_j(N_B, N_C) = \frac{N_j}{\phi_P}, \quad j = \{B, C\}
\]  

(26)

For Region \( BSCU \) we have \( \phi_C = 0 \) and thus from Equation (3b) we obtain

\[
\phi_B = \phi_P - \frac{N_C}{n_C(N_B, N_C)},
\]  

(27a)

where \( n_C \) is derived from Equation (6) as

\[
n_C(N_B, N_C) = \frac{n_B^2 - n_B(N_B, N_C)^2}{n_B(N_B, N_C)}.
\]  

(27b)

For finding \( n_B, \phi_C = 0 \) and Equations (27a) and (27b) are inserted into in Equation (3a) and therefore

\[
n_B = \frac{\omega_B N_C - \sqrt{m}}{2(N_B + N_C - \omega_B \phi_P)},
\]  

(27c)
where \( m = (\omega_B N_C)^2 - 4(N_B + N_C - \omega_B \phi_P)(\omega_B \phi_P - N_B)\bar{n}_B^2 \).

It can be shown that for this region that the following holds true
\[
\begin{align*}
\frac{\partial n_C(N_B, N_C)}{\partial N_B} &= \left( -1 - \frac{\bar{n}_B^2}{n_B(N_B, N_C)^2} \right) \frac{\partial n_B(N_B, N_C)}{\partial N_B}, \\
\frac{\partial n_C(N_B, N_C)}{\partial N_C} &= \left( -1 - \frac{\bar{n}_B^2}{n_B(N_B, N_C)^2} \right) \frac{\partial n_B(N_B, N_C)}{\partial N_C}.
\end{align*}
\]
(27d)
(27e)

In region \( BSCS \), the concentrations inside the fluid do not change. The concentrations are the value at \( N_t \), i.e.
\[
n_B(N_B, N_C) = \bar{n}_B, \quad n_C(N_B, N_C) = \bar{n}_C.
\]
(28)
Therefore, all the derivatives are zero.

**B  Eigenproblem**

We seek the solution of the eigenvalue problem \( \mathbf{J} r_p = \lambda_p r_p \) where \( \lambda_p \) and \( r_p \) denote the \( p \)-th eigenvalue and eigenvector, respectively, for the Jacobian matrix of the flux functions as defined Appendix A.

In region \( \text{BU}
, we obtain a diagonal matrix for \( \mathbf{J} \) with both diagonal entries as \( 1/\phi_p \). Therefore, \( \lambda_1 = \lambda_2 = 1/\phi_p \) and the directions of the eigenvectors are arbitrary.

In region \( BSCS \) the problem is trivial since \( \mathbf{J} \equiv 0 \).

For region \( \text{BCU} \), it can be shown
\[
\frac{\partial n_B(N_B, N_C)}{\partial N_C} = \omega_B \phi_P - N_B \frac{\partial n_B(N_B, N_C)}{\partial N_B} \frac{\partial n_C(N_B, N_C)}{\partial N_B}.
\]
(29)

After some algebraic calculation, we obtain
\[
\frac{\partial n_B}{\partial N_B} \frac{\partial n_C}{\partial N_C} - \frac{\partial n_B}{\partial N_B} \frac{\partial n_C}{\partial N_B} = \left( -\frac{n_B^2}{n_B^2} - 1 \right) \frac{\partial n_B}{\partial N_B} - \left( -\frac{n_B^2}{n_B^2} - 1 \right) \frac{\partial n_B}{\partial N_C} = 0,
\]
i.e., the determinant of \( \mathbf{J} \) is zero and thus \( \lambda_1 = 0 \). The other eigenvalue is the trace of \( \mathbf{J} \). It is possible to show, using simple algebraic calculations that, \( \lambda_2 = \left( \frac{\partial n_B}{\partial N_B} \right)_{N_C} + \left( \frac{\partial n_C}{\partial N_C} \right)_{N_B} = \frac{1}{\phi_p - \phi_B} \).

The second eigenvector is
\[
r_1 = \left( \lambda_1 - \mathbf{J} \right)_{21} = \left( -\mathbf{J} \right)_{21} = \left( \frac{\partial n_B}{\partial N_C} \frac{\partial n_C}{\partial N_B} \right) = \left( \bar{n}_B^2 + 1 \right) \frac{\partial n_B}{\partial N_B} \left( \phi_p - \phi_B \right) \phi_B - N_B \phi_B \right) \phi_B - N_B \phi_B \right).
\]
This means \( r_1 \) is parallel to the line \( I_1 = \{(N_B, N_C)| N_C = \frac{-N_B}{\phi_p - \phi_B} \phi_B (N_B - \phi_B) \} \) and therefore the family of lines emerging from \( \phi_B(N_B, N_C) \) are slow integral curves.

Using the partial derivatives of the flux functions for this region, we obtain
\[
r_2 = \left( -\frac{1}{\phi_p - \phi_B} \right).
\]

Using the expression Equations (27a) to (27c) we can evaluate \( \nabla_{(N_B, N_C)} \phi_B = \left( \frac{\partial n_B}{\partial N_B} \frac{\partial n_C}{\partial N_C} \right)^T \) and show \( \nabla_{(N_B, N_C)} \phi_B \cdot r_2 = 0 \) for the curve \( \phi_B(N_B, N_C) \equiv \phi \). Therefore, iso-porosity curves are fast integral curves.

**C  Admissible and inadmissible shocks**

**Theorem 1** (Slow shocks). A wave with the left state in \( \text{BU} \) and the right state in \( \text{BCU} \) is a slow shock, provided that left and right states and \( \left( \frac{\phi_B - \phi_B}{\phi_B} \right) \) form a straight line.

**Proof.** For \( N_t = \left( \frac{N_B}{N_C} \right) \in \text{BU} \), we chose an arbitrary point \( N_r = \left( \frac{N_B^i}{N_C} \right) \in \text{BCU} \) on the line
\[
l_B = \left\{ (N_B, N_C)| N_C = \frac{N_C^i}{N_B} - \omega_B \phi_B (N_B - N_B^i) + N_C^i \right\}
\]
(30)
and show that this point belongs to $\mathcal{H}_1(\mathcal{N}_l)$.

The expressions for the coordinates of the left and right states together with the equation of the line can be simplified to obtain

$$\frac{n_B - n_B'}{N_B - N_B'} = \frac{n_C - n_C'}{N_C - N_C'}.$$  

In words, the arbitrary point satisfies the Rankine-Hugoniot condition.

Since the slope of $l_B$ in Equation (30), $-\omega_B/\phi_B$, is negative, $N_C < N_C'$ holds true. This allows us to show

$$\hat{\nu}(\mathcal{N}_l; \mathcal{N}_r) = \left(\frac{N_C'}{\phi_p - \phi_p} - \frac{\phi_C'}{\phi_p}\right) / \left(N_C' - N_C''\right) < \frac{1}{\phi_p} = \lambda_1(\mathcal{N}_r).$$

On the other hand, if we express $\phi_B$ in terms of $N_B$ and $N_C'$, we can show $\hat{\nu}(\mathcal{N}_l; \mathcal{N}_r) > 0 = \lambda_1(\mathcal{N}_l)$.  

From the above theorem, a shock with left state in $BUCU$ and right state in $BSCU$ is stable. In addition, a shock with the left state in $BSCS$ and the right state in $BSCU$ is unstable because, for $\mathcal{N}_l \in BSCS$, $\lambda_1(\mathcal{N}_l) = \lambda_2(\mathcal{N}_l) = 0$ and therefore any shock violates Lax entropy condition.

**Theorem 2** (Detached $\mathcal{H}$). For a point in $BSCU$, the detached branch of the Hugoniot loci is not admissible.

**Proof.** We prove, by contradiction, that a shock with the right state on the detached branch of $\mathcal{H}$ is unstable. For a given point $\mathcal{N}_l = \left(\frac{N_B}{N_C}; \frac{N_C}{N_B}\right) = \left(n_B^l(\phi_p - \phi_p^l) + \phi_p \omega_B\right) / n_C^l(\phi_p - \phi_p^l) \in BSCU$, let $\mathcal{R}$ be the set all points in the detached $\mathcal{H}$. It can be directly shown that $\exists \mathcal{N}_r \in \mathcal{R}$ such that $N_B^r = N_B^l = 0$. In addition, $\mathcal{N}_s = \left(\frac{N_B}{N_C}; \frac{N_C}{N_B}\right) = \left(n_B^s(\phi_p - \phi_p^s) + \phi_p \omega_B\right) / n_C^s(\phi_p - \phi_p^s)$, where $n_C^s = \bar{\nu}C$ because the fluid is only saturated with $C$ and does not contain any $B$. The proof has three parts:

**I-** First, we prove that

$$\arg \min_{\mathcal{N}_r \in \mathcal{R}} \lambda_2(\mathcal{N}_r) = \mathcal{N}_s.$$  

From Appendix B, we know $\lambda_2(\mathcal{N}_r) = \frac{1}{\phi_p - \phi_p^s}$. Therefore, we only need to prove $\min_{\mathcal{N}_r} \phi_C^s = \phi_C^s$, i.e., the lower end of the detached $\mathcal{H}$ curve has the lowest porosity. Since the other end of the curve has the lowest porosity and the curve is continuous, it remains to show that no other point has porosity equal to that of $\mathcal{N}_s$. We prove this by contradiction: Suppose $\exists \mathcal{N}_r \in \mathcal{H}(\mathcal{N}_l), \mathcal{N}_r \neq \mathcal{N}_s$ such that $\phi_C^r = \phi_C^s$. Since $\mathcal{N}_s \in \mathcal{H}(\mathcal{N}_l)$ we can derive a relation for $\phi_C^s$. Replacing this for $\mathcal{N}_r$ we obtain two expressions for $n_B^r$ and $n_C^r$

$$n_B^r = \frac{n_B^l \bar{\nu}C - n_C^l}{\bar{\nu}C - n_C^l},$$

$$n_C^r = \bar{\nu}C - \frac{n_B^r}{n_B^l}(\bar{\nu}C - n_C^l),$$

which do not satisfy the charge balance equation (Equation (6)). Therefore, we have proved by contradiction that such a point does not exist.

**II-** Next, we show that

$$\arg \max_{\mathcal{N}_r \in \mathcal{R}} \hat{\nu}(\mathcal{N}_l; \mathcal{N}_r) = \mathcal{N}_s.$$  

Since $\forall \mathcal{N}_r \in \mathcal{R}, \mathcal{N}_r \neq \mathcal{N}_s$ we have

$$\hat{\nu}(\mathcal{N}_l - \mathcal{N}_s) - \hat{\nu}(\mathcal{N}_l - \mathcal{N}_r) = \frac{n_B^l - n_B'^l}{N_B^l - N_B'^l} = \frac{-n_B^l \phi_B^l}{N_B^l(N_B^l - N_B'^l)} + \frac{n_B'^l \phi_B^l}{N_B^l(N_B^l - N_B'^l)} = \frac{n_B^l \phi_B^l}{N_B^l(N_B^l - N_B'^l)} > 0.$$  

**III-** Last, we know that

$$\lambda_2(\mathcal{N}_l) > \hat{\nu}(\mathcal{N}_l; \mathcal{N}_r),$$

$$\lambda_2(\mathcal{N}_r) > \hat{\nu}(\mathcal{N}_l; \mathcal{N}_r),$$

i.e., all $\mathcal{N}_r \in \mathcal{R}$ violate the Lax entropy condition and therefore the shock is not admissible.
The following two lemmas are used to prove the uniqueness of the solution to case 10 (Theorem 3).

**Lemma 1** (bifurcation line \( z \)). Suppose \( N_l \in BUCU \) and \( N_r \in BSCS \). Let \( z \) be the line passing through \( N_r \) and \( N_l = \left( \frac{N_{N_l}}{N_{N_r}} \right) = \left( \frac{v_{B} \phi_{r}}{v_{B} \phi_{r}} \right) \). Let also \( N_{IB} = \mathcal{H}(N_l) \cap \mathcal{H}(N_r) \cap BSCU \) and \( N_{IC} = \mathcal{H}(N_l) \cap \mathcal{H}(N_r) \cap BUCS \). If \( N_l \in l \) then \( \bar{v}(N_l; N_{IB}) = \bar{v}(N_{r}; N_{r}) \) and \( \bar{v}(N_l; N_{IC}) = \bar{v}(N_{r}; N_{r}) \).

**Proof.** The proof is tedious with trivial algebraic calculations. We only sketch the outline of the proof for \( \bar{v}(N_l; N_{IB}) = \bar{v}(N_{r}; N_{r}) \). The other equality \( \bar{v}(N_l; N_{IC}) = \bar{v}(N_{r}; N_{r}) \) can be proved similarly. To do this, a system of 5 equations with 5 unknowns need to be solved. The unknowns are the coordinates of \( N_{IB} \) in the hodograph plane (2), its fluid concentrations (2) and the amount of precipitate B. The equations are
1. Total concentration for \( N_{IB} \),
2. Charge balance for \( N_{IB} \),
3. \( N_{IB} \in \mathcal{H}(N_l) \),
4. \( N_{IB} \in \mathcal{H}(N_r) \).

**Lemma 2** (Diversion from the bifurcation line \( z \)). Suppose \( N_r \in BSCS \) and \( N_l \in BUCU \) lies on the line \( z \) defined in Lemma 1. Let \( l_{BSCU} \) be part of \( \mathcal{H}_1(N_l) \) that lies in \( BSCU \). Then, for any point \( N_{\xi} \) with \( N^c_{\xi} > N^l_{\xi} \) that lies on line \( l_{BSCU} \) we obtain \( \bar{v}(N_{\xi}; N_{IB}) > \bar{v}(N_{IB}; N_r) \). The resulting inequality is inverse when \( N^c_{\xi} < N^l_{\xi} \).

**Proof.** Consider the case where \( N^c_{\xi} > N^l_{\xi} ; N_{IB} \), or the intermediate point in the region \( BSCU \), is identical for both points \( N_l \) and \( N_{\xi} \).

From Lemma 1, we obtain that \( W_1 \) and \( W_2 \) in \( N_{l} \xrightarrow{W_1} N_{IB} \xrightarrow{W_2} N_{r} \) have equal velocities \( \bar{v}(N_l; N_{IB}) = \bar{v}(N_{IB}; N_r) = \frac{v_{B} \phi_{l} - v_{B} \phi_{r}}{N^l_{B} - N^l_{B}} \). On the other hand, since the intermediate points for both cases coincide, \( W_2 \) in \( N_{l} \xrightarrow{W_1} N_{IB} \xrightarrow{W_2} N_{r} \) and \( W_2 \) are identical. It remains to show \( \bar{v}(N_{\xi}; N_{IB}) > \bar{v}(N_l; N_{IB}) \). The later is possible to prove because \( \phi_{l} < 1 \) and therefore
\[
n^l_{B} - n^l_{B} > N^c_{\xi} - N^l_{\xi} > 0,
\]

Similarly, opposite results could be obtained by assuming \( N_{\xi} \) on the left of \( N_l \) or
\[
n^l_{B} - n^l_{B} < N^c_{\xi} - N^l_{\xi} < 0.
\]

**Theorem 3.** For a Riemann Problem with \( N_r \in BSCS \) and \( N_l \in BUCU \) below the bifurcation line \( z \) defined in Lemma 1 (case 10 in the section Solutions of the Riemann Problem), the intermediate state lies in \( BSCU \).

**Proof.** Since, \( N_l \in BUCU \), \( \exists N^*_l \in BUCU \) that also lies on \( l_{BSCU} \) (defined in the proof of Lemma 2), i.e \( \mathcal{H}_1(N_l) = \mathcal{H}_1(N^*_l) \). Therefore, we have
\[
M(N_l; N_r) = M(N^*_l; N_r) = N_{IB},
\]

where by \( M(N_l; N_r) \), denotes the intermediate state of the Riemann Problem with initial states \( N_l \) and \( N_r \). From Lemmas 1 and 2 we obtain
\[
\bar{v}(N^*_l; N_{IB}) = \bar{v}(N_{IB}; N_r) > \bar{v}(N_l; N_{IB})
\]

In addition, (again from Lemmas 1 and 2):
\[
\forall N_l, \exists N^{**}_l \in l_{BUCU} \text{ s.t. } BUCS \ni M(N_l; N_r) = M(N^{**}_l; N_r) = N_{IC},
\]

\[
\Rightarrow \bar{v}(N^{**}_l; N_{IC}) = \bar{v}(N_{IC}; N_r) < \bar{v}(N_l; N_{IC})
\]

Therefore the stable solution is the one with the intermediate point in \( BSCU \).
Theorem 4. For case 11, when the left state does not belong to region $\alpha$ (Figures 13a and 14a), the solution with intermediate state in BUCS is not admissible.

Proof. The proof is tedious with trivial algebraic calculations, so a sketch of the proof is presented instead. First, we take the left state exactly on the extension of $C^{BS}$ and we show that $S_1$ and $S_2$ the velocity of the shocks from $N_l$ to $N_{i1}$ and from $N_{i1}$ to $N_{i2}$ are equal. Moving $N_l$ along the trajectory $(\phi^0_{\rho,\omega,C})$ and $N_l$, the solution to the Riemann Problem would yield an identical intermediate point. Therefore, the velocity of the second shock (from $N_{i1}$ to $N_{i2}$) remains constant whereas the first velocity, due to Lemma 2 increases. This violates our admissibility condition. To show that the velocities are the same when $N_l$ is exactly on the extension of $C^{BS}$, one has to solve a system of 5 equations:

1. $N_{i1} \in H(N_l)$,
2. $N_{i2} \in H(N_{i1})$,
3. Charge balance for $N_{i1}$ i.e. $n_{i1}^B(n_{i1}^B + n_{i1}^C) = k_C$,
4. Charge balance for $N_{i2}$ i.e. $n_{i2}^B(n_{i2}^B + n_{i2}^C) = k_C$,
5. $N_{i2} \in C^{BS}$.

We have not considered $\phi_{\beta}^i$ in the set of knowns because $N_{i2} \in I_2(N_r)$ implies $\phi_{\beta}^i = \phi_{\beta}^r$. Solving this system gives us the elements we need to show $\bar{v}(N_r; N_{i1}) = \bar{v}(N_{i1}; N_{i2})$. □

References


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Figure 1: Phase plane (hodograph plane) and the separating curves defined in Equations (10) and (11) for parameter values $k_B = 1 \text{mol}^2 \text{lit}^{-2}$, $k_C = 0.67 \text{mol}^2 \text{lit}^{-2}$, $\omega_B = 3 \text{mol} \text{lit}^{-1}$, $\omega_C = 2 \text{mol} \text{lit}^{-1}$ and $\phi_P = 0.4$. The diagonal line ($\phi_B + \phi_C = \phi_P$) is the limit line at which porosity vanishes. Each of the regions $BUCU$, $BSCU$, $BUCS$ and $BSCS$ are bounded by the separating curves and the main axes.
Figure 2: (a) Distribution of total concentration at initial time $t_1$ (solid blue) and at $t_2$ (dashed red) for a batch of precipitate B (concentration $N_B^q$) bounded from both sides by unsaturated fluid ($N_p^B$). The total concentration for the saturated fluid is shown by a horizontal black dashed line. (b) Flux function vs. total concentration (thick solid blue) and its derivative (dashed red), shock composition path (solid red) and its slope (thin solid blue) for the same problem.
Figure 3: Slow (dashed red) and fast (solid blue) integral curves in the hodograph plane for points in the regions $BSCU$ and $BUCS$. 
Figure 4: (a) Slow shock curves for the left state in $BUCU$ and the right state in the other three regions. If $N_l$ lies in region $\alpha$, then the branch of $H_1$ in $BSCU$ is not possible. (b) Fast shock curves (solid and dashed blue) for two left states in $BSCU$ and two in $BUCS$ and right states in $BSCS$. 
Figure 5: Detached Hugoniot locus $\mathcal{H}$ in $BUCS$ for a state $N_p$ and inadmissible Hugoniot locus $\mathcal{H}$ in $BUCU$ (solid red) and inadmissible $\mathcal{H}s$ for state $N_q$ in other three regions (dashed red).
Figure 6: Clogging boundaries for $H_2$ in BSCS and BUCS. The system parameters are $k_B = 0.5 \text{mol}^2 / \text{lit}^2$, $k_C = 0.71 \text{mol}^2 / \text{lit}^2$, $\omega_B = 1 \text{mol} / \text{lit}$, $\omega_C = 5 \text{mol} / \text{lit}$ and $\phi_P = 0.4$. 
Figure 7: Example solution for case 3; (a) on the hodograph plane, (b) profile of concentration of ions, (c) profile of volume fractions of the precipitates. In Figure (a) \( N_i \) is on the boundary of BSCU and BUCU. The waves are shown by arrows and the slow integral curve by a dashed magenta line. In Fig. (b) the labels are for the profiles of \( N_B \) and \( N_C \).
Figure 8: (a) Solution for case 7 on the hodograph plane. $N_1$ is on the intersection of $I_1(N_l)$ (magenta) and $I_2(N_r)$ (blue). (b) Profile of the solution on $N-v$ plane and (c) on $\phi-v$ plane.
Figure 9: Solution for case 9 on the hodograph plane with the upstream fluid saturated with both fluids and the downstream fluid unsaturated. Note that directions of the integral curves are arbitrary in both regions $BUCU$ and $BSCS$. 
Figure 10: (a) Construction of the solution for case 10 on the hodograph plane. Magenta lines show $H_1(N_l)$ and blue curves show $H_2(N_{iB})$ and $H_2(N_{iC})$ passing through $N_r$. The state $N_l$ is below the bifurcation line $z$ and $N_{iB}$ is the intermediate state. (b) Profile of the solution on the $N-v$ plane and (c) on the $\phi-v$ plane.
Figure 11: (a) Profile of the solution of five Riemann Problems with $\mathbf{N}_r = (0.5, 0.3)^T$ and $\mathbf{N}_l = (N_B^l, 0.15)^T$ with slightly different values for $N_B^l$. (b) Structure of the solution on the hodograph plane. Note that the structure of the solution is discontinuous with respect to the initial condition on hodograph plane. However, this is the case if we only look at the hodograph plane, because the velocities are continuous as shown in Figure (a).
Figure 12: (a) Solution for case 10 when the shock wave $C_2$ causes the more reactive and less dense salt B to precipitate. The structure is analogous to Figure 10. However, here the intermediate point is very close to the boundary of the domain. For the given $N_r$, the problem has no solution if $N_l$ lies in the yellow shaded region. (b) Profile of the concentrations. (c) Profile of the precipitates in the $\phi - v$ plane. The increase in B precipitate almost fills the available void space. The parameters are $k_B = 0.5 \text{ mol}^2 \text{m}^{-2}, k_C = 0.71 \text{ mol}^2 \text{m}^{-2}, \omega_B = 1 \text{ mol} \text{m}^{-2}, \omega_C = 5 \text{ mol} \text{m}^{-2}, \phi_P = 0.4$. 
Figure 13: (a) Construction of the solution for case 11 on the hodograph plane when there is a direct path from $N_l$ to $BSCU$. The magenta line shows $H_1(N_l)$ and the blue curve shows $H(N_r)$. (b) Solution of the same problem on the $N$-$v$ plane and (c) on the $\phi$-$v$ plane.
Figure 14: (a) Construction of the solution for case 11 on the hodograph plane when there is not a direct path from $N_l$ to $BSCU$, i.e. when $N_l$ is in region $\alpha$ (shaded blue region). The magenta line shows $H_1(N_l)$ and the blue curves represent $H_2(N_{i1})$ and $I_2(N_r)$. $N_{i2}$ is on the boundary and therefore belongs to both $H_1(N_{i1})$ and $I_2(N_r)$. (b) Solution of the same problem on $N-v$ plane and (c) on $\phi-v$ plane.
Figure 15: (a) Construction of the solution for case 13 on the hodograph plane when \( \mathbf{N}_r \) can be the right state of a shock with the left state in BSCU. The magenta line depicts \( I_1(\mathbf{N}_l) \) and the blue curve show \( \mathcal{H}(\mathbf{N}_r) \) and \( \mathbf{N}_i \) marks the intersection of them. (b) Solution of the same problem on the \( \mathbf{N}-\nu \) plane and (c) on the \( \phi-\nu \) plane. The system parameters are \( k_B = 1.5 \text{ mol}^2 \text{ m}^{-2} \), \( k_C = 2 \text{ mol}^2 \text{ m}^{-2} \), \( \omega_B = 1 \text{ mol} \text{ m}^{-1} \), \( \omega_C = 0.4 \text{ mol} \text{ m}^{-1} \) and \( \phi_P = 0.4 \).
Figure 16: (a) Construction of the solution for case 13 on the hodograph plane when $N_r$ cannot be the right state of a shock with the left state in BSCU, i.e., when $N_r$ belongs to the green shaded region $\beta$. The magenta lines show $I_1(N_l)$ and $H_1(N_{i1})$. The state $N_{i2}$ is the intersection of $H_2(N_r)$ (blue curve) with $H_1(N_{i1})$. The two first waves $C_1, S_1$ are the two parts of the slow compound wave. (b) Solution of the same problem on the $N-v$ plane and (c) on the $\phi-v$ plane. The parameter values are $k_B = 1.5 \text{mol}^2 \text{lit}^{-2}, k_C = 2 \text{mol}^2 \text{lit}^{-2}, \omega_B = 1 \text{mol} \text{lit}^{-1}, \omega_C = 0.4 \text{mol} \text{lit}^{-1}$ and $\phi_P = 0.4$. 

(k) solution on hodograph plane

(b) concentrations profile

(c) precipitates profile

(a) solution on hodograph plane
Figure 17: (a) Construction of the solution for case 15 on the hodograph plane when the intermediate points are connected by a slow shock. The magenta lines shows $H_1(N_l)$ and $H_1(N_{i1})$. The state $N_{i2}$ is the intersection of $I_2(N_r)$ (blue) with $H_1(N_{i1})$. The waves $C_1$ and $S_1$ are the two parts of the slow compound wave. (b) Solution of the same problem on the $N-v$ plane and (c) on the $\phi-v$ plane. The parameter values are $k_B = 1.5 \text{mol}^2 \text{m}^{-4}$, $k_C = 2 \text{mol}^2 \text{m}^{-4}$, $\omega_B = 1 \text{mol} \text{m}^{-4}$, $\omega_C = 0.4 \text{mol} \text{m}^{-4}$ and $\phi_P = 0.4$. 
Figure 18: (a) Construction of the solution for case 15 on the hodograph plane when the intermediate points are connected by a fast shock. Blue curves show $I_2(N_r)$ and $H_2(N_{i2})$. The state $N_{i1}$ is the intersection of $I_1(N_l)$ (magenta) with $H_2(N_{i2})$. The waves $S_2$ and $C_2$ are the two parts of the fast compound wave. (b) Solution of the same problem on the $N$-$v$ plane and (c) on the $\phi$-$v$ plane. The parameter values are $k_B = 0.33 \, \text{mol}^2 \, \text{lit}^{-1}$, $k_C = 1 \, \text{mol}^2 \, \text{lit}^{-1}$, $\omega_B = 2 \, \text{mol} \, \text{lit}^{-1}$, $\omega_C = 3 \, \text{mol} \, \text{lit}^{-1}$ and $\phi_P = 0.4$. 
Figure 19: Necessary and sufficient condition curves to avoid clogging in the space of molar density ratio vs equilibrium constant ratio. Four different pairs of two minerals are shown as examples. B, C and S for the systems in the legend are in the form B-S, C-S respectively with S being the common ion.
Table 1: Possible cases for the initial states of Riemann Problem (Equation (17))

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