Laboratory Characterization of Chemico-osmotic, Hydraulic and Diffusion Properties of Rocks: Apparatus Development - 9134

M. Takeda, T. Hiratsuka, K. Ito
Institute for Geo-Resources and Environment,
National Institute of Advanced Industrial Science and Technology (AIST)
Higashi 1-1-1 Central 7, Tsukuba, Ibaraki 305-8567
Japan

ABSTRACT

Excess fluid pressures induced by chemical osmosis in natural formations may have a significant influence on groundwater systems in a geological time scale. Examinations of the possibility and duration times require characterization of the chemico-osmotic, hydraulic and diffusion properties of representative formation media under field conditions. To develop a laboratory apparatus for chemical osmosis experiments that simulates *in-situ* conditions, typical lithostatic and background pore pressures, a fundamental concept of the chemical osmosis experiment using a closed fluid circuit system (referred to as a closed system hereafter) was revisited. Coupled processes in the experiment were examined numerically. In preliminary experiments at atmospheric pressure a chemical osmosis experiment using the closed system was demonstrated. An approximation method for determining the chemico-osmotic property was attempted. Based on preliminary examinations, an experimental system capable of loading the confining and pore pressures on the sample was thus developed.

INTRODUCTION

Precise characterization and modeling of groundwater flow systems are necessary for a realistic performance assessment of radioactive waste disposal. In groundwater flow modeling, the gravity potential is commonly assumed as the dominant driving force of regional groundwater flow. However, the gravity potential flow model has a limited ability to reconstruct the excess fluid pressure distributions occasionally observed in sedimentary formations [1, 2]. To reconstruct these excess pressures for groundwater flow models, geologic processes such as compaction disequilibrium, tectonic forces and diagenetic reactions have been invoked [3]. On the other hand, in clay-rich formations with vertical salinity gradients, chemical osmosis has recently been considered as one of the driving forces of groundwater flow and a factor that causes excess pressures [4].

If a formation medium acts as a semi-permeable membrane then chemical osmosis induces a fluid movement in the direction of increasing salinity [5]. Consequently, fluid pressure could increase where salinity is high and decrease where it is low. Thus chemical osmosis could induce a fluid flow that counters the pressure-driven flow in the formation. Where osmotic- and pressure-driven flows equilibrate, the net flow ceases while fluid pressures remain in disequilibrium. This means that the direction of groundwater flow might be misinterpreted without differentiating osmotically-induced pressure from those induced by other causes [6]. However, formation media are not perfect membranes as they allow solute diffusion that accord with salinity gradients. As a result, osmotic pressure would dissipate as solutes diffuse from high to low concentrations. The time period during which the osmotic pressures are held in the formation depends on hydraulic and diffusive properties in addition to the chemico-osmotic property of the formation media.

This study focuses on the development of a laboratory experimental system to estimate the chemico-osmotic, hydraulic and diffusive properties of formation media under deep underground conditions. The apparatus is designed according to a preceding study by Keijzer et al. (1999) [7] in which an apparatus was developed to determine the chemico-osmotic property for compacted clayey materials under near surface conditions. Keijer et al. adopted the closed system and this enabled observations of osmotic pressure evolution and dissipation. We added a function to our apparatus that simulates loading confining pressures and background pore pressures corresponding to those in the deep underground on the sample. Loading such confining and pore pressures on the sample is technically feasible using a closed system as seen in laboratory permeability tests [e.g., 8]. However, when performing the chemical osmosis experiment using the closed system the reservoir compressible storage affects the variations of osmotically induced pressures. This was shown in the experiment by Keijer et al. and hence their effects have to be considered in designing experimental configurations.

For an appropriate design of the experimental system we revisited the fundamental concept of the chemical osmosis experiment using the closed system. Coupled processes in the chemical osmosis experiment were numerically examined using a mathematical model that accounted for the reservoir compressible storage. In preliminary experiments at atmospheric pressure the chemical osmosis experiment using the closed system was carried out and an approximation method for determining the osmotic property was attempted. Finally, a newly-developed apparatus was introduced and potential problems related to parameter estimations are discussed. This research project has been conducted under the research contract with the Nuclear and Industrial Safety Agency (NISA).

CHEMICAL OSMOSIS EXPERIMENT USING THE CLOSED SYSTEM

Coupled Processes

A schematic of the chemical osmosis experiment using the closed system is shown in Fig. 1. The solute concentration difference between reservoirs induces a chemical osmosis flux in the sample from the low concentration reservoir to the high concentration reservoir. The fluid movement causes an increase in pressure in the high concentration reservoir and a decrease in pressure in the low concentration reservoir. The resulting pressure differences between the reservoirs causes a pressure-driven flux that counters the chemical osmosis flux. If the sample is an ideal membrane, once the osmosis-and pressure-driven fluxes equilibrate the net flux stops leaving a pressure and concentration difference between reservoirs. For a semi-permeable membrane, however, solutes migrate by diffusion. Solutes are eventually distributed uniformly throughout the system and the induced pressure dissipates in the reservoirs and the sample.

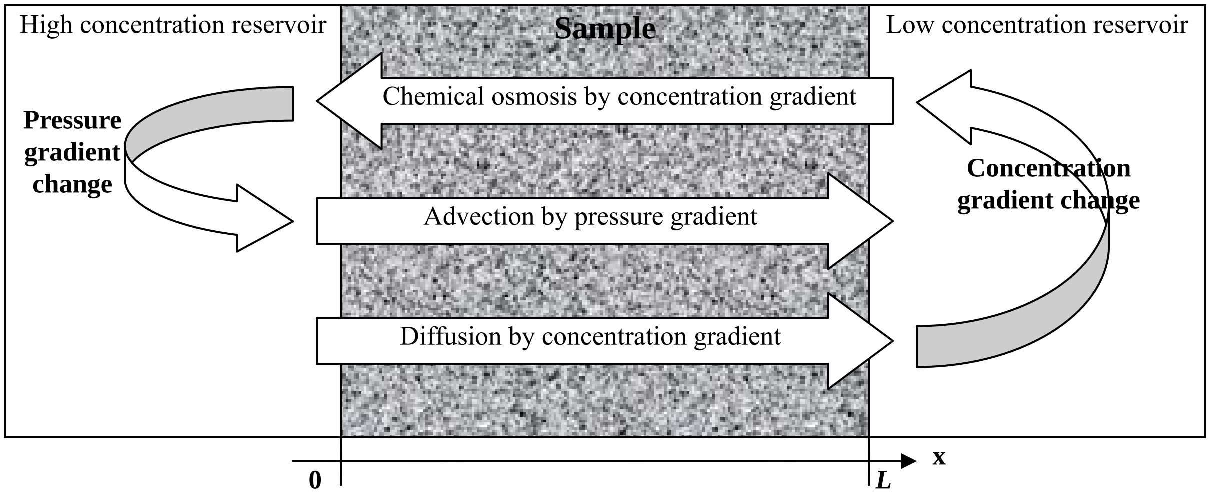

Fig. 1. A schematic diagram of the chemical osmosis experiment using a closed system.

Mathematical Formulation

The net fluid flux, including the osmosis- and pressure-driven fluxes, in a semi-permeable membrane may be described as an extension of Darcy's law using the van't Hoff approximation for osmotic pressure [4]:

$$q = -\frac{k}{\mu} \cdot \left(\frac{\partial P}{\partial x} - \sigma \cdot \nu \cdot R \cdot T \cdot \frac{\partial C}{\partial x} \right) \qquad \text{(Eq. 1)}$$

where q is the net fluid flux ($\mathrm{m \cdot s^{-1}}$), P is the pressure (Pa), C is the solute concentration ($\mathrm{mol \cdot L^{-1}}$), x is the distance (m), k is the intrinsic permeability ($\mathrm{m^2}$), μ is the dynamic viscosity of fluid (Pa·s) and σ is the reflection coefficient (-) ranging from 1 for an ideal membrane to 0 for a material exhibiting no membrane properties, ν is the number of chemical species (-), R is the gas constant ($\mathrm{Pa \cdot L \cdot mol^{-1} \cdot K^{-1}}$) and T is the temperature (K). The mass conservation equation for the fluid is expressed as [4]:

$$\frac{k}{\mu} \cdot \left(\frac{\partial^2 P}{\partial x^2} - \sigma \cdot \nu \cdot R \cdot T \cdot \frac{\partial^2 C}{\partial x^2} \right) = \frac{Ss}{\rho \cdot g} \cdot \frac{\partial P}{\partial t} \qquad \text{(Eq. 2)}$$

where Ss is the specific storage ($\mathrm{m^{-1}}$), ρ is the fluid density ($\mathrm{kg \cdot m^{-3}}$) and g is the gravitational acceleration ($\mathrm{m \cdot s^{-2}}$).

Assuming that the solute transport is dominated by diffusion, the mass conservation equation for the solutes may be expresses as [4]:

$$D_\mathrm{e}^{*} \cdot \frac{\partial^2 C}{\partial x^2} = \alpha \cdot \frac{\partial C}{\partial t} \qquad \text{(Eq. 3)}$$

where D_e^{*} is the effective diffusion coefficient ($\mathrm{m^2 \cdot s^{-1}}$) and α is the capacity factor (-). For the diffusion process in the semi-permeable membrane solutes are partially sieved by the membrane effect and the effective diffusivity of the membrane is dependent on σ [e.g., 9]. According to Bader and Kooi (2005) [10] the simplest form of the dependency is expressed as:

$$D_\mathrm{e}^{*} = D_\mathrm{e} \cdot (1 - \sigma) \qquad \text{(Eq. 4)}$$

where D_e is the effective diffusion coefficient ($\mathrm{m^2 \cdot s^{-1}}$) excluding the membrane effect.

In the mass conservation equations membrane properties are represented as the reflection coefficient, σ. For a porous medium without membrane properties, σ is zero and Eqs. 2 and 3 reduce to the conventional mass conservation equations for groundwater flow and solute transport [11].

Numerical Modeling

Assuming constant compressible storages for reservoirs [e.g., 12], the fluid mass balance between the sample and reservoirs are expressed as:

$$S_\mathrm{h} \cdot \frac{\partial P}{\partial t} = -A \cdot q \big|_{x=0} \qquad \text{(Eq. 5)}$$

$$S_\mathrm{l} \cdot \frac{\partial P}{\partial t} = A \cdot q \big|_{x=L} \qquad \text{(Eq. 6)}$$

where S_h and S_l are the compressible storages of high and low concentration reservoir ($\mathrm{m^3 \cdot Pa^{-1}}$), and A is the cross-sectional area of sample ($\mathrm{m^2}$). Similarly, the solute mass balance between the sample and reservoirs are expressed as [e.g., 13]:

$$V_{\mathrm{h}} \cdot \frac{\partial C}{\partial t} = D_e^* \cdot A \cdot \left.\frac{\partial C}{\partial x}\right|_{x=0} + C_0 \cdot V_h \cdot \delta(t) \qquad \text{(Eq. 7)}$$

$$V_{\mathrm{l}} \cdot \frac{\partial C}{\partial t} = -D_e^* \cdot A \cdot \left.\frac{\partial C}{\partial x}\right|_{x=L} \qquad \text{(Eq. 8)}$$

where V_{h} and V_{l} are the volumes of high and low concentration reservoir (m^3). The initial conditions are:

$$P(x, t=0) = 0 \qquad \text{(Eq. 9)}$$

$$C(x>0, t=0) = 0 \qquad \text{(Eq. 10)}$$

$$C(x=0, t=0) = C_0 \qquad \text{(Eq. 11)}$$

where C_0 is the initial solute concentration in the high concentration reservoir ($\mathrm{mol \cdot L^{-1}}$).

Solving the problem defined by Eqs. 2 and 3 together with Eqs. 5 thorough 11, semi-analytical solutions for the chemical osmosis experiment using the closed system were derived. Using these derived solutions a hypothetical experiment was simulated. Conditions for the hypothetical experiment and the simulated results are shown in Fig. 2. Figure 2 (a) shows that a pressure difference rapidly develops when a large concentration difference exists between reservoirs and reaches a maximum at about t=3x10^5 s. The developed pressure difference decreases as the concentration difference becomes small. Figure 2 (b) and (c) shows that pressures induced in the sample decrease as solutes distribute across the sample. At t=3x10^5 s, both solutes and pressure are distributed almost linearly along the length.

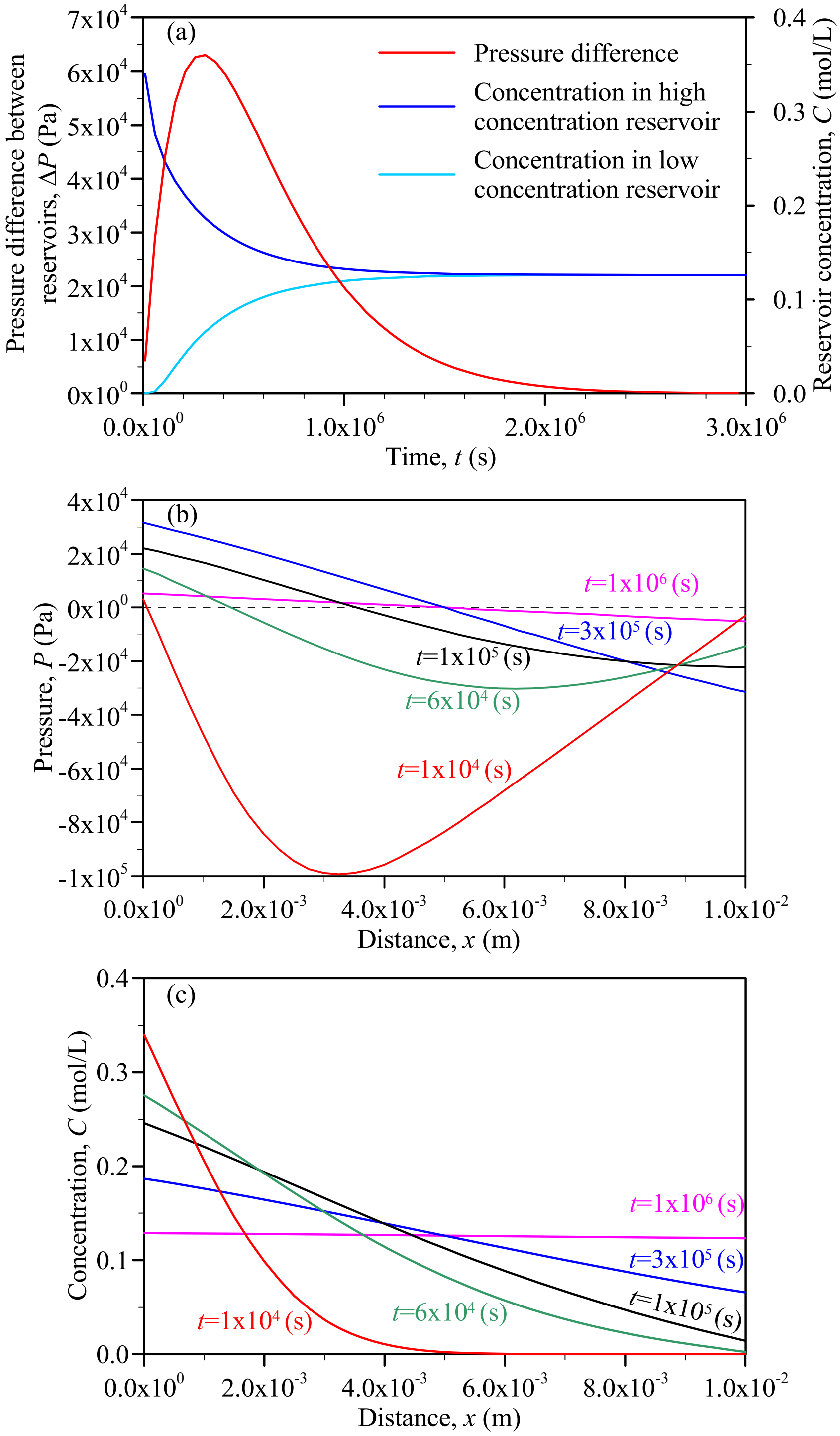

Fig. 2. Transient variations of (a) pressure differences between reservoirs and reservoir concentrations and distributions of (b) pressures and (c) concentrations within the sample simulated under conditions, σ=0.1 (-), k=5x10^{-18} (m^2), Ss=1x10^{-7} (1/m), D_e^*=1x10^{-10} (m^2/s), α=0.6 (-), L=0.01 (m), A=3.12x10^{-3} (m^2), S_h=S_l=1x10^{-9} (m^3/Pa), and V_h=V_l=1.6x10^{-5} (m^3).

PRELIMINARY EXPERIMENT

Material and Instrument

A disc-shaped argillaceous rock was used as a sample. The diameter and thickness were 63 mm and 10 mm, respectively. The porosity was estimated as approximately 0.6 using mercury intrusion porosimetry. The sample was mounted into an acrylic holder (inner diameter of 65 mm and height of 10 mm) and the remaining space between the sample and the holder was filled with a silicon-sealant. After the accretion of silicon-sealant, the sample was saturated in a vacuum chamber. Then the sample, embedded in the holder, was placed between acrylic solution reservoirs. For a tight seal, Viton O-rings were put between the holder and reservoirs, and the assembly was tightened by a set of six bolts. The assembly is shown in Fig. 3. Reflective index sensors for salinity measurements were inserted into each reservoir. A differential pressure transducer was connected to each reservoir for measuring the pressure differences. The reflective index was calibrated using NaCl solutions with concentrations from 0 to 0.5 M.

Experimental Procedures

Experiments were performed using two methods differing in initial conditions of pressure and solute concentrations. In the first experiment (referred to as experiment I hereafter) the sample and reservoirs were filled with distilled water and pressure in the reservoirs and the sample were set to atmospheric pressure before the experiment. The experiment was initiated by replacing the distilled water in a reservoir with a 0.4 M NaCl solution and by closing the reservoir. These initial concentration and pressure conditions correspond to those used for the numerical modeling in the previous section. The second experiment (referred to as experiment II hereafter) was conducted after experiment I. Experiment I was stopped before pressures and concentrations equilibrated between reservoirs. At commencement of experiment II the solution in the high concentration reservoir was replaced with a 0.4 M NaCl solution and reservoir pressures were set to atmospheric pressure again. In both experiments, reservoir concentrations and pressure differences between reservoirs were measured. Experiments were conducted at room temperature of 298.15±0.5 K.

Experimental Results

Observed pressure differences and reservoir concentrations are shown in Fig. 4. (a). In experiment I the pressure difference rapidly increased and reached a maximum at about t=2x10^4 s. The developed pressure difference gradually decreased until the measurement stopped. The concentration in the high concentration reservoir decreased quickly and the time period was almost the same as that required for the pressure difference to reach a maximum.

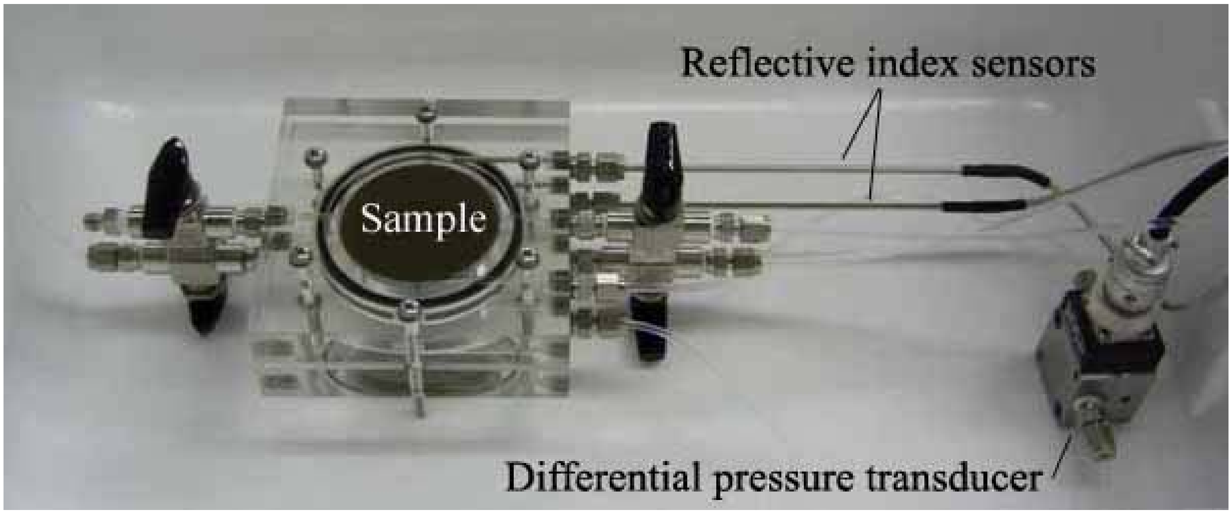

Fig. 3. A photograph of the experimental assembly for preliminary chemical osmosis experiments using a closed system.

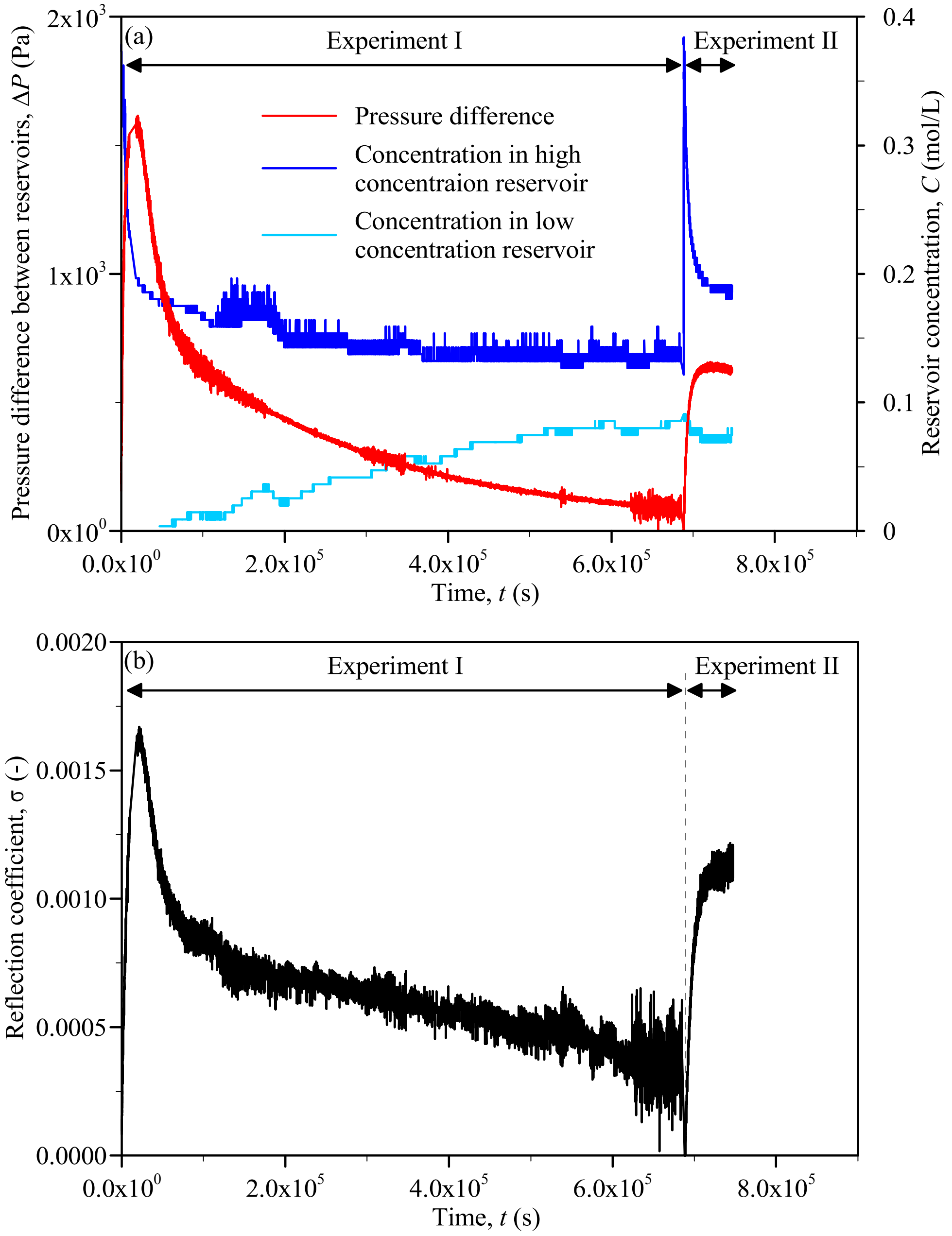

Fig. 4. (a) Pressure differences between reservoirs and reservoir concentrations observed in experiments I and II and (b) the reflection coefficient, σ, as approximated by Eq. 5.

Concentrations in the high and low concentration reservoirs gradually decreased and increased, respectively. In experiment II pressure differences developed within almost the same time period as that observed in experiment I.

In experiment I, the pressure difference and the reservoir concentrations varied in a similar way to that predicted in the numerical model. Assuming that pressures and concentrations were distributed linearly along the sample after pressure differences reached their maxima and that the net fluxes were negligibly small in experiments I and II the reflection coefficient σ was estimated based on its definition [14]:

$$\sigma = \left.\frac{\Delta P}{\Delta \Pi}\right|_{q=0} \qquad \text{(Eq. 12)}$$

where ΔP is the pressure difference (Pa) for zero net flux and $\Delta \Pi$ is the theoretical osmotic pressure (Pa). According to the Van’t Hoff expression the theoretical osmotic pressure for a single-salt system is given as follows [5]:

$$\Delta \Pi = \nu \cdot R \cdot T \cdot \Delta C \quad \text{(Eq. 13)}$$

Calculated reflection coefficients are shown in Fig. 4 (b). The reflection coefficients were expected to be constant for each data point after the pressure difference reached a maximum. However, the values decreased in a similar way to the decrease in pressure difference in experiment I. Although the reflection coefficients for experiment II were almost constant at $1.1\text{x}10^{-3}$, these values would have decreased if the measurement had been continued until the pressure difference decreased. This indicates that the net fluxes were not negligibly-small or that Eq. 12 is not applicable to the experimental methods adopted in this study.

APPARATUS DEVELOPMENT

An apparatus was designed to enable chemical osmosis experiments under deep underground conditions. The notable difference from the previously mentioned experimental system is that experiments can be performed considering loading confining and pore pressures on samples. System components were selected according to the paper of Keijzer et al. (1999) [7] in which an apparatus that simulates near surface conditions was developed. The newly developed apparatus is shown in Fig. 5. It mainly consists of a stainless-steel pressure vessel, magnetically coupled gear pumps, pressure transducers, reflective index sensors, a differential pressure transducer and a syringe pump. The stainless-steel pressure vessel can support hydrostatic pressures of up to 60 MPa and can accommodate a cylindrical specimen with a diameter of 5 cm and lengths ranging from 1 to 10 cm. The syringe pump is used in the calibration test to determine the reservoir compressible storages. Additionally, the syringe pump enables permeability tests to be performed separately. Each reservoir contains a gear pump, a pressure transducer, a reflective index sensor, a sintered stainless-steel porous stone and stainless-steel tubing, manifold and valves. The high and low concentration reservoirs are made symmetrically. The developed system is currently being checked using an acrylic pressure vessel.

CONCLUDING REMARKS

For chemical osmosis experiments using closed systems, both the pressure difference and reservoir

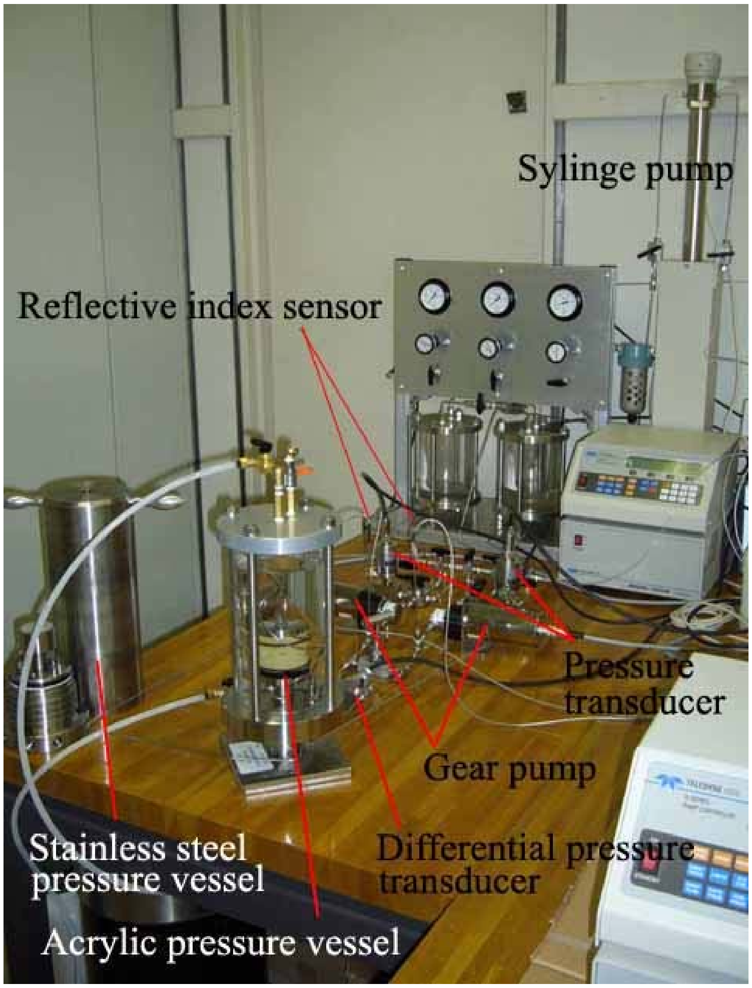

Fig. 5. A pictorial view of the experimental apparatus for chemical osmosis experiments that was developed in this study.

concentrations vary over time and their behavior is dependent on the chemico-osmotic, hydraulic and diffusion properties of the sample and of the system constants such as the compressible storage and volumes of the reservoirs. A pressure difference dependency on the reservoir compressible storages was observed in an experiment performed by Keijzer et al. (1999) [7]. The influence of reservoir volumes on concentration variations has also been explained by Takeda et al. (2008) [13]. However, system constants have not been considered in mathematical models for the chemical osmosis experiment in the laboratory. In this study compressible storage and volumes of reservoirs were incorporated into a mathematical model.

Numerical modeling of a hypothetical experiment indicated that pressures and concentrations in the sample are linearly distributed along the length after the pressure difference reaches a maximum (Fig. 2. (b) and (c)). However, the reflection coefficient approximated by Eq. 12 was time dependent in the preliminary experiments. To determine the reflection coefficient from the experimental data, at which the pressure and concentration gradients are supposed to be linear to the distance, an analytical solution should be developed. Analytical solutions for permeability and diffusion tests have previously been derived from mathematical models assuming linear gradients [15, 16]. Thus it will also be possible to derive an analytical solution for the chemical osmosis experiment by modifying the mathematical models for the permeability and diffusion tests.

To discuss osmotic pressures and their duration times in formations at least five related parameters, i.e., σ, k, Ss, D_e^*, and α are necessary (Eqs. 2 and 3). To obtain these parameters for the chemical osmosis experiment system constants should also be measured separately by calibration tests. Treating all parameters as unknown and inversely determining them from a set of pressure and concentration data might be possible by using the numerical model. Increasing the number of unknown parameters may, however, decrease the reliability of the parameter estimation. Therefore, each parameter should be determined separately. Coupled processes in the chemical osmosis experiment are supposed to be dominated by diffusion and hence the effective diffusion coefficient, D_e^*, can be uniquely determined from concentration differences between reservoirs where the solute sorption onto the solid phase is considered to be negligible [13]. The intrinsic permeability, k, and the specific storage, Ss, can also be estimated from the permeability tests, which can be performed by the newly-developed apparatus. The remaining parameters, i.e., the reflection coefficient, σ, and the capacity factor, α, have to be inversely determined from the experimental data. Therefore, an analytical solution capable of uniquely determining the reflection coefficient should be developed for further study using analytical models.

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