Mixing-Induced Precipitation in Brine Mining: Reactive Transport Modeling

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INTRODUCTION

Continental brines have become the leading raw material for lithium production worldwide. Lithium-bearing brines are found in salt aquifers (mainly halite) in the nucleus of salars (salt flats). Because of extremely high evaporation rates, the primary discharge occurs by evaporation keeping the water table below the surface.

Brines are exploited through pumping wells or ditches excavated in halite aquifers and evaporation of the brine in solar ponds to further concentration. In this type of mining, such as that in Atacama (Chile), a fast and drastic loss in the hydraulic efficiency of the pumping wells threatens the feasibility of the exploitation. We postulate here that the hydraulic efficiency loss is due to salt precipitation induced by brine mixing. The effects of mixing solutions has only been considered to explain carbonate dissolution at the seawater intrusion front in coastal aquifers (Sanford & Konikow, 1989), and two explain the deep cavity formation required to allocate Mississippi Valley-type deposits (Corbella et al., 2004).

The aim of this work is to study the feasibility of the hypothesis of brine mixing and mineral precipitation in the brine exploitation of the Atacama Salar, by means of reactive transport modeling.

STUDY SITE

The Atacama Salar is a closed saline basin which forms part of the current inner fore arc of northern Chile. With a 1400 km² outcrop area, the salt nucleus constitutes a multilayer halite aquifer. It can be distinguish (Fig. 1): (I) Unit A is an unconfined aquifer mainly composed of pure halite with several discontinuity planes (probably stratification planes). It is 12 to 15 m thick and has high hydraulic conductivities. (II) A less permeable body of 2 to 8 m thick acting as an aquitard which consist of halite that may have gypsum levels. (III) Unit B is a semi-confined aquifermade up of halite, 8 to 11 m thick and highly conductive. (IV) A lowpermeability body is at the bottom of the mined system.

Two different brines are identified in aquifers "A" and "B" with a transition brine in the aquitard separating those aquifers. Brine extraction is carried out via brine pumping fields, i.e. horizontal drains (1 km length) connected with vertical extraction well (Fig. 1). Hundreds of pumping wells are distributed according to a regular grid. Due to consistency of halite rock, no casing is used.

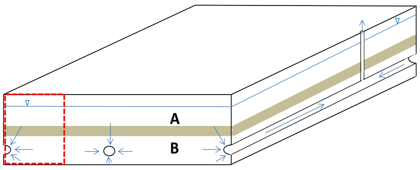

fig 1. Sketch of the brine exploitation, with two aquifers, A and B, separated by an aquitard. The area within the dotted line represents the modeled domain.

During the brine extraction, a drop in the brine level in the well is observed. The level drop is caused by an exponential decrease inhydraulicconductivity and causes a rapid decrease in the brine pumping efficiency. This level drop is satisfactorily modeled assuming an 'skin effect', i.e., the existence of a low permeability skin around the pumping well. Indeed, massive precipitation of salts is observed in and around the wells and drains (Fig. 2).

fig 2. Gypsum precipitates around in a well.

REACTIVE TRANSPORT MODELING

A reactive transport modeling of a transversal section of the horizontal drain has been used to investigate the processes leading to salt precipitation in the surroundings of a drain. To solve the multisolute reactive transport RETRASO code (Saaltink et al., 1998) has been used.

For each time increment, the porosity is updated according to the molar volume of the precipitated phases. Porosity variation modifies permeability in the simulations according to Kozeny'sequation:

$$k = k_0 \frac{\emptyset^3}{(1-\emptyset)^2} \frac{(1-\emptyset_0)^2}{\emptyset_0^2}$$

where $\emptyset_0$ is the initial porosity and k_0 the intrinsic permeability for matrix $\emptyset_0$.

The model domain is 40 x 500 m section normal to the drain. Because the symmetry of the problem under consideration only half of the transversal section to the drain is modeled (see modeled section in Fig. 1). The model simulates 90 days of pumping with a pumping rate of 0.01

palabras clave: Salmuera, Mezcla, Precipitación, Yeso, Halita, Atacama, Permeabilidad, Colmatación, Transporte Reactivo

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L/s in the center of the drain. No flow is considered through the top and bottom boundaries, and constant head at the boundary opposite to pumping. Pitzer ion-ion interaction model has been used in the geochemical calculations.

RESULTS AND DISCUSSION

According to field observations, the reactive transport calculations predict a thin mixing zone and gypsum precipitation in the aquitard between units A and B (Fig. 3). However, most of gypsum precipitation takes place around the drain (Fig. 3). Precipitation is not symmetrical. There is a zone with a low rate of gypsum precipitation which can be called "no reactive channel" (Fig. 3). Halite precipitation is two orders of magnitude lower than gypsum (not represented). Porosity decreases towards the drain from 5%, as the initial porosity, to 0.18 % in the drain wall. Within the "no reactive channel" the porosity remains above 2%.

Pumping generates hydraulic gradients forcing the upper brine to flow through the aquitard unit towards the lower aquifer (Unit B). This flow fieldproduces a mixing of the brines A and B. The mixing of two brines in equilibrium with a salt produces supersaturation and precipitation of the salt. Indeed, Fig. 4 shows the representation of the gypsum equilibrium equation ($x*y=K$). Although activities should be represented instead molalities, the total salinity is almost constant, and therefore the activity coefficients and the activity of water can be assumed constant and included in K. Any brine equilibrated with gypsum, such as A and B, will plot within the equilibrium line. Any brine with higher Ca and/or SO_4 will be supersaturated. In contrast, any mixture of two brines equilibrated with gypsumwill plot within the straight segment AB, and therefore in the supersaturation field. Because of gypsum stoichiometry, precipitation will move the mixture to the equilibrium around a 1:1 slope line. The distance from the conservative line to the equilibrium line determines the mass of gypsum precipitated. It is easy to see that: 1) the more different Ca and SO_4 concentrations are in the mixing brines, the moreprecipitation occurs; and 2) 50% mixing results in maximum amount of mass precipitated. The same discussion can be made for halite. However, Cl and Na concentration in A and B brines are relatively similar, their mixing line is almost coincident with the equilibrium curve, and only a small amount of halite precipitates.

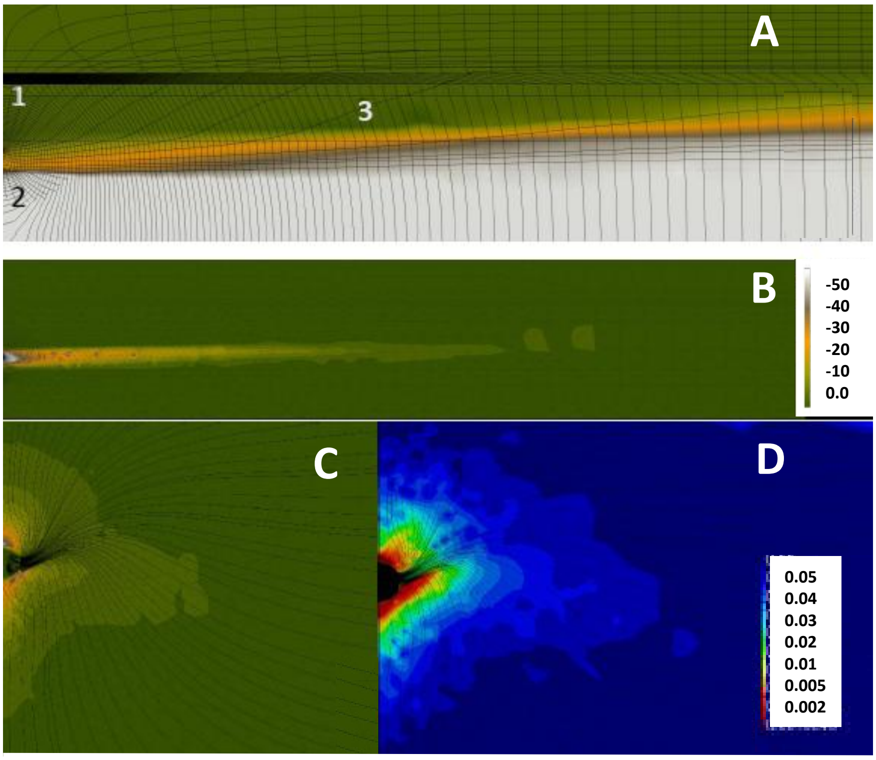

fig 3. *A) Zones with brine A (green), B (white) and mixture of both (orange) marked by the concentration of a conservative element. Isopotential lines are plotted in the background. B) Mass of gypsum precipitated (mol/m3). Flow lines plotted in the background. C) Detail of B around the drain. D) Porosity .All the graphics correspond to results after 90 days calculation.*

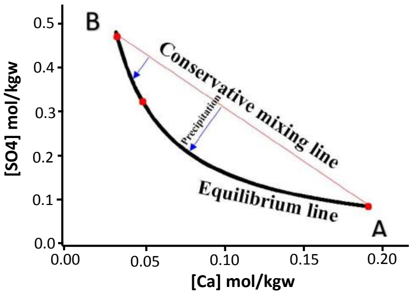

fig 4. *Ideal mixing of two brines (A and B) that are in equilibrium with gypsum. If mixing is non-reactive, theresulting mixture will be supersaturated. Returning to equilibrium requires precipitation.*

Close to the drain, descending brine. A (path 1 of Fig. 3) invades the aquifer with brine B, high mixing occurs and massive gypsum (and minor halite) precipitates in the area abovethe drain during the initial 15 days (Fig. 3). Meanwhile, brine B flows from far regions through more permeable aquifer B towards the drain. It mixes with descending brine A, which has invaded the drain area, and precipitated gypsum below the drain (path2 of Fig. 3). In between these two paths, brines A and B have been mixed up during their flow to the drainprecipitating small amounts of salts along the mixing (path 3 in Fig. 3). The mixture has exhausted most of its precipitation potential and forms a 'non-reactive' channel.

As hydraulic conductivity changes with porosity, after approximately 15 days top and bottom environments of the drain has undergone mineral clogging, and very small flow rates cross clogged areas. In this setting, ascending and descending flow paths are forced to flow towards the "no reactive channel". The thickness of this channel progressively wanes, and the efficiency of the well exponentially drops.

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