

Capítol 2

DISSOLUCIÓ DE CARBONATS PROFUNDS PER MESCLA DE FLUIDS

RESUM

L'existència de cavitats reblertes de minerals en roques carbonàtiques és un tret molt comú en reservoris de petroli i en jaciments de plom-zinc. Com que l'aigua subterrània s'equilibra ràpidament amb carbonats, la presència de cavitats de dissolució en carbonats profunds és una paradoxa. A la literatura hi ha proposats dos processos geoquímics per dissoldre els carbonats a una certa profunditat: l'oxidació d'àcid sulfhídric a àcid sulfúric i la precipitació de sulfurs metàl·lics. El balanç de massa entre el carbonat dissolt i els minerals que hi precipiten, però, es contradiu amb el d'aquests models.

Amb l'ajut de la modelització geoquímica estudiem els efectes que es produeixen en una mescla hidrotermal deguts al contrast entre la química de les dues solucions; són l'algebraic, el de salinitat i el de pH. Demostrem que la mescla de dues solucions calentes i saturades en carbonat forma una nova solució que dissol la roca encaixant carbonàtica. Però per a diferents proporcions dels dos fluids extrems la mescla pot resultar ser una solució supersaturada en carbonat i que, per tant, rebliria la cavitat. El procés de mescla és generalment més efectiu en la dissolució de carbonats que els altres esmentats. A més a més, el resultat de la mescla és consistent amb el ventall de textures i proporcions dels minerals observats en les cavitats.

Chapter 2

ROLE OF FLUID MIXING IN DEEP DISSOLUTION OF CARBONATES

ABSTRACT

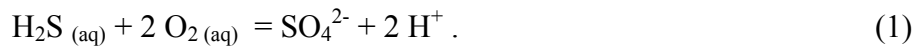
The presence of cavities filled with new minerals in carbonate rocks is a common feature in oil reservoirs and lead-zinc deposits. Since groundwater equilibrates rapidly with carbonates, the existence of dissolution cavities in deep carbonate host rocks is a paradox. Two alternative geochemical processes have been proposed to dissolve carbonates at depth: hydrogen sulfide oxidation to sulfuric acid, and metal sulfide precipitation.

With the aid of geochemical modeling we demonstrate that mixing two warm solutions saturated in carbonate results in a new solution that dissolves the host rock. Variations in the proportion of the end-member fluids can also form a supersaturated mixture and fill the cavity with a new generation of carbonate. Mixing is in general more effective in dissolving carbonates than the aforementioned processes. Moreover, mixing is consistent with the wide set of textures and mineral proportions observed in cavity infillings.

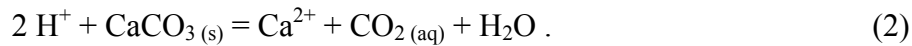
INTRODUCTION

Carbonates have a fast dissolution kinetics. Thus, groundwater circulating over long distances in carbonate-hosted aquifers is in equilibrium with calcite and/or dolomite (Back and Hanshaw, 1971; Deike, 1990). By contrast, dissolution of carbonate takes place in deep environments, where hydrocarbon traps or Mississippi Valley type (MVT) base metal deposits occur (Hill, 1995; Anderson, 1973).

Two scenarios have been proposed for carbonate dissolution. The first scenario is hydrogen sulfide oxidation, which creates sulfuric acid speleogenesis and forms carbonate reservoirs (Hill 1990; 1995). A similar model was employed by Barnes (1983) to explain the dissolution of the carbonate host of MVTs in the Upper Mississippi Valley (UMV). The mixture of a reduced solution rich in hydrogen sulfide with a more oxidizing one leads to the oxidation of sulfide to sulfate, and the release of protons:



When this reaction occurs in a carbonate host rock dissolution of carbonates takes place:



The second scenario is based on sulfide precipitation (mainly sphalerite and galena) in MVT deposits (Anderson, 1975):



As a result of proton release, reaction (2) takes place. The sulfur is added to the metal-bearing brine with the other solution or as a result of the “in situ” reduction from sulfate ions. According to reactions (1) to (3), a mole of carbonate is dissolved for each mole of hydrogen sulfide oxidized or metal sulfide precipitated.

However, the processes described above are difficult to reconcile with many observations in nature. First, the textures indicate that the minerals filling the cavities grew in open spaces. Therefore, part or the entire volume of the cavities was formed prior to the filling. Second, since sulfide minerals are not the only ones filling the cavity the amount of sulfide precipitated is insufficient to meet the mass balance requirements of reaction (3). The volume of sulfides is usually larger than that of the other minerals. However, some districts, such as the UMV or Silesia-Cracow, have cavities only filled with carbonates (Heyl et al. 1959; Leach et al. 1996), and other districts, such as the European Alpine, the English Pennines, the Appalachians, the Irish or Polaris, have cavities that are mostly filled with fluorite or barite (Schroll, 1996; Dunham, 1983; Kesler, 1996; Hitzman and Beaty, 1996; Randell and Anderson, 1996). Third, gypsum, which is expected to form from reactions (1) and (2), is only found in a few localities, and in very small amounts (Lu et al. 1995). All these

observations suggest that at least some of the processes that generated the cavities are not related to those causing the precipitation of the infilling minerals. Therefore, additional processes not considered to date must account for these observations.

The mixing of two fluids saturated in a particular mineral may bring about changes in the saturation state of the new solution. Raup (1970) describes an experiment where halite precipitates at the interface of two brines in equilibrium with this mineral. Mixing of fresh and sea water has been interpreted as being responsible for carbonate corrosion at the salt intrusion front in coastal aquifers (Back et al., 1979; Sandford and Konikow, 1989; Anthony et al., 1989, Wicks and Herman, 1996). We postulate that the mixing of two fluids in deep aquifers is much more important for carbonate dissolution-precipitation than the changes induced by the oxidation of H₂S or the precipitation of sulfides. The aim of this paper is to evaluate, by means of geochemical modeling, the effects of the chemical reactions described (1 to 3), and to compare them with the effect of pure mixing of the two solutions involved.

THE EFFECTS OF TWO MIXING FLUIDS

We assume that the mixing occurs between a basinal brine and a less saline groundwater in accordance with the conceptual models described for MVT deposits (e.g. Anderson, 1975; Garven and Freeze, 1984; Barnes, 1983; Sverjensky, 1986). The compositions of these solutions are given in Table 1 and Figure 1.

The chlorine, sodium and calcium concentrations of the brine (BR in Fig. 1) are estimated from the fluid inclusions trapped in the precipitated minerals (McLimans, 1977). The total amounts of iron, zinc and sulfide are those of typical hydrothermal brines (Giordano and Barnes, 1981; Sverjensky, 1987; Anderson and Garven, 1987; Plumlee et al. 1994). The assemblage K-feldspar-muscovite-quartz, commonly observed in fractures (Heyl et al., 1959), constrains the pH of the brine. The concentration of potassium is taken from fluid inclusion data (McLimans, 1977). The

total carbon concentration is calculated in equilibrium with calcite also following the MVT conceptual models (Anderson, 1975). The pH and solute concentrations are consistent with the data for basinal saline fluids (Hanor, 2001). Following Anderson and Garven (1987), Sverjensky (1987), Plumlee et al. (1994) and Appold and Garven (2000), the oxidation state of the brine is considered to be in the field of hydrocarbon species, represented here by methane (Fig. 1). The oxygen fugacity (fO_2) is further constrained to 10^{-51} bar to meet the concentration of C_{org} measured in the inclusion fluids (McLimans, 1977).

The other end fluid (GW1 and GW2 in Fig. 1) consists of slightly saline groundwater. Total carbon is again calculated in equilibrium with calcite. The pH is not constrained

TABLE 1. CHEMICAL COMPOSITION OF END-MEMBER SOLUTIONS

Cases	1. Mixing		2. H ₂ S oxidation		3.Sulfide precipitation: H ₂ S addition		4.Sulfide precipitation: SO ₄ ²⁻ addition and reduction	
	gw	br	gw	br	gw	br	gw	br
Cl	1.0	5.0	1.0	5.0	1.0	5.0	1.0	5.0
Na	0.99	3.5	0.99	3.5	0.99	3.5	0.99	3.5
Ca	0.05	0.5	0.05	0.5	0.05	0.5	0.05	0.5
C _{inorganic}	<u>6 10⁻⁴</u>	<u>0.015</u>	<u>3 10⁻⁴</u>	<u>0.015</u>	<u>6 10⁻⁴</u>	<u>0.015</u>	<u>3 10⁻⁴</u>	<u>0.015</u>
C _{organic}	5 10 ⁻⁴	0.013	5 10 ⁻¹¹	0.013	5 10 ⁻⁴	0.013	5 10 ⁻¹¹	0.013
S	10 ⁻¹⁰	10 ⁻¹⁰	10 ⁻¹⁰	10 ⁻³	10 ⁻⁴	10 ⁻¹⁰	10 ⁻⁴	10 ⁻¹⁰
Fe	2 10 ⁻⁷	10 ⁻¹⁰	2 10 ⁻⁷	10 ⁻¹⁰	2 10 ⁻⁷	10 ⁻¹⁰	2 10 ⁻⁷	10 ⁻¹⁰
Zn	10 ⁻¹⁰	10 ⁻¹⁰	10 ⁻¹⁰	10 ⁻¹⁰	10 ⁻¹⁰	10 ⁻⁴	10 ⁻¹⁰	10 ⁻⁴
K	2 10 ⁻⁴	0.3	2 10 ⁻⁴	0.3	2 10 ⁻⁴	0.3	2 10 ⁻⁴	0.3
fO ₂ (bar)	10 ⁻⁵¹	10 ⁻⁵¹	10 ⁻⁴²	10 ⁻⁵¹	10 ⁻⁵¹	10 ⁻⁵¹	10 ⁻⁴²	10 ⁻⁵¹
pH	6.5	5.0	6.5	5.0	6.5	5.0	6.5	5.0

Note: Concentration units are mol/kg. The underlined numbers have been calculated to fulfill the condition of calcite equilibrium. gw: groundwater; br: brine.

and may vary between 6.0 and 7.5 for a chlorinity of 1.0 in accordance with the analyses of basinal fluids (Hanor, 2001). We work with a pH value of 6.5 and subsequently analyze the sensitivity of the results with respect to pH. Two oxidation states are assumed to account for two different scenarios: H₂S-bearing water with a fO_2 value similar to that of the brine described above (GW1), and a SO₄-bearing water, with fO_2 of 10^{-42} bar in equilibrium with goethite (GW2). Variations in fO_2 of GW2 do not significantly affect the results of the calculations, provided that SO₄²⁻ is the predominant species. A temperature of 150°C, commonly reported in fluid inclusion microthermometry (McLimans, 1977), was assumed for both brine and groundwater.

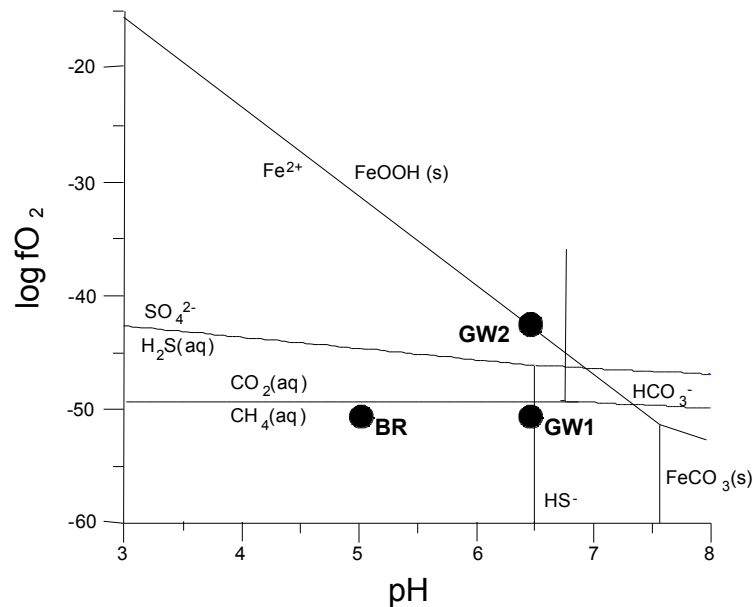


Figure 1. Location of the brine (BR) and two possible regional groundwaters (GW1 and GW2) in a pH-log fO_2 (bar) diagram at 150°C. Total concentrations of carbon and iron of 10^{-2} and 10^{-7} m, respectively, are used.

The calculations are performed with the geochemical simulator RETRASO. This is a Fortran code capable of handling a multicomponent solute transport coupled with

chemical reactions (Saaltink et al. 1998; Ayora et al. 1998). Mixing is simulated assuming diffusion between two end-member solutions of fixed composition. The aqueous species included in the calculations and the thermodynamic data for chemical reactions were those compiled in the EQ3NR database (Wolery, 1992), which allow calculations from 0 to 300°C. The activity coefficients of aqueous species are calculated according to the B-dot expression (Helgeson and Kirkham, 1974). The minerals considered are: calcite as a representative of the carbonate host, sphalerite as a representative of the metal sulfides that precipitate in MVT deposits, and K-feldspar, muscovite, quartz and kaolinite, as found in the country rocks. For the flux rates expected in deep aquifers (~ 1m/a, Garven and Freeze, 1984), and the temperatures modeled (150°C), the mineral-solution reactions are assumed to be fast enough to reach equilibrium.

We present the results as the saturation index of the mixture with respect to calcite; this mineral is not allowed to dissolve or to precipitate because we are only interested in showing the potential of the mixture to dissolve/precipitate calcite. The exact locus of dissolution and precipitation depends on the relative values of the fluxes of the two fluids. Since this depends on each site, the results for particular flow systems will be analyzed elsewhere through reactive transport modeling.

RESULTS

The mixing of two fluids at low temperature (10 to 25°C) has been discussed by Wigley and Plummer (1976). They isolated the intrinsic factors that affect the dissolution and precipitation of calcite by mixing waters. According to our calculations, these factors are equally valid at 150°C, and are summarized below (additional figures 6 to 9 at the end of the chapter illustrate the effects).

MIXING OF FLUIDS WITH DIFFERENT SALINITY

The result of mixing two calcite saturated solutions that only differ in their salinity is a new solution subsaturated in calcite. The subsaturation increases with the difference in salinity. This is due to the variation in the activity coefficients as the ionic strength of the solution varies.

MIXING OF FLUIDS WITH DIFFERENT Ca CONCENTRATION

Two fluids that are both equilibrated with calcite but have a different Ca concentration must also have a different pH or pCO₂. The resulting mixtures are always supersaturated in calcite. This occurs because of the so-called algebraic effect described by Wigley and Plummer (1976). Let us assume a fluid equilibrated with a mineral that is composed of two ions, A and B. The ion activity product (IAP) is:

$$\text{IAP} = A \cdot B = K \quad (4)$$

A different fluid that contains b-times of ion A will also be equilibrated with the same mineral if equation (5) holds:

$$\text{IAP} = b \cdot A \cdot B / b = K \quad (5)$$

It is easily demonstrated that the IAP of any linear mixture of these two fluids is always higher than K, indicating that the mixture is supersaturated. The maximum supersaturation occurs for equal proportions of the two fluids, and IAP increases with increasing b, i.e., the difference in Ca concentrations in the original solutions.

MIXING OF FLUIDS WITH DIFFERENT pH AND pCO₂

The mixture of two fluids in equilibrium with calcite that differ in their pH and pCO₂ is a solution undersaturated with respect to calcite at acidic to neutral pH. The pH variation of the mixture is not linear although the pCO₂ variation between the two end-term solutions is linear. This is due to the speciation of carbon: when the pCO₂ is low the pH drops fast, but as the total carbon increases a higher amount of H⁺ is consumed

in carbonic speciation reactions (HCO_3^- to $\text{CO}_{2(\text{aq})}$), and the pH decrease is slow. The concentration of CO_3^{2-} also follows a non-linear pattern: it decreases initially because of the drop in pH, but recovers as total carbon increases and the pH decrease slows. The evolution of calcite saturation parallels that of the CO_3^{2-} concentration since Ca^{2+} is constant. The CO_3^{2-} concentration is higher under slightly basic conditions than under acidic ones for the same Ca concentration with the result that the mixture of slightly basic fluids will be more easily supersaturated than the mixture of more acidic ones.

MIXING OF FLUIDS WITH DIFFERENT TEMPERATURE

The behavior of the system at different temperature depends on the property that varies to ensure the calcite saturation of the end-members. Thus, if the pCO_2 remains constant, the variation in pH and/or Ca will lead to supersaturated mixtures. If the pCO_2 varies together with pH, subsaturation may appear. However, according to convection experiments and theory (Nield and Bejan, 1992), if we assume that the warm brine acts as a heat source in deep environments, temperature variations exceeding 10°C are not expected within the range of a few meters (the scale of the carbonate cavities). For these differences in temperature, the variations in the saturation of the mixtures are negligible and were ignored in our calculations.

GENERAL CASE: MIXING FLUIDS WITH DIFFERENT PARAMETERS

As shown in Fig. 2, the mixing effect of the two fluids selected as brine and groundwater (case 1 of Table 1) causes subsaturation in calcite along the entire mixture. According to the literature, there is a range of variation in the parameters listed in Table 1. On the one hand, the pH value of the brine is calculated from the muscovite-K feldspar-quartz equilibrium. Although abundant, there is no evidence that these minerals coexist in equilibrium everywhere. Moreover, variations in potassium concentration also affect the pH value obtained for the brine. On the other hand, the pH of groundwater remains broadly unconstrained. Therefore, the saturation index of

calcite will be calculated for other pH values of the two end fluids. A more acidic brine (pH 4.5) leads to an increasing subsaturation (case B, Fig. 2) due to the more important pH-pCO₂ effect. A more acidic groundwater (pH 6) leads to a similar subsaturation pattern (case C, Fig. 2) due to the fewer differences between groundwater and brine. As expected, for a more basic groundwater (pH 7) or brine (pH 6) there is supersaturation along the entire mixing (case D and E, Fig 2). Finally, a more diluted groundwater can lead to supersaturation and subsaturation (case F, Fig.2) owing to the increasing role of the Ca algebraic effect.

Therefore, the combination of the different non-linear effects described above leads to trends that are impossible to predict 'a priori': calcite subsaturation, supersaturation or both. When both occur, supersaturation takes place in the higher pH terms, which correlate with more diluted solutions (Hanor, 2001), whereas subsaturation predominates in the more acidic and more saline solutions. Henceforth, we will employ a reference case where the effect of mixing is moderate (case A in Fig. 2).

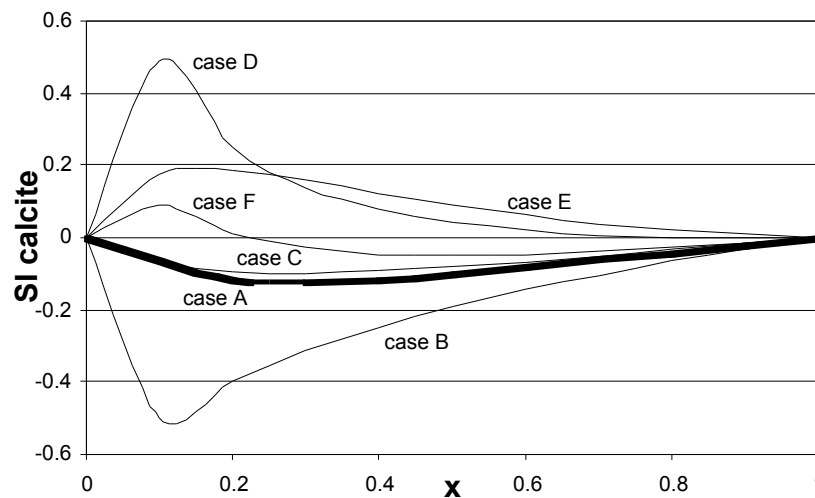


Figure 2. Calcite saturation index of the mixture of a groundwater (left hand side) and a brine (right hand side) of different pH and salinity. Case A) Composition of the end members as case 1 in Table 1; case B) pH of 6.5 and 4.5; case C) pH of 6 and 5; case D) pH of 7 and 5; case E) pH of 6.5 and 5.5; case F) Cl of 0.25 and 5 m; Ca of 0.006 and 0.5 m, respectively.

THE EFFECT OF H₂S OXIDATION

In this model, H₂S carried by the brine is oxidized when mixing with groundwater. The oxidation state of the resulting mixture depends on the amount of H₂S in the brine and on the concentration of oxidant agents in the groundwater. Barnes (1983) proposed O_{2(aq)} as the oxidant agent. However, water from many aquifers lacks detectable oxygen; in such cases, the oxidizing capacity of water is controlled by redox pairs, such as Fe(III)-Fe(II), U(VI)-U(IV), SO₄²⁻-H₂S, etc. (Grenthe et al.,1992). The low amount of oxygen assumed for the groundwater in our modeling ($\sim 10^{-42}$ mol/kg) is not expected to play a significant role as an oxidant agent.

We model the effect of oxidation of H₂S by Fe(III), which may be a more abundant solute in groundwater. The total Fe concentration is assumed to be 10⁻⁷ mol/kg, from the equilibrium with goethite (GW2 in Fig. 1). Compared with pure mixing calcite subsaturation increases slightly, but the effect of H₂S oxidation is very minor (Fig. 3).

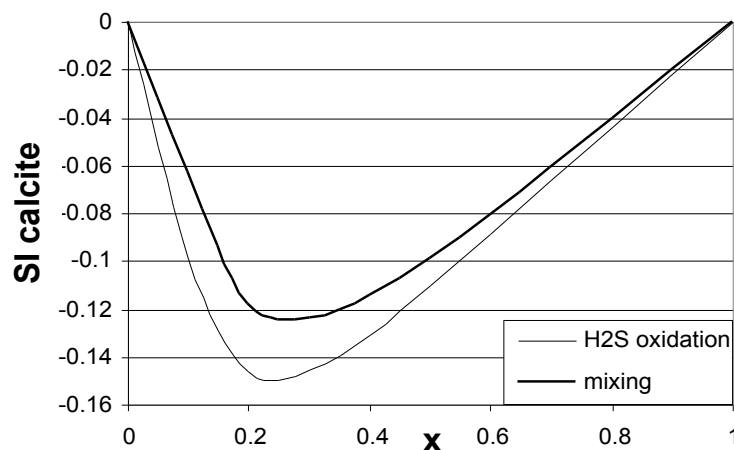


Figure 3. Effect of H₂S oxidation on calcite saturation index: variation of calcite saturation index with different mixing proportions between a groundwater (left hand side) and a brine (right hand side). The compositions of the end member fluids are found in table 1, case 1 and 2.

It is interesting to note, however, that this effect is not dependent on Fe concentration or on fO_2 but on pH and H_2S concentration. This is so because the increase in calcite subsaturation is not attributed to H_2S oxidation to SO_4 , but to sulfur speciation:



Since S is only present in the brine and H_2S is the predominant species at the pH of the brine, reaction (6) releases additional protons to the mixture, increasing the calcite subsaturation (see additional figure 9 for the plots that clarify this argument).

THE EFFECT OF SULFIDE PRECIPITATION

In this case, the brine is assumed to carry Zn but is sulfur-free (Anderson, 1975). Thus, Zn-sulfide precipitates when mixing with a sulfide-rich groundwater (GW1 in Fig.1). One consequence of sulfide precipitation is calcite subsaturation (reaction 3). According to our calculations, however, this subsaturation is smaller than that obtained from the pure mixing effect, and depends on the brine-groundwater proportions (Fig. 4).

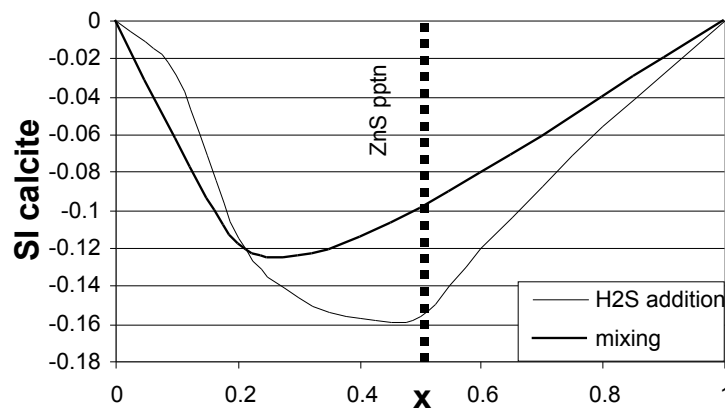


Figure 4. Effect of ZnS precipitation on calcite saturation index: variation of calcite saturation index with different mixing proportions between a groundwater (left hand side) and a brine (right hand side). The compositions of the end member fluids are found in Table 1, examples 1 and 3. The H_2S is carried by the groundwater, and the Zn by the brine. The dotted line marks the proportion where most sphalerite precipitates.

Where there is an excess of sulfur, i.e., in the groundwater-rich terms of the mixture, the pH decreases less than in the pure mixing case because of the buffering effect of sulfide species. Thus, HS^- is the predominant species at the pH of groundwater and the reverse of reaction (6) favors the consumption of hydrogen ions in the alkaline groundwater-rich terms of the mixture, increasing the saturation of calcite. Subsaturation of calcite increases at even proportions of S and Zn (at $x=0.5$ in our example) due to the precipitation of sulfides. Furthermore, in the Zn-rich terms of the mixture the formation of ZnOH^+ slightly increases the amount of free H^+ in solution, enhancing the subsaturation of calcite (additional figure 10). Higher or lower concentrations of S and Zn in the end-member solutions lead to mixtures with a more or less pronounced effect over the saturation of calcite.

In an alternative hypothesis, the H_2S could be added due to the reduction of SO_4^{2-} supplied by groundwater (GW2) at the expense of the organic matter from the brine (Jackson and Beales, 1967; Anderson, 1975). Unlike the previous case, the mixture

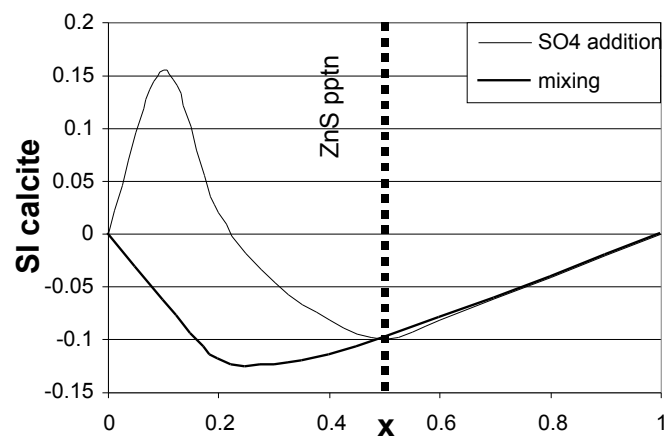
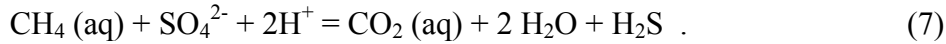


Figure 5. Effect of ZnS precipitation on calcite saturation index: variation of calcite saturation index with different mixing proportions between a groundwater (left hand side) and a brine (right hand side). The composition of the end member fluids are found in Table 1, cases 1 and 5. The H_2S is formed after reduction of groundwater SO_4^{2-} by organic matter from the brine. The dotted line marks the proportions of groundwater and brine where most sphalerite precipitates.

becomes less subsaturated, and even supersaturated for some proportions of fluids, as metal sulfide precipitates (Fig. 5). This is due to the proton consumption in the organic matter oxidation reaction:



Nothing is known on the kinetic feasibility of this reaction at high temperature and confined environments. In the Zn-rich terms of the mixture, the H^+ ions freed in the formation of ZnOH^+ compensate the ones consumed in reaction (7) with the result that the final pH and subsaturation of the mixture is very similar to that in the pure mixing case (additional figure 11).

CONCLUSIONS

According to our calculations, the mixing of warm solutions has effects on calcite solubility similar to those described by Wigley and Plummer (1976) for low temperature fluids. Three competing effects over calcite saturation could occur simultaneously when mixing two calcite-saturated solutions of high temperature and disparate chemistry. The algebraic effect causes supersaturation of the mixture, and the salinity and the pH-pCO₂ effects result in subsaturation of calcite in the final solution. The combination of these effects could lead to supersaturation or subsaturation.

Our calculations confirm the dissolution of carbonates when a reduced brine mixes with a more diluted and more oxidizing water. This is not attributed to the H₂S oxidation (Barnes, 1983; Hill, 1990), but is essentially due to the mixing effect.

When H₂S is supplied by the groundwater, our results corroborate that sulfide precipitation promotes calcite dissolution (Anderson, 1975). However, they again show that dissolution mainly occurs because of the mixing effect. Moreover, subsaturation increases with respect to the pure mixing only where a sulfide-rich fluid meets a zinc-

rich brine. When H₂S is produced from the reduction of sulfate by organic matter, less calcite is dissolved (and sometimes precipitates) compared with the pure mixing case.

Therefore, with respect to carbonate dissolution, mixing is in general more effective than chemical reactivity between the components of the solutions. Mixing can form cavities regardless of H₂S oxidation and sulfide precipitation. Mixing explains the textures that demonstrate the filling of open cavities, and for the wide variety of minerals and proportions encountered.

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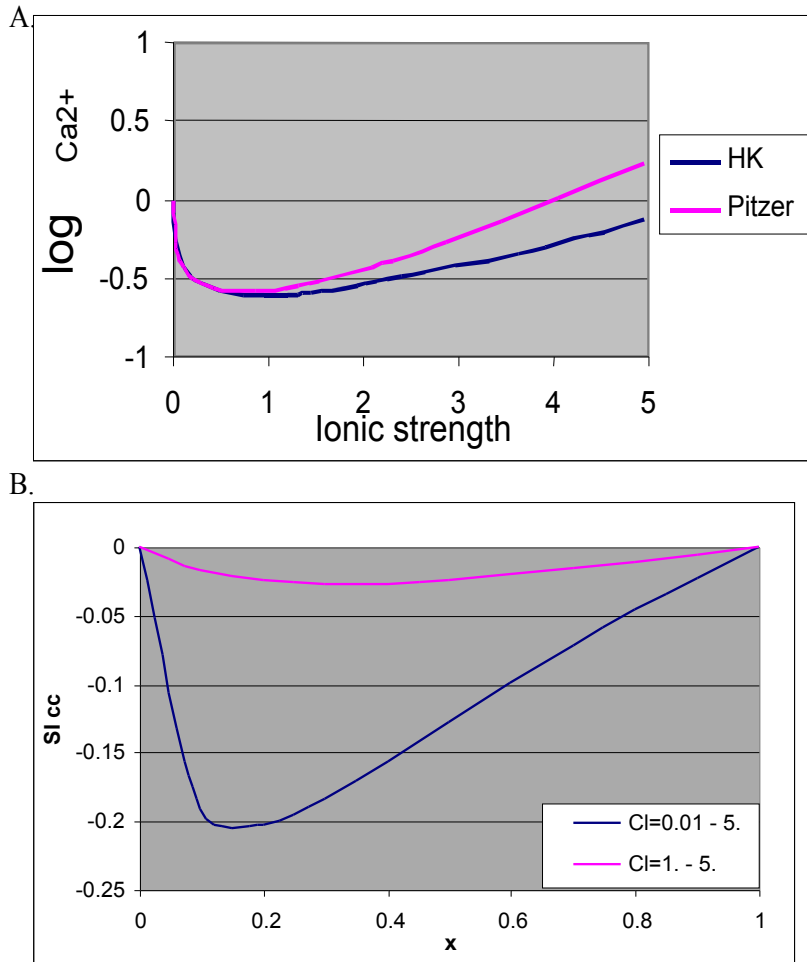
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Additional figure:

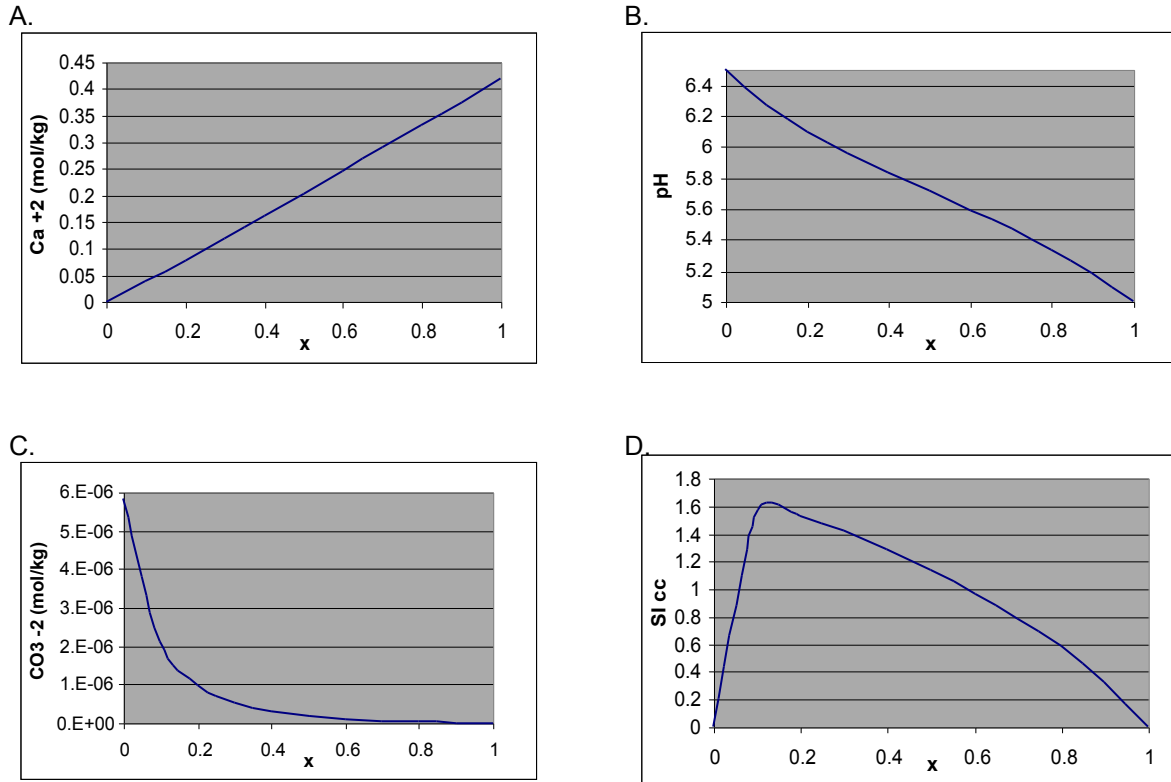
Figure 6. A. Activity coefficient for Ca^{2+} in solutions of different ionic strength at 25°C: comparison of the values calculated with the models of Helgeson and Kirkham (1974) and Pitzer. The value of the calcium activity coefficients is lower for intermediate salinities, as a mixture of a brine and a dilute water would have, than for extreme salinities. Consequently, after the definition of saturation index of calcite:

$$SI = \log \frac{IAP}{K_{eq}} = \log \frac{m_{Ca^{2+}} m_{CO_3^{2-}}}{K_{eq}}$$

for low activity coefficients, the value of SI is also low. That is, the mixture of two fluids equilibrated in calcite with different salinity will have lower $a_{Ca^{2+}}$ than the extremes and will result subsaturated in calcite.

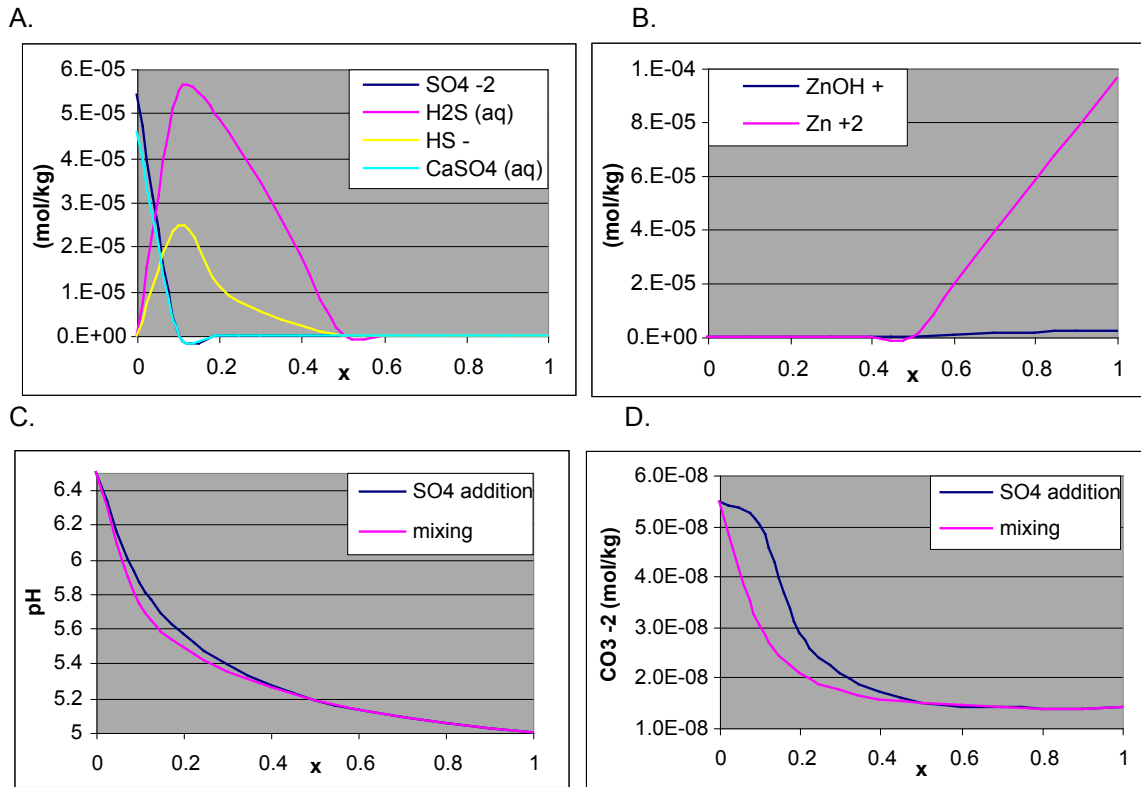
B. Saturation index of calcite in mixtures composed of a dilute groundwater ($x=0$) and a fluid of variable salinity, mainly due to chlorine concentration ($Cl=0.01, 1.0$ or 5.0 mol/kg).

Subsaturation increases with the difference in salinity of the extremes.



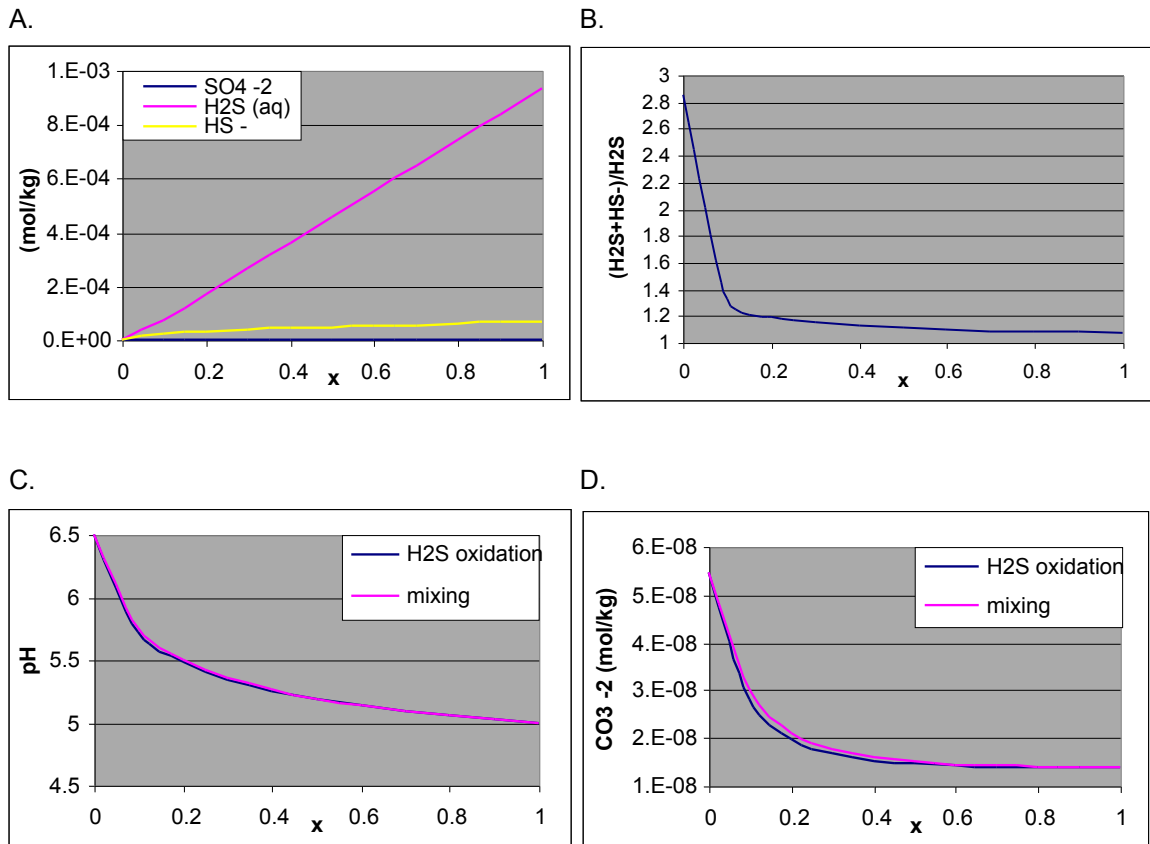
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Figure 7. Mixing of two fluids with different Ca concentration. Total carbon concentration is approximately 0.01 mol/kg in both end-members. Since Ca speciation does not vary with pH, the variation of Ca^{2+} and pH of the mixture are practically linear (A and B). Opposite to the calcium trend, for a constant total carbon value, the concentration of CO_3^{2-} decreases in the mixture as its pH decreases (C). The product of Ca^{2+} and CO_3^{2-} in the mixtures results in supersaturation (algebraic effect, D).



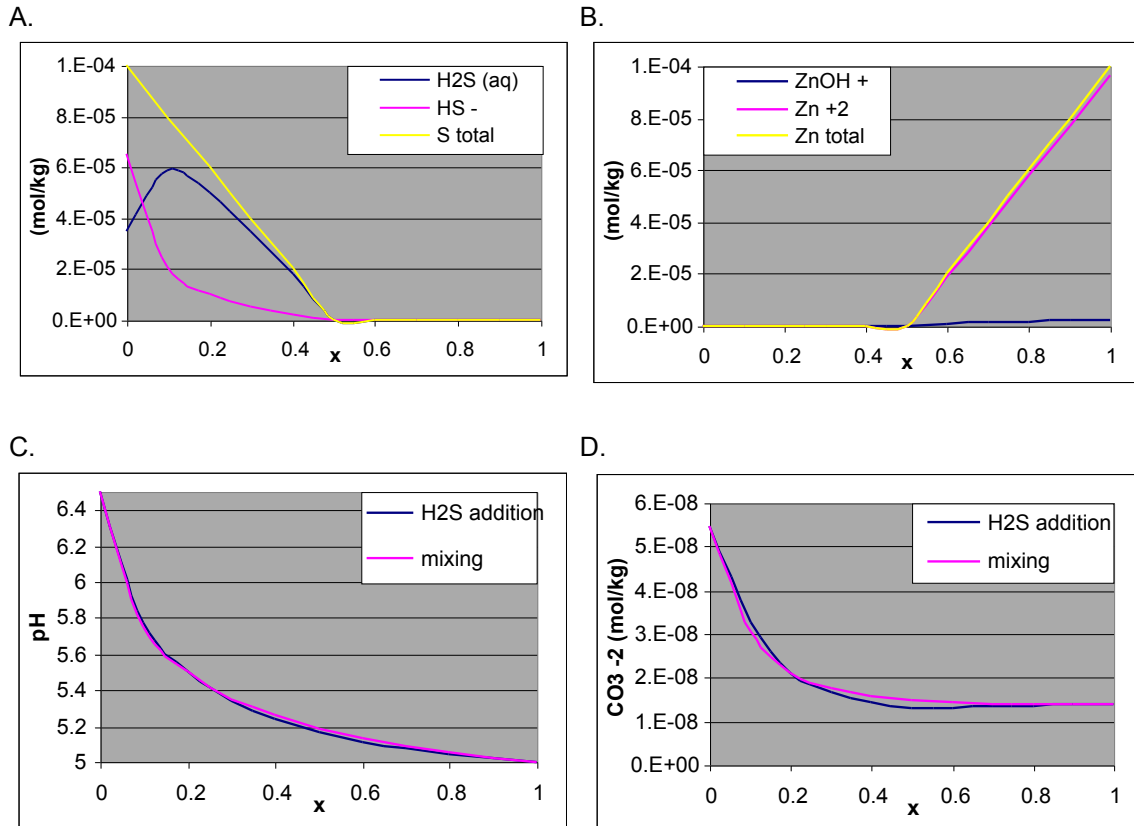
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Figure 8. Mixing of two fluids with different pH and p_{CO_2} . The total Ca concentration is 0.05 mol/kg. The total carbon variation between the two end-term solutions is linear (A). The pH variation, however, is not linear (B). This is due to the speciation of carbon: when the amount of total carbon is low the pH drops fast, but as the total carbon increases a higher amount of H^+ is consumed in the speciation reactions (HCO_3^- to $\text{CO}_{2(\text{aq})}$), and the pH decreases slowly. The concentration of CO_3^{2-} also follows a non-linear pattern: it initially decreases because of the pH drop, but it recovers as the total carbon increases and the pH increase slows down (C). Since Ca^{2+} concentration is constant, the evolution of calcite saturation parallels that of CO_3^{2-} concentration (D).



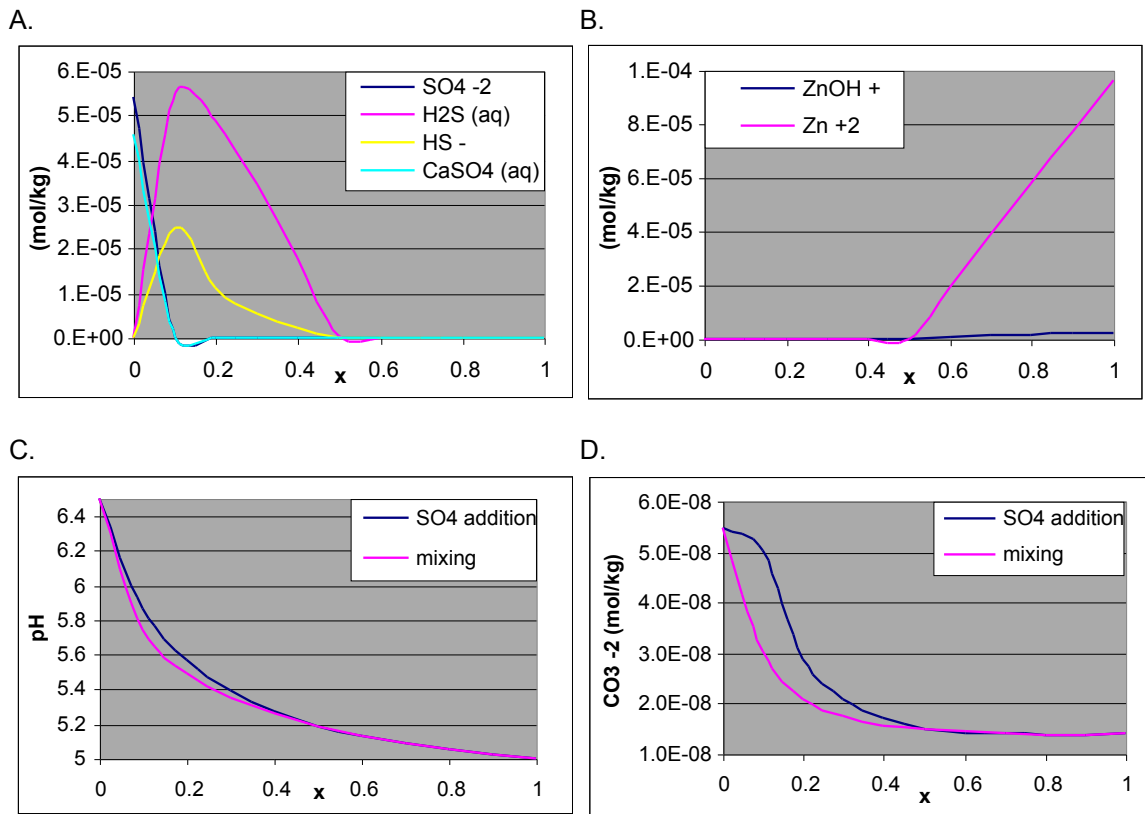
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Figure 9. Species concentration resulting from mixing an oxidizing groundwater (with $2 \cdot 10^{-7}$ mol/kg of total iron) and a reduced brine; comparison with the case of mixing alone (groundwater and sulfur-poor brine). Sulfur species concentration increases with the total sulfur in solution; sulfate species only predominate over sulfide ones at $x=0.0$, which is not even noticeable in plot A. Thus, sulfur is only oxidized at $x=0.0$, where all Fe(III) appears in the form of $\text{Fe}(\text{OH})_2^+$. At other proportions of groundwater and brine ($x > 0.0$) the iron in solution is reduced predominantly to Fe^{2+} and FeCl_4^{2-} . The larger proportion of H_2S than HS^- in the mixture towards $x=0.0$ (B), that is, when it is more basic, produces the relative enrichment in H^+ that leads to a slight decrease in pH respect to the mixing case (C). This reduces the CO_3^{2-} concentration too (D), and thus causes an increase in the subsaturation of calcite in the mixture relative to that of the mixing with a sulfur-free brine.



Additional figure:

Figure 10. Species concentration resulting from mixing a sulfide-rich groundwater and a Zn-rich brine; comparison with the case of pure mixing (sulfide-poor groundwater and Zn-poor brine). Sulfide species concentration decreases with the total sulfur concentration (A) to a minimum at $x=0.5$ where the maximum precipitation of sphalerite would occur. ZnOH⁺ concentration increases from that proportion of fluids towards the brine-rich side with the total Zn in solution (B). The speciation reaction between H₂S and HS⁻ tends to diminish the amount of free hydrogen ions in the mixture, while the formation of hydroxide slightly contributes to the increase in free ions because of the precipitation reaction. Thus the pH of the mixture is slightly smaller in the groundwater-rich side and slightly higher at even proportions than in the sulfide addition model (C). As a result, the concentration of CO₃²⁻ follows similar trends (D), so that the final subsaturation of calcite rises in the left hand side and diminishes, as the model predicts, at about $x=0.5$.



Additional figure:

Figure 11. Species concentration resulting from mixing a sulfate-rich groundwater and a Zn-rich brine; comparison with the case of pure mixing (sulfate-poor groundwater and Zn-poor brine). Sulfate species concentration decrease with the total sulfur concentration and with the generation of sulfide species (A), indicating that sulfate is reduced to sulfide. Zinc species concentration increase with the total zinc concentration in the mixture (B). Total sulfur and zinc concentrations bottom up near $x=0.5$, where the maximum precipitation of ZnS and the maximum dissolution of calcite would occur. The formation of $\text{H}_2\text{S}_{(\text{aq})}$ at expenses of HS^- and H^+ contributes to the depletion of free H^+ ions in the groundwater-rich mixture mainly due to the sulfate reduction and organic matter oxidation reaction (8). Consequently, the pH there rises compared to that of the pure mixture (C). At even proportions of groundwater and brine, and in the brine-rich terms, the generation of some ZnOH^+ , thus that of H^+ , compensates the H^+ consumption from reaction (8) and causes the pH to be similar to that of the pure mixture. CO_3^{2-} concentration (D) follows a similar pattern to the pH, and is responsible for the final rise in the calcite saturation index with respect to that of the pure mixing.