



HAL
open science

Modelling approaches for anion-exclusion in compacted Na-bentonite

Christophe Tournassat, C. A. J. Appelo

► **To cite this version:**

Christophe Tournassat, C. A. J. Appelo. Modelling approaches for anion-exclusion in compacted Na-bentonite. *Geochimica et Cosmochimica Acta*, 2011, 75 (13), pp.3698-3710. 10.1016/j.gca.2011.04.001 . hal-00597084

HAL Id: hal-00597084

<https://brgm.hal.science/hal-00597084>

Submitted on 31 May 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Supporting information B. C-program for calculating the model results.

Template for parameter input file (name = graph.in)

```
0.1      | NaCl Concentration for Graph
0.02     | density increment for Graph
0.2      | minimum density (kg/dm3)
1.9      | maximum density (kg/dm3)
|crystallographic ssa
748.9|
|charge
-0.81 |
|Input for models 1 and 2
ssa | nc | nb_Debye      |
748.9| 3 | 2          |
|Input for models 3 and 4
ssa | ncmin | nb_Debye | dporemin (nDL) | hint_min |
748.9| 1.5 | 2          | 5.51          | 0.31e-9 |
```

C. file

```
#include <stdio.h>
#include <math.h>
#include <float.h>
#include <stdlib.h>

double rhomm = 2.841; /* kg/dm3 */

int main() {

/***** Graph characteristics - start *****/

    static int get_line(char *s, int lim, FILE *f_in);
    static int copy_until(int start_pos, char *in, char *out, char stop);

    double Concentration = 0;
    double delta_rho = 0;
    double rho_min = 0;
    double rho_max = 0;
    char line[1000], l1[50], stop_char;
    int start_pos;
    double ssa_cryst;
    double charge_model;
    double ssa_model1, ssa_model2;
    double nc_model1, ncmin_model2;
    double nb_debye_model1, nb_debye_model2;
    double dpore_min, hint_min;
    static double Debye_length(double C0);
    static double C_Donnan(double C0, double q);
```

```

static double h_int(double C0, double rho);
static double Volume_Donnan(double surf, double nb_Debye, double C0);
static double Calculate_nc(double rho, double C0, double surf, double ncm, double nDL);
static double model(double rho, double C0, double charge, double surf, double nb_debye,
double ncm, double nDL, double hintmin);
double rho;
double por_tot, por_inta, por_intb;
double hint;
double model0, model1, model2, model3, model4;
double nca, ncb;

FILE *graphout, *graphin = fopen("Graph.in", "r");
stop_char = "|";

/* NaCl Concentration */
get_line(line, 1000, graphin); copy_until(0, line, 11, stop_char);
Concentration = atof(11);
/* Density increment */
get_line(line, 1000, graphin); copy_until(0, line, 11, stop_char);
delta_rho = atof(11);
/* Min density */
get_line(line, 1000, graphin); copy_until(0, line, 11, stop_char);
rho_min = atof(11);
/* max density*/
get_line(line, 1000, graphin); copy_until(0, line, 11, stop_char);
rho_max = atof(11);

/***** Graph characteristics - end *****/

/***** Model inputs - start *****/

// double ssa_cryst;
get_line(line, 1000, graphin);
get_line(line, 1000, graphin); copy_until(0, line, 11, stop_char);
ssa_cryst = atof(11);

// double charge_model;
get_line(line, 1000, graphin);
get_line(line, 1000, graphin); copy_until(0, line, 11, stop_char);
charge_model = atof(11);

// double ssa_model1, ssa_model2;
// double nc_model1, ncm_model2;
// double nb_debye_model1, nb_debye_model2;
// double dpore_min, hint_min;

get_line(line, 1000, graphin);
get_line(line, 1000, graphin);
get_line(line, 1000, graphin);
start_pos = copy_until(0, line, 11, stop_char); ssa_model1 = atof(11);

```

```

start_pos = copy_until(start_pos, line, l1, stop_char); nc_model1 = atof(l1);
copy_until(start_pos, line, l1, stop_char); nb_debye_model1 = atof(l1);

get_line(line, 1000, graphin);
get_line(line, 1000, graphin);
get_line(line, 1000, graphin);
start_pos = copy_until(0, line, l1, stop_char); ssa_model2 = atof(l1);
start_pos = copy_until(start_pos, line, l1, stop_char); ncmin_model2 = atof(l1);
start_pos = copy_until(start_pos, line, l1, stop_char); nb_debye_model2 = atof(l1);
start_pos = copy_until(start_pos, line, l1, stop_char); dpore_min = atof(l1);
copy_until(start_pos, line, l1, stop_char); hint_min = atof(l1);

printf (" NaCl Concentration: \t%.5f mol/L\n density increment: \t%.5f kg/dm3\n min
density: \t%.5f kg/dm3\n max density: \t%.5f kg/dm3\n", Concentration, delta_rho,
rho_min, rho_max);
printf (" ssa_cryst: \t%.5f m2/g\n charge: \t%.5f molc/kg\n ssa model 1: \t%.5f m2/g\n
nc model 1: \t%.5f\n nb debye model 1: \t%.5f\n", ssa_cryst, charge_model, ssa_model1,
nc_model1, nb_debye_model1);
printf (" ssa model 2: \t%.5f m2/g\n nc min model 2: \t%.5f\n nb debye model 2: \t%.5f\n
dpore min: \t%.12f * DL\n hint min: \t%.12f m\n", ssa_model2, ncmin_model2,
nb_debye_model2, dpore_min, hint_min);

fclose(graphin);
/***** Model inputs - end *****/

/***** Output -start *****/

// static double Debye_length(double C0);
// static double C_Donnan(double C0, double q);
// static double h_int(double C0, double rho);
// static double Volume_Donnan(double surf, double nb_Debye, double C0);
// static double Calculate_nc(double rho, double C0, double surf, double ncmin, double
nDL);
// static double model(double rho, double C0, double charge, double surf, double nb_debye,
double ncmin, double nDL, double hintmin);
// double rho;
// double por_tot, por_inta, por_intb;
// double hint;
// double model0, model1, model2, model3;
// double nca, ncb;

nca = 3;
ncb = 25;

/*FILE */graphout = fopen("Graph.out", "w");

fprintf (graphout, "NaCl (mol/L)\tDensity (kg/dm3)\tTotal porosity\tth int (nm)\tInterlayer
porosity nc = 3 and ssa_cryst\tInterlayer porosity nc = 25 and ssa_cryst\tModel BK\tModel
1\tModel 2\tModel 3\tModel 4\n");

```

```

for (rho = rho_min; rho <= rho_max + delta_rho; rho += delta_rho) {

    por_tot = 1 - rho / rhomm;
    hint = h_int(Concentration, rho);
    por_inta = hint * ssa_cryst * 1000000 * rho * (1 - 1/nca) / 2;
    if (por_inta > por_tot)
    {
        por_inta = por_tot;
    }
    por_intb = hint * ssa_cryst * 1000000 * rho * (1 - 1/ncb) / 2;
    if (por_intb > por_tot)
    {
        por_intb = por_tot;
    }
    hint = h_int(Concentration, rho);
    /* Birgersson & Karnland, all porespace is Donnan... */
    model0 = model(rho, Concentration, charge_model, ssa_cryst, 1500, 1, 0, 0);

    model1 = model(rho, Concentration, charge_model, ssa_model2, 1500, 8.4, 0, 0) ;
    model2 = model(rho, Concentration, charge_model, ssa_model2, nb_debye_model1, 2.48,
0, 0.0) ;
    model3 = model(rho, Concentration, charge_model, ssa_model2, nb_debye_model2,
ncmin_model2, dpore_min, 0.62e-9) ;
    model4 = model(rho, Concentration, charge_model, ssa_model2, nb_debye_model2,
ncmin_model2, dpore_min, hint_min) ;

    fprintf                                     (graphout, "
%.5f\t%.5f\t%.5f\t%.5f\t%.5f\t%.5f\t%.12f\t%.12f\t%.12f\t%.12f\t%.12f\n  ", Concentration,
rho, por_tot, hint*1e9, por_inta, por_intb, model0, model1, model2, model3, model4) ;
    }

    fclose(graphout);
    return 0;
}

```

```

/***** Output *****/
*****/

```

```

/***** Functions for calculation -start *****/

```

```

double Debye_length(double C0) {
    return pow( (2.0 * pow(96485, 2) * 1e3 * C0 / (8.314 * 298 * 0.00000000069328)), -0.5);
}

```

```

double C_Donnan(double C0, double q) {
    return (2*C0*C0 / (-q + pow( (q*q + 4* C0*C0), 0.5)));
}

```

```

}

double h_int(double C0, double rho) {
    double x2, x3, rho_lim;
    rho_lim = 1.3 - 3 * C0;
    x3 = 1.0; x2 = 0.0;
    if (rho > rho_lim)
    {
        x2 = (rho - rho_lim) / (1.6 - rho_lim);
        x3 = 1 - x2;
    }
    if (rho > 1.6)
    {
        x3 = 0.0; x2 = 1.0;
    }
    return (x2 * 0.62 + x3 * 0.94) * 1e-9;
}

double Volume_Donnan(double surf, double nb_Debye, double C0) {
    return surf * nb_Debye * Debye_length(C0) * 1e3;
}

double Calculate_nc(double rho, double C0, double surf, double ncmin, double nDL) {
    double nc2 = ncmin;
    double dpore;
    double vol_int, surf_int, vol_stern, vol_ext, surf_ext;

    surf_int = surf * (nc2 - 1)/nc2 * rho * 1000;      /* in m2 */
    vol_int = surf_int * h_int(C0, rho) * 1000 / 2;   /* in dm3 */
    surf_ext = surf / nc2 * rho * 1000;              /* in m2 */
    vol_stern = 0; /* surf_ext * 1.84e-10 * 1000; */
    vol_ext = 1 - vol_int - vol_stern - rho / rhomm;  /* in dm3 */
    if (vol_ext < 0)
    {
        vol_ext = 0;
    }

    dpore = 2 * vol_ext / 1000 / surf_ext;           /* in m */

    while ((nc2 < 30) && (dpore < nDL * Debye_length(C0)))
    {
        nc2 += 0.01;
        surf_ext = surf / nc2 * rho * 1000;
        surf_int = surf * (nc2 - 1)/nc2 * rho * 1000;
        vol_int = surf_int * h_int(C0, rho) * 1000 / 2;
        vol_stern = 0; /* surf_ext * 1.84e-10 * 1000; */
        vol_ext = 1 - vol_int - vol_stern - rho / rhomm;
        dpore = 2 * vol_ext / 1000 / surf_ext;
    }
    return nc2;
}

```

```
}
```

```
/****** Functions for calculation - end *****/
```

```
/******  
***** Models -start  
******/
```

```
/******  
***** Model  
******/
```

```
double model(double rho, double C0, double charge, double surf, double nb_debye, double  
ncmin, double nDL, double hintmin) /*** surface in m2/g, charge in molc/kg *****/
```

```
{
```

```
double vol_int, surf_int, vol_stern, vol_ext, surf_ext, vol_Donnan, vol_free, q;  
double nc2 = ncmin;  
double result;  
double hint;  
double dpore;
```

```
nc2 = Calculate_nc(rho, C0, surf, ncmin, nDL);  
hint = h_int(C0, rho);
```

```
surf_int = surf * (nc2 - 1)/nc2 * rho * 1000; /* in m2 */  
vol_int = surf_int * hint * 1000 / 2; /* in dm3 */  
surf_ext = surf / nc2 * rho * 1000; /* in m2 */  
vol_stern = 0; /*surf_ext * 1.84e-10 * 1000;*/  
vol_ext = 1 - vol_int - vol_stern - rho / rhomm; /* in dm3 */  
dpore = 2 * vol_ext / 1000 / surf_ext;
```

```
while ((hint > hintmin) && (dpore < nDL * Debye_length(C0)))
```

```
{  
hint -= 0.001e-9;  
vol_int = surf_int * hint * 1000 / 2;  
vol_ext = 1 - vol_int - vol_stern - rho / rhomm;  
dpore = 2 * vol_ext / 1000 / surf_ext;  
}
```

```
if (vol_ext < 0)
```

```
{  
vol_ext = 0;  
}
```

```
vol_Donnan = Volume_Donnan(surf_ext, nb_debye, C0); /* in dm3 */
```

```
if (vol_Donnan > vol_ext)
```

```
{  
vol_Donnan = vol_ext;  
}
```

```
vol_free = vol_ext - vol_Donnan;
```

```

if (vol_Donnan == 0)
{
    result = 0;
}
else
{
    q = charge / nc2 * rho / vol_Donnan;
    result = (vol_free + vol_Donnan * C_Donnan(C0, q) / C0);
}
return result;
}

```

```

/*****                               Models                               -end                               of                               models
*****/

```

```

/***** Procedures for files reading - start *****/

```

```

int get_line(char *s, int lim, FILE *f_in) {
    int i, c, space;
    space = c = 1;
    for (i = 0; i < lim && (c = fgetc(f_in)) != EOF && c != (int) '\n'; i++) {
        s[i] = (char) c;
        if (space && c != 32) space = 0;
    }
    if (space) i = 0;
    s[i] = '\0';
    if (i == 0 && c == EOF)
        return EOF;
    else
        return 0;
}

```

```

int copy_until(int i, char *in, char *out, char stop) {
    int j;
    j = 0;
    while ((in[i] != stop) && (out[j] = in[i]) != '\0') {
        i++; j++;
    }
    out[j] = '\0';
    return ++i;
}

```

```

/***** Procedures for files reading - end *****/

```