Supplementary Information for

Pore topology, volume expansion and pressure development in chemically-induced foam cements

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Supplementary Appendix A. Porosity of Foam Cement

**Final Porosity** $n_f$ Let us consider a cement paste that has an initial volume $V_o$ composed of volume of void $V_V$ and volume of solid $V_S$ (i.e., $V_o = V_S + V_V$).

![Figure A1. Simplified phase diagram for foam cement.](image)

The initial porosity $n_o$ is the ratio between volume of void $V_V$ and the initial volume $V_o$

$$n_o = \frac{V_V}{V_o} = \frac{V_V}{V_V + V_S} \quad \text{(A-1)}$$

Assuming the initial degree of saturation $S_o = 100\%$, the initial porosity $n_o$ is

$$n_o = \frac{V_V}{V_o} = \frac{V_w}{V_w + V_C + V_B + V_A} \quad \text{(A-2)}$$

where $V_V = V_w$ and subscripts $W$, $C$, $B$, and $A$ indicate water, cement, bentonite, and aluminum respectively. In terms of mass densities $\rho = M/V$,

$$n_o = \frac{M_W}{\rho_W \left( \frac{M_W}{\rho_W} + \frac{M_C}{\rho_C} + \frac{M_B}{\rho_B} + \frac{M_A}{\rho_A} \right)}$$

$$= \frac{M_W / M_C}{\rho_W \left( \frac{M_W}{\rho_W} / \rho_C + \frac{M_C}{\rho_C} / \rho_C + \frac{M_B}{\rho_B} / \rho_B + \frac{M_A}{\rho_A} / \rho_A \right)} \quad \text{(A-3)}$$

$$= \frac{\mu_{WC}}{\rho_w \left( \frac{\mu_{WC}}{\rho_w} + \frac{1}{\rho_C} + \frac{\mu_{BC}}{\rho_B} + \frac{\mu_{AC}}{\rho_A} \right)} = \frac{\mu_{WC}}{\frac{1}{\rho_C} + \frac{\mu_{BC}}{G_B} + \frac{\mu_{AC}}{G_A}}$$
where the parameter $\mu$ denotes the mass ratio between the mass of each component and the mass of cement $M_C$ (e.g., water-cement ratio $\mu_{WC} = M_W/M_C$), and the specific gravity of each phase is $G = \rho/\rho_w$. After foaming, the volume expansion ratio $\beta$ relates the final volume $V_f$ of foam cement to the initial volume $V_o$

$$\beta = \frac{V_f}{V_o} = \frac{V_G + V_o}{V_o} = \frac{V_G}{V_o} + 1 \quad (A-4)$$

where $V_G$ indicates the volume of gas bubbles. Then, the final porosity $n_f$ after volume expansion is the ratio between $(V_G + V_f)$ and $V_f$

$$n_f = \frac{V_G + V_f}{V_f} = \frac{V_G + V_f}{\beta V_o} = \frac{V_o}{\beta} = \frac{(\beta - 1) + n_o}{\beta} \quad (A-5)$$

Note that this first order approximation assumes that the volume of solid remains constant.

For example, consider a cement paste that has water-cement mass ratio $\mu_{WC} = 1$, bentonite-cement mass ratio $\mu_{BC} = 0.08$, and aluminum-cement mass ratio $\mu_{AC} = 0.04$ (see Table 1). Specific gravities are: $G_C = 3.15$ for cement, $G_B = 2.7$ for bentonite and $G_A = 2.7$ for aluminum. Then, the initial porosity is $n_o = 0.734$ for all cases in Figure 2c (Equation A-4).

$$n_o = \frac{\mu_{WC}}{\mu_{WC} + \frac{1}{G_C} + \frac{\mu_{BC}}{G_B} + \frac{\mu_{AC}}{G_A}} = \frac{1}{1 + \frac{1}{3.15} + \frac{0.08}{2.7} + \frac{0.04}{2.7}} = 0.734 \quad (A-6)$$

For the cement paste with aluminum chip size $d_{50} = 0.04$mm, the volume expansion ratio is $\beta = V_f/V_o = 1.5$ (see Figure 2c). Then, the final porosity is

$$n_f = \frac{n_o + \beta - 1}{\beta} = \frac{0.734 + 1.5 - 1}{1.5} = 0.823 \quad (A-7)$$
Supplementary Appendix B. Pressure Generation

Let us make the following assumptions to obtain a first-order estimate of pressure generation (See Innocentini et al. 2003 for a similar analysis):

- Constant temperature and constant slurry volume \( V_o \) = constant, i.e., the volume of liquid and solid in the slurry does not change during the reaction.
- The empty cell volume \( V_{cell} - V_o \) is initially filled with air. Air and the generated hydrogen will occupy this volume after the reaction.
- Assuming Dalton's law, the final pressure created by the gas mix will be the sum of their partial pressures: \( P_{max} = P_{air} + P_{H_2} \). Air does not experience volume change thus \( P_{air} \) remains at \( P_{air} = 1 \) atm; therefore, the change in \( P_{max} \) is controlled by the partial pressure of hydrogen \( P_{H_2} \).
- The change in hydrogen pressure with respect to volume under constant temperature follows Boyle-Mariotte's law for ideal gas behavior without correction for molecular size (i.e., Van der Waals equation - Note: precise equations of state for hydrogen gas typically involves the integration along the pressure-temperature trajectory). Then, for hydrogen only:

\[
P_{H_2} = P_{1atm} \frac{V_{1atm}}{V_{cell} - V_o} = P_{1atm} \frac{V_{1atm}}{M_H} \frac{M_H}{V_{1atm}} \left( V_{cell} - V_o \right)
\]

where 1atm refers to one atmosphere. The density of hydrogen at one atmosphere is \( \rho_{1atm} = M_H / V_{1atm} = 8.9 \times 10^{-5} \) g/cm³.

The reaction of 1 mol of aluminum results in 3 mols of H-atoms. Given their atomic masses Al\( \approx 27 \)g/mol and H\( \approx 1 \)g/mol, we can conclude that 27 g of Al generates 3 g of H. Consequently, the mass of hydrogen \( M_H \) is related to the mass of reacted aluminum as \( M_H = M_A / 9 \)
\[ P_{H_2} = P_{\text{atm}} \frac{M_H}{\rho_{\text{atm}} (V_{\text{cell}} - V_o)} = \frac{1}{9} P_{\text{atm}} \frac{M_A}{\rho_{\text{atm}} (V_{\text{cell}} - V_o)} \]  

(B-2)

Then, the maximum pressure in the cell is the sum of partial pressures

\[ P_{\text{max}} = P_{\text{air}} + P_{H_2} = P_{\text{atm}} \left(1 + \frac{M_A}{9 \cdot \rho_{\text{atm}} (V_{\text{cell}} - V_o)}\right) \]  

(B-3)

When the fraction of reacted aluminum is \( \lambda = \frac{M_{\text{react}}}{M_A} \), then the generated pressure becomes

\[ P_{\text{max}} = P_{\text{air}} + P_{H_2} = P_{\text{atm}} \left(1 + \frac{\lambda \cdot M_A}{9 \cdot \rho_{\text{atm}} (V_{\text{cell}} - V_o)}\right) \]  

(B-4)

where the approximation on the right applies when the pressure generation is high.

For example, consider \( P_{\text{atm}} = 101.3 \text{ kPa} \), \( \lambda = 1 \), \( M_A = 1 \text{ g} \), \( \rho_{\text{atm}} = 8.9 \times 10^{-5} \text{ g/cm}^3 \), \( V_{\text{cell}} = 120 \text{ cm}^3 \) and \( V_o = 55 \text{ cm}^3 \); in this case, the maximum pressure \( P_{\text{max}} \) the reaction will create within the chamber is \( P_{\text{max}} = 2047 \text{ kPa} \).
Supplementary Table S1. Chemical composition of the cement.

| Name of compound     | Molecular formula | Percent % |
|----------------------|-------------------|-----------|
| Silicon dioxide      | SiO₂              | 24.47     |
| Aluminum oxide       | Al₂O₃             | 6.79      |
| Ferric oxide         | Fe₂O₃             | 5.26      |
| Calcium oxide        | CaO               | 53.08     |
| Magnesium oxide      | MgO               | 3.98      |
| Sulfur trioxide      | SO₃               | 3.03      |
| Potassium oxide      | K₂O               | 0.22      |
| Sodium oxide         | Na₂O              | 0.89      |
| Loss on ignition     | L.O.I             | 1.32      |

Note: The cement used in this study is type 1 Portland cement, manufactured by Arabian Cement - Rabigh.
Supplementary Table S2. Aluminum content for aluminum chips of different sizes estimated from energy-dispersive X-ray spectroscopy EDS.

| Aluminum No. | ① | ② | ③ | ④ | ⑤ |
|--------------|----|----|----|----|----|
| Aluminum d$_{50}$ [mm] | 0.04 | 0.11 | 0.29 | 0.64 | 2.00 |
| Oxygen O | 38.2 | 44.7 | 38.7 | 31.2 | 37.7 |
| Aluminum Al | 28.4 | 18.5 | 19.0 | 51.3 | 45.0 |
| Silicon Si | 10.2 | 9.9 | 7.9 | 14.4 | 13.6 |
| Sodium Na | 0.46 | 0.97 | 0.94 | 0.92 | 0.85 |
| Magnesium Mg | 0.66 | 0.62 | 0.78 | 1.1 | 0.85 |
| Carbon C | 21.7 | 24.2 | 31.8 | 1.0 | 1.2 |
Supplementary Figure S1. Expansion tests at constant pressure (Figure 2a) - Initial $V_o$ and terminal $V_t$ volumes for cement-water-aluminum mixtures for different aluminum mass ratios $\mu_{AC} = M_A/M_C$ prepared with chip size $d_{50} = 0.29$ mm. Note: All mixtures: water-cement ratio $\mu_{WC} = M_W/M_C = 100\%$. 
Supplementary Figure S2. Expansion tests at constant pressure (Figure 2b) - Initial $V_o$ and terminal $V_t$ volumes for cement-water-aluminum-bentonite mixtures for five different bentonite mass ratios $\mu_{BC} = M_B/M_C$ at aluminum mass ratio $\mu_{AC} = M_A/M_C = 4\%$. Note: All mixtures: water-cement ratio $\mu_{WC} = M_W/M_C = 100\%$. 

Initial volume $V_o$ at time $t = 0$

Terminal volume $V_t$ at time $t = 500$ min

Bent. 0 g 0.08 g 0.16 g 0.24 g 0.32 g

Bent. 0 g 0.08 g 0.16 g 0.24 g 0.32 g
Initial volume $V_o$ at time $t = 0$

Supplementary Figure S3. Expansion tests at constant pressure (Figure 2c) - Initial $V_o$ and terminal $V_t$ volumes for cement–water–aluminum–bentonite mixtures for five different aluminum chip sizes $d_{50}$ prepared with aluminum mass ratio $\mu_{AC} = M_A/M_C = 4\%$, bentonite mass ratio $\mu_{BC} = M_B/M_C = 8\%$. Note: All mixtures: water-cement ratio $\mu_{WC} = M_W/M_C = 100\%$. 

Terminal volume $V_t$ at time $t = 225$ min
Supplementary Figure S4. Normalized volume expansion versus elapsed time for cement-water-aluminum mixtures for different aluminum mass ratios $\mu_{AC} = M_A / M_C$ prepared with chip size $d_{50} = 0.29$ mm (Figure 2a). Note: All mixtures: water-cement ratio $\mu_{WC} = M_W / M_C = 100\%$. 
**Supplementary Figure S5.** Normalized volume expansion versus elapsed time for cement-water-aluminum-bentonite mixtures for five different bentonite mass ratios $\mu_{BC} = M_B / M_C$ at aluminum mass ratio $\mu_{AC} = M_A/M_C = 4\%$ (Figure 2b). Note: All mixtures: water-cement ratio $\mu_{WC} = M_W/M_C = 100\%$. 
Supplementary Figure S6. Normalized volume expansion versus elapsed time for cement-water-aluminum-bentonite mixtures for five different aluminum chip sizes $d_{50}$ prepared with aluminum mass ratio $\mu_{AC} = M_A/M_C = 4\%$, bentonite mass ratio $\mu_{BC} = M_B/M_C = 8\%$ (Figure 2c). Note: All mixtures: water-cement ratio $\mu_{WC} = M_W/M_C = 100\%$. 
Supplementary Figure S7. Conceptual drawing of volume expansion mechanisms in a gassy cement mixture.