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Energy Procedia 4 (2011) 5267–5274

**Energy
Procedia**

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GHGT-10

Experimental Results of Diffusion Coefficient of Sulfate Ions in Cement Type 10 and Class G

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Abstract

This paper presents the results of lab experiments done with cement samples in sulfate environment. About 350 samples of cement type 10 and class G were prepared and placed into three temperatures conditions (30, 55, and 75°C) and three sulfate concentrations (3,000; 6,000; and 30,000 ppmW) for periods of 2, 4, 6, 8, and 10 months. Sulfur concentration (profile) was measured using the scanning electron microscope; SEM. Diffusion coefficient was calculated by matching lab profiles with curves obtained from a Matlab code created for this purpose. Apart from obtaining the values for diffusion coefficient for sulfate, another main finding was the relationship of sulfate concentration and temperature. At certain threshold temperature, the effects of sulfate diffusion on cement deterioration were more pronounced. The results show that the diffusion coefficient for SO₄ was in the order of $3.0 \times 10^{-12} \text{ m}^2/\text{s}$ to $4.2 \times 10^{-12} \text{ m}^2/\text{s}$ with small differences in cement type 10 and class G. Also it was noticed that samples exposed at temperature equals to 55°C, and sulfate concentration equals to 6,000 ppmW had more significant changes when compared to the results obtained from tests conducted at the all other experimental conditions.

© 2011 Published by Elsevier Ltd. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).*Keywords:* carbon dioxide capture and storage, geologic sequestration, cement deterioration, sulfate, SEM, profile modelling

1. Introduction

Wellbores have been identified as the components with the highest risk of leakage in the geologic storage of carbon dioxide. Among the main factors contributing to this assumption is the natural deterioration of the cement used for setting casings and for plugging. Well cement industry has developed a strong expertise while dealing with different factors found in oilfields; however long-term geologic storage of CO₂ is a new technology with new challenges.

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Cement deterioration due to the presence of sulphates in reservoir fluids have been studied for decades and as matter of fact, the American Petroleum Institute, API has a classification for cement types resistant to sulphates (API 2006a). In spite of this know-how, technical literature offers limited reference to practical experiments dealing with deterioration of cement due to the presence of sulphates. One of the factors that help defining the long-term performance of any cement is the diffusion coefficient (Buenfeld, Newman 1987, Samson et al. 1999). Knowing the behaviour or reaction of cement to sulphates may be useful to estimate the long-term performance and also will help in adopting corrective measurements for particular conditions where the risks of leakage may be high.

2. Technical background

Portland is the most common type of hydraulic cement. Such cement sets and develops compressive strength as a result of hydration, which involves chemical reactions between water and the compounds present in the cement (Barret, Bertrandie 1986, Richardson 2000). The deterioration of compressive strength is produced by several factors, being sulphate attack one of the most important ones.

In fluid reservoirs, brines commonly contain magnesium and sodium sulphates. These sulphates react with precipitated calcium hydroxide to form magnesium and sodium hydroxides and calcium sulphate which can, in turn react with the aluminates to form ettringite (Gerdemann, Dahlin & O'Connor 2002). This compound may produce expansion which is beneficial for reducing permeability and increasing bonding, but when uncontrolled, it may lead to loss of compressive strength, cracking, and damage as it is illustrated in Figure 1 (Kurtis, Monteiro & Madanat 2000).

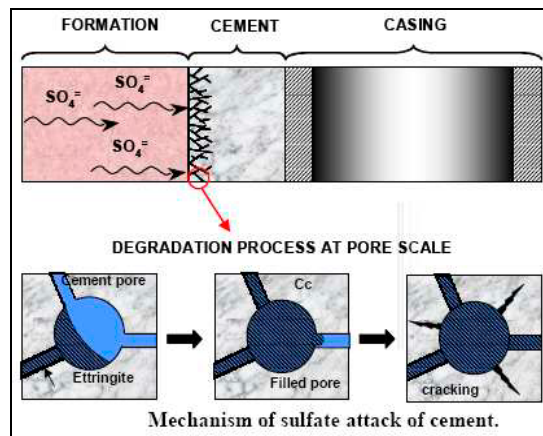


Figure 1 Mechanism of sulphate attack of cement

Three main factors influence the formation of ettringite: temperature, permeability, and cement composition (Batic et al. 2000). Sulphate attack is decreased when temperature increases. Studies on concrete have shown that when the temperature is higher than 65°C, ettringite is soluble and does not precipitate (Divet, Randriambololona 1998). On the other hand, studies have demonstrated that reducing permeability makes cement more resistant to sulphate attack (Mehta, Schiessl & Raupach 1992, Sirivivatnanon, Khatri 1999). Regarding to cement composition, the resistance to sulphate attack increases with the reduction of tri-calcium aluminate, C_3A . Other factors that also may affect the sulphate resistance are the pore solution alkalinity and the water/cement ratio (Smith 1990)

2.1 Modelling the diffusion of sulphate ions

Several models for sulphate attack have been proposed by researchers using approaches based on different scientific fields: engineering, mechanics, physics, and mathematics. This diversity in approaches explains the different

assumptions and the various mechanisms considered (Samson et al. 1999, Wooda, Gladdenb 2002, Samson, Marchand & Beaudoin 1999, Samson, Marchand & Snyder 2003, Gospodinov 2005). In this paper, the diffusion of sulphate in cement is modelled as a product of chemical reactions (Tixier, Mobasher 2003a, Tixier, Mobasher 2003b):

- Decalcification
- Formation of expansive products (mono-sulphate, ettringite and thaumasite)

These two reactions are linked and in this paper are treated as one while modelling. The reactions start when portlandite, $\text{Ca}(\text{OH})_2$, is reached by sulphate ions, which leads to the formation of gypsum. Next, part of the content of tri-calcium aluminate, C_3A , may react with the formed gypsum to produce ettringite. This ettringite may then react with the remaining C_3A to transform part of it into calcium mono-sulphate-aluminate hydrate which finally may react again with the remaining sulphates to produce secondary ettringite and thaumasite. Figure 2 illustrates these reactions. This figure shows that sulphate attack is a progressive phenomenon from the surface inwards (Yang, Buenfeld 2000, Sibbick, Fenn & Crammond 2003, Kakali et al. 2003). The intensity of the ion flow depends on the concentration of various species and the porosity of the cement, as well as the changes in porosity caused by chemical reactions (Buenfeld, Newman 1987, Clifton, Frohnsdorff & Ferraris 1999).

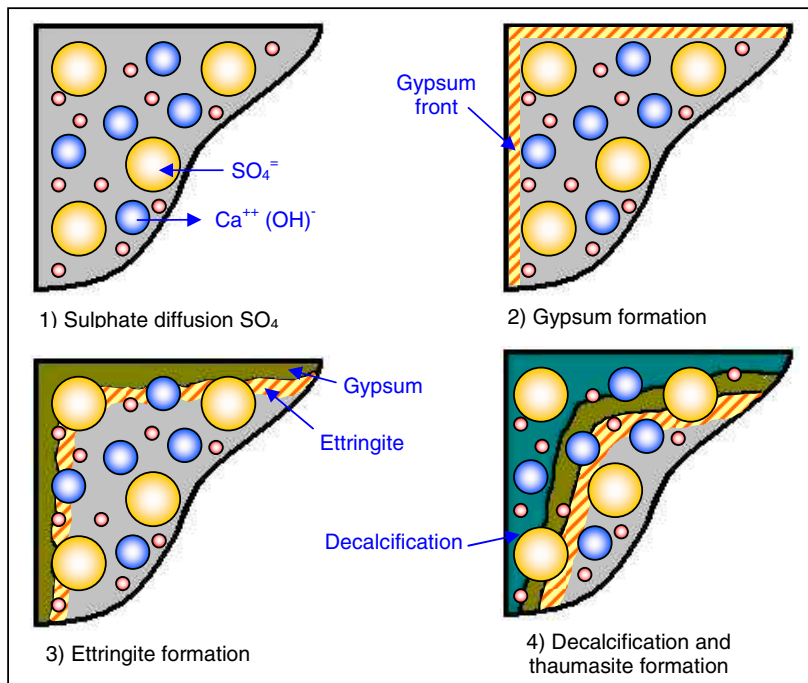


Figure 2 Representation of sulphate attack

The modeling approach used in this study is based on the general conservation equation involving diffusion, convection, sorption, and chemical reaction, as the phenomena governing the transfer of mass through cement (Astarita 1967)

$$\underbrace{D \Delta c}_{\text{molecular transport}} = \underbrace{u \nabla c}_{\text{convection}} + \underbrace{\frac{\partial c}{\partial t}}_{\text{accumulation}} + \underbrace{r}_{\text{reaction rate}} \dots \dots \dots \text{Equation 1}$$

Where: u , velocity; c , concentration; t , time; D , diffusion coefficient; Δ , non-infinitesimal change; and ∇ , gradient of a scalar function. The term molecular transport corresponds to diffusion, and it is produced due to a difference in concentration between two regions. Considering the laboratory conditions under which experiments were conducted (dilute solutions, no pressure or temperature gradient and assuming first order chemical reaction) the convection term is eliminated. Then, the general form of Equation 1 becomes:

$$\frac{\partial U}{\partial T} = D \frac{\partial^2 U}{\partial X^2} - kU \dots\dots\dots \text{Equation 2}$$

Where: U , molar concentration; T , time; and k , rate of reaction. The solution for this equation is given as:

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - r u^2 + r u z \dots\dots\dots \text{Equation 3}$$

With: $r = \frac{k L^2 U_0}{q D}$

Boundary Conditions :

$$\left. \begin{matrix} t > 0 \\ x = 0 \\ x = 1 \end{matrix} \right\} u = 1$$

Initial Conditions :

$$\left. \begin{matrix} t = 0 \\ 0 < x < 1 \end{matrix} \right\} u = 0$$

3. Experimental set-up

The goal for this set of experiments was to investigate the change in the composition of cement as a result of diffusion of sulphate. In total, about 350 samples were prepared using two classes of cement (A and G) following the standard API 10-B (API 2006b). These samples were placed in recipients at three temperatures and three sulphate concentrations. The measurement of sulphate concentration was done for periods of 2, 4, 6, 8, and 10 months. The qualitative and quantitative analyses were completed using a Scanning Electron Microscope, SEM, in conjunction with the Energy Dispersive X-ray Spectroscopy, (EDS) (Bell, Garratt-Reed 2003). In total, there were 18 different environments to be analysed as shown in the Table 1 and the set-up illustrated in Figure 3.

Table 1 Set up conditions for lab experiments

Cement class	A	G	
Temperature	30°C	55°C	75°C
Sulphate concentration	3,000 ppm (w)	6,000 ppm (w)	30,000 ppm (w)

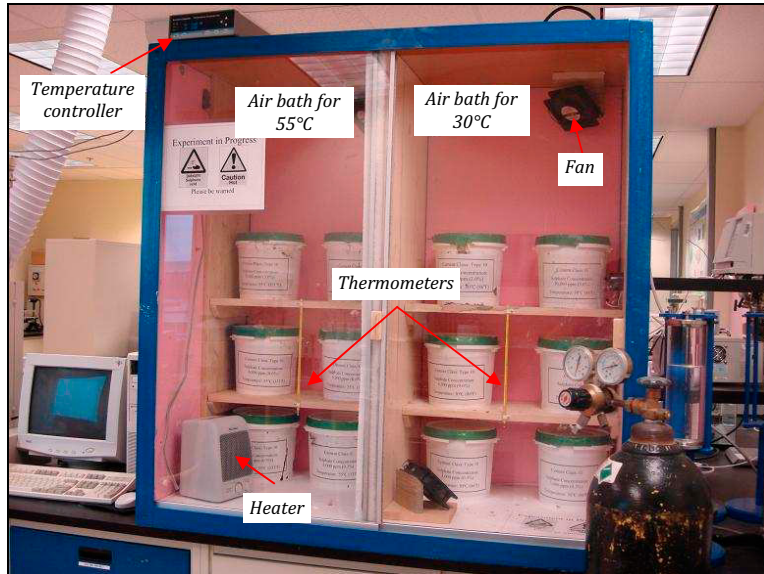


Figure 3 Set-up for samples at 30°C and 55°C

Each sample, once dried, was cut and measured the sulphur concentration every 4 millimetres using the SEM. That concentration was plotted into an axis to define sulphur profile as illustrated in the Figure 4.

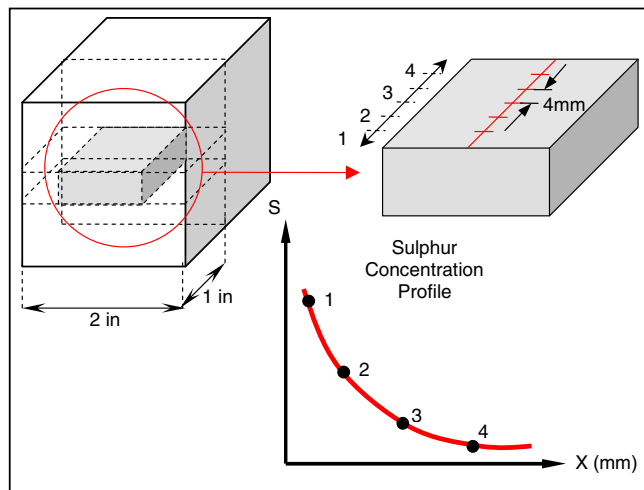


Figure 4 Sulphur concentration profile

4. Mathematical modelling

Based on the solution for Equation 3, a MatLab code was developed to model the chemical reactions at the interior of cement cores (Appendix A). The diffusion coefficient (D) in the MatLab code defines the shape of the curve. A process of matching between the SEM measurements and the curve generated through the code was done in order to see which value of diffusion coefficient fits best as illustrated in Figure 5. Table 2 presents diffusion coefficients of

sulphate based on the numerical model for Type 10 and Class G cements. Some constants were taken from technical literature (Gospodinov 2005):

- Rate constant of reaction k: 1.00E-08 m³/(mol.s)
- Sulphates initial concentration U₀: 30.61 mol/m³
- Calcium initial concentration Ca: 82.5 mol/m³

Table 2 Diffusion coefficients for sulphate environment

Cement Type 10	Cement Class G
D: 3.00E-12 m ² /s at T=30°C	D: 2.90E-12 m ² /s at T=30°C
3.80E-12 m ² /s at T=55°C	3.50E-12 m ² /s at T=55°C
4.20E-12 m ² /s at T=75°C	3.90E-12 m ² /s at T=75°C

Also it was noticed that samples exposed at temperature equals to 55°C, and sulfate concentration equals to 6,000 ppmW had more significant changes when compared to the results obtained from tests conducted at the all other experimental conditions

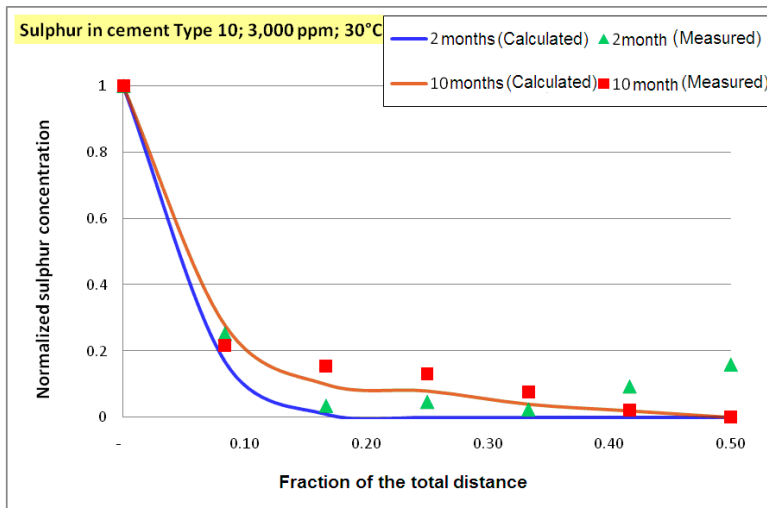


Figure 5 Matching sulphur profiles for diffusion coefficient

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Appendix A

MatLab source for the diffusion of SO₄

```

L=25.4e-3;% thickness of slab [meters]
D=3.61e-12;% diffusion coefficient [m^2/s]
k=1e-8;% rate constant of reaction [m3/(mol.s)]
U0=30.61;% sulphates initial concentration [mol/m3]
r=k*L^2*U0/(3*D); p=-r;
M=25 ;% number of time increments.
N=25;% number of distance increments.
dx=0.5/(N+0); dt=dx*0.08; K=dx^2/dt; l=[0:N+0];x=dx*l;
u=[1;zeros(N,1)];%initialize u
z0=-3*Ca/U0; rf1=dt/dx^2; rf2=0.4;pbhat=fix(rf1/rf2)+1;
rc=rf1/pbhat;
z=z0*ones(N+1,1);%initialize Z
dm=[rc*1;zeros(N-1,1)];% compute terms vector d, then matrix Am
Am=(+diag(rc*ones(N-1,1),1)+ diag(rc*ones(N-1,1),-1)+diag((1-
2*rc)*ones(N,1)));
Am(N,N-1)=2*rc;
for j=[1:M]% begin iterations
zz=z(2:N+1,j);
for kk=[1:pbhat] % VSIET procedure
zz=Am*zz+dm;
end
z(2:N+1,j+1)=zz; z(1,j+1)=1;
end
for j=[1:M]% begin iterations
% call analytical solution of Fick's 2nd law
% compute forward projection of u to half-level of time
UH(N)=u(N+1,j)+(2*u(N,j)-(2+(r*u(N+1,j)+p*z(N+1,j+1))*dx^2)*u(N+1,j))/(2*K);
for i=[2:N]
UH(i-1)=u(i,j)+(u(i+1,j)+u(i-1,j)-
(2+(r*u(i,j)+p*z(i,j+1))*dx^2)*u(i,j))/(2*K);
end
% compute terms of main diagonals of matrices A and B
a=-r*UH*dx^2-2*(1+K); b=2+r*UH*dx^2-2*K;
% compute terms of vector d
d(1)= 2*p*z(2,j+1)*dx^2*UH(1)-2 ;
d(2:N)= 2*p*z(3:N+1,j+1)*dx^2.*(UH(2:N))';
% build matrices A and B
A=sparse(diag(ones(N-1,1),1)+ diag(ones(N-1,1),-1)+diag(a));
A(N,N-1)=2;
B=sparse(-diag(ones(N-1,1),1)-diag(ones(N-1,1),-1)+diag(b));
B(N,N-1)=-2;
% solve system
u(2:N+1,j+1)=A\ (B*u(2:N+1,j)+d'); u(1,j+1)=1;
if rem(j,5)==0 % pick here number of plots
plot(x,u(:,j))
title('Sulphur Profile'); xlabel('x [mm]');ylabel('S concentration')
hold on; end; end;
hold off

```