Developing ERICA FF2 for sulfate in cementitious systems

Masood Valavi

*Supervisor: Professor **Paul Bowen***

*Co-supervisor: Dr. **Sandra Galmarini** (EMPA, CH)*

Powder Technology Group (PTG)

Construction Materials Laboratory (LMC),

Swiss Federal Institute of Technology (EPFL),

Lausanne, Switzerland

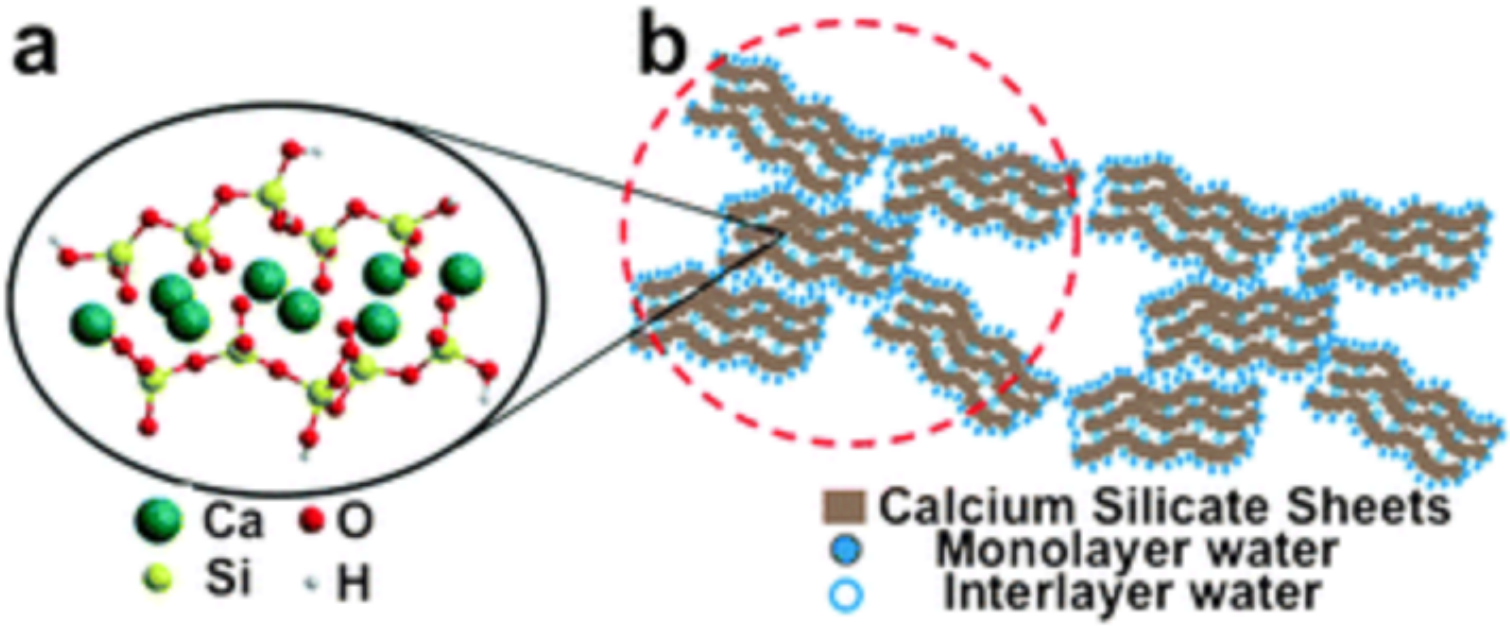
Sep 2019

Outline

- ESR3 goals
- Force field improvement and validation for Water-Sulfate-Portlandite solutions (ERICA FF1)
- Development of ERICA FF2 and Validation
- Future Plans
- Secondments

ESR 3

A lot of ions such at SO4

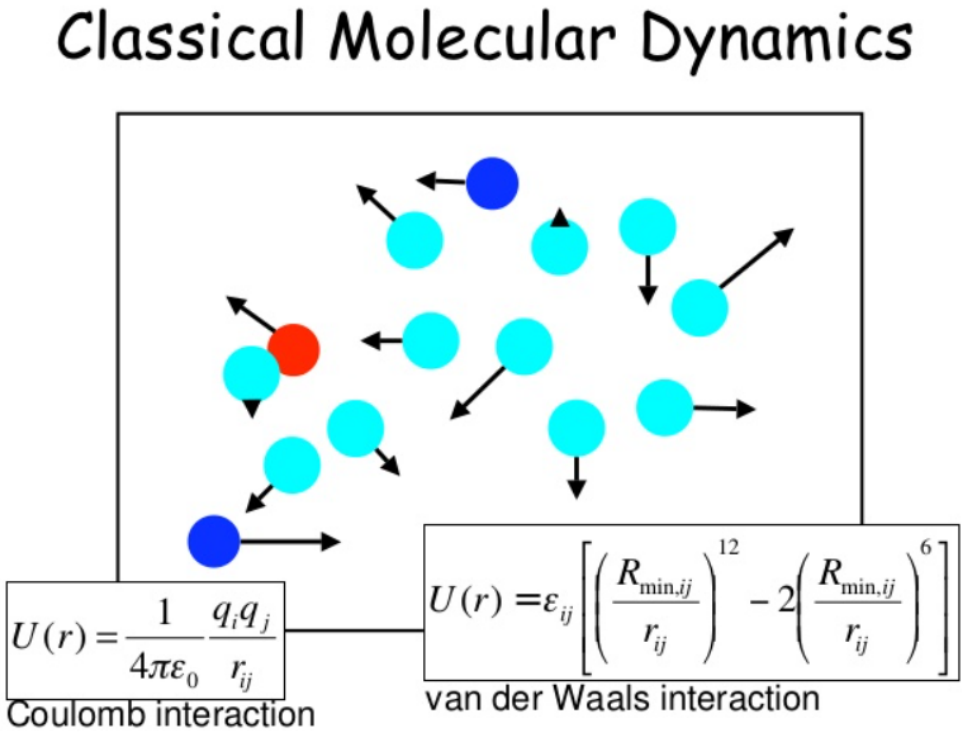


Goal: interaction of ions such as sulfate with surfaces of C-S-H

ERICA FF1:Force Field Validation for Aqueous System of Portlandite and Sulfate

Force Field Overview:what is Force Field

- Assembly of interatomic potentials
- Conclusions depending on the force field
- force field should be validated carefully

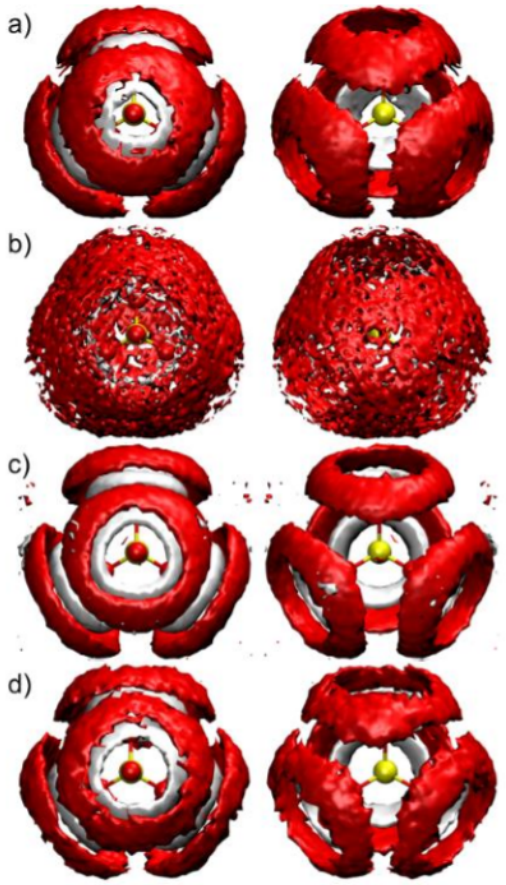


Force Field Overview Field

- The first step -the simulation of Portlandite growth in the presence of sulfate -develop an accurate empirical force field (FF).
- interaction of Portlandite- water, sulfate-water and sulfate-Portlandite must be captured correctly
- several force fields which can be used in the interactions of Portlandite-water :Clay FF and SPC/E,Cement FF and TIP4P2005
- Sulfate:Duvail(Polarizable) and Gale FF(non-polarizable)

Force Field Overview Field

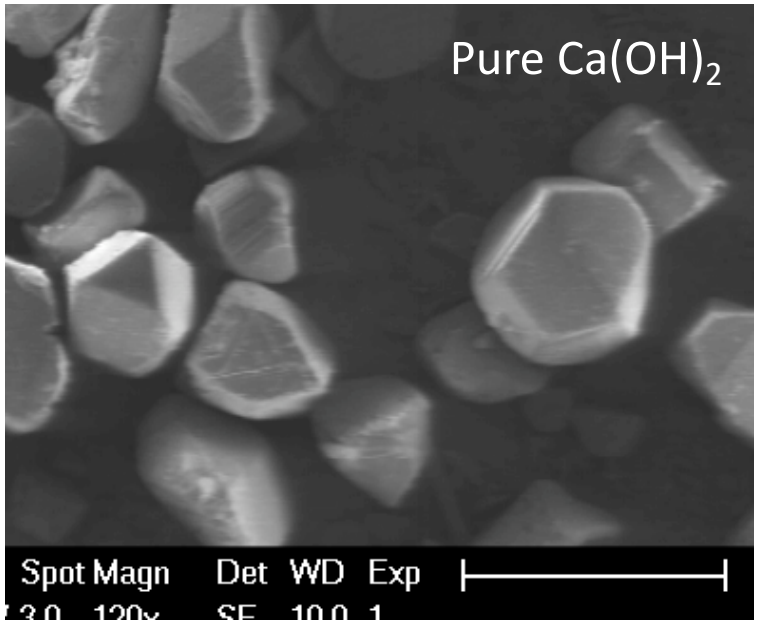
- Gale model captured the structure of water around sulfate correctly
- A)FF1
- B)FF2
- C)AMOEBA
- D)DFT

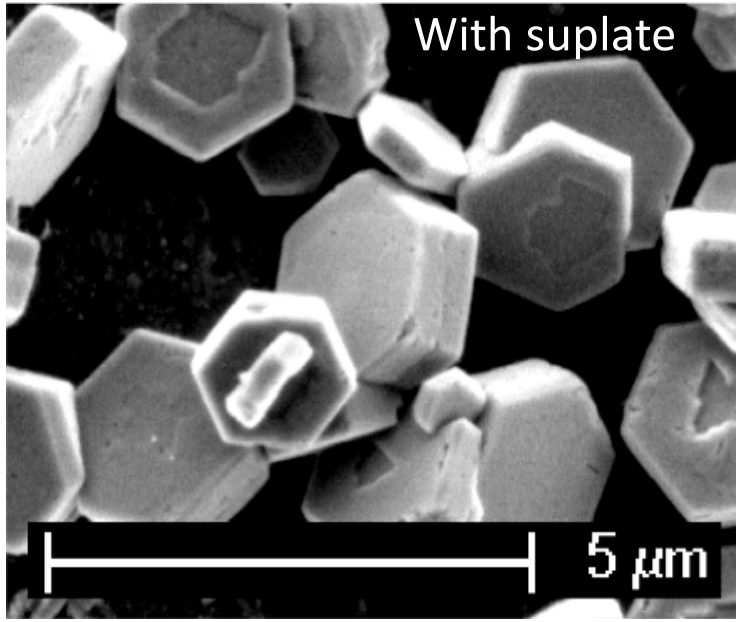


.Representations of the 3D water structure around the sulfate ion

Why important?

- Force field developed during
- Sandra Galmarini thesis CEMENT FF1
- Does not have Al, Mg, SO_4^{2-}
- Needs developments….
- Significant effect of sulfate on $Ca(OH)_2$ morphology*
- Can influence porosity – hence transport properties & strength….
- Training for adsorption on C-S-H



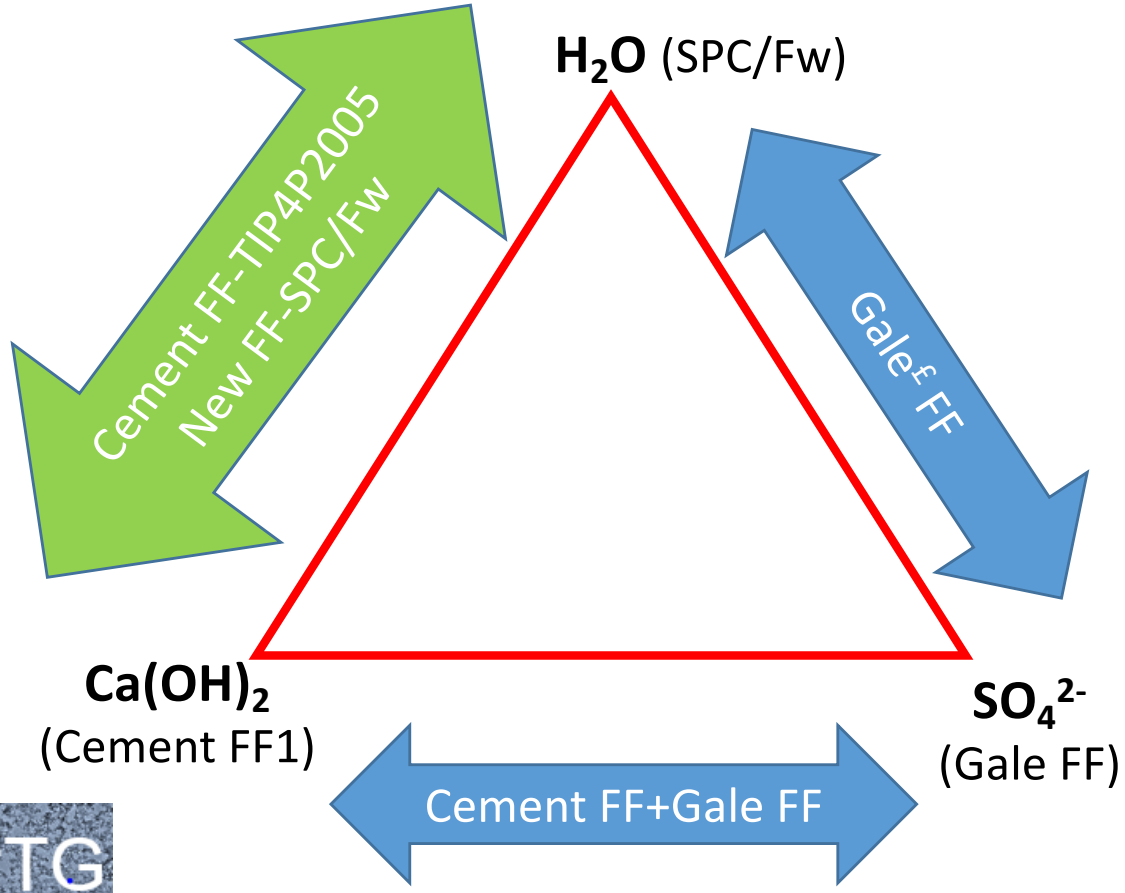


Galmarini et al CCR. 41 p1330 (2011) & CCR 71, p61 (2014).
Galmarini & Bowen CCR 81,p16 (2016)

Force Field Development

Criteria for good force field

- %5-6 on the length parameters
- 10 degrees of angles



Development of non-polarizable force fields for phosphates and sulphates

£E. H. Byrne, P. Raiteri, and **J. D. Gale**, "Computational Insight into Calcium-Sulfate Ion Pair Formation," *J. Phys. Chem. C*, 2017

Benchmarks for validation

- Experimental data for benchmarking performance of force field = a set of atomistic potentials

Structural

- Portlandite – $Ca(OH)_2$
- Gypsum – $Ca\ SO_4 \cdot 2H_2O$
- Anhydrite – $Ca\ SO_4$
- Coordination numbers
- Average bond lengths

Thermodynamic

- Heats of dissolution

ERICA FF2 development and validation

Need for development of ERICA FF2

- Including Al and Si in the potential and interaction of these 2 atoms with other atoms
- Simulation of C-A-S-H is now accessible
- OH-SO4 validation for ERICA FF1 was missing-It has been done now by simulation of Ettrinigite

ERICA FF 2

(J.am.Ceram soc,1999)**Nora de Leeuw FF**

Cement FF 1(cement and concrete research 2011,Sandra et al)

(J.phys.chem.c,2017)
Julian Gale FF

Cement FF 2
(cement and concrete research 2017,Aslam et al)

(J.Chemical Physics 2006)**SPC/Fw FF**

Cement FF 3(Aslam et al, Under preparation)

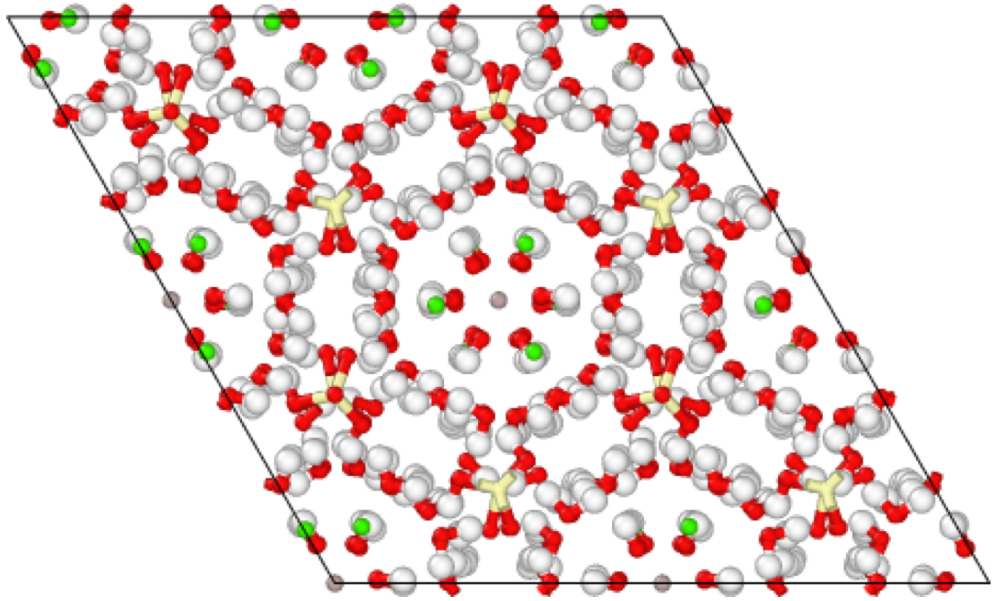
ERICA FF 2 validation by simulation of Ettrinigite

Ettrinigite Bulk simulation of a 2x2x1 box

Total run of 1ns

1000 Atoms in the box

Figure in Z direction



Grey: Aluminium
Green: Calcium
Yellow: Sulfur
Red: Oxygen
White: Hydrogen

ERICA FF 2 validation by simulation of Ettrinigite

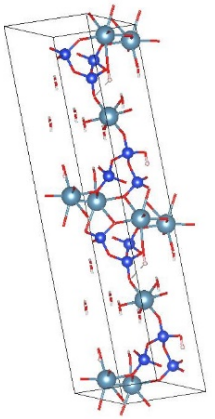
	EM (A)	MD(A)	EXP(A)	Relative and abdolute e error EM	Relative and absolute error MD
a	11.47	11.67	11.23	2.1%	3.9%
b	11.38	11.63	11.23	1.3%	3.6%
c	21.67	21.6	21.48	0.8%	0.5%
alfa	90.34	89.88	90	0.34 abs	0.12 abs
betta	90.33	90.58	90	0.33 abs	0.58 abs
gamma	120.11	120.17	120	0.11 abs	0.17 abs

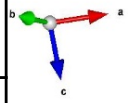
ERICA FF 2 validation by simulation of Ettrinigite

Average bond	MD	exp	relative error%
Ca-Ooh	2.52	2.53	0.35
Ca-Ow	2.31	2.41	4.14
Al-Ooh	1.85	1.79	3.35
S-Os	1.61	1.56	3.2
Ow-Hw	0.9976	1.03	3.1
Ooh-Hoh	0.9318	0.9756	4.0

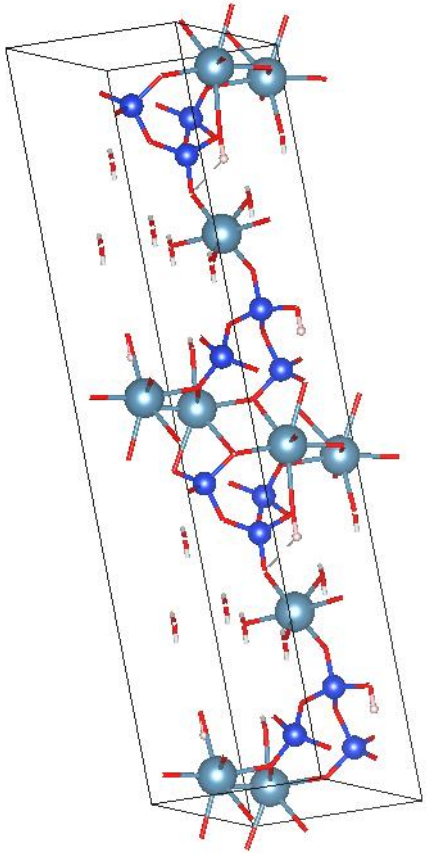
Tobermorite bulk simulation of a 4x4x1 box
Total run of 600 ps

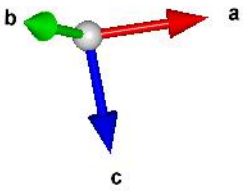
	EM	MD	Exp	Relative error EM	relative error MD
a	6.75	6.81	6.73	0.001	0.002
b	7.37	7.39	7.42	0.004	0.003
c	31.11	31.62	30.65	0.011	0.015
alfa	110.48	112.47	111.34		
beta	87.04	87.12	87.37		
gamma	123.36	122.22	123.25		





Why we are not happy by simulation of 14 A Tobermorite





Why we are not happy by simulation of 14 A Tobermorite

Future Plans

- Simulation of adsorption of sulfate into three surface of portlandite by MD and MTD

- Simulation of adsorption of sulfate into surfaces of C-S-H

Secondments

- April 2020 2 weeks at Usurrey
- October 2020 1-2 months at CHRYSO

Outreach Activity

- Amirkabir University in Iran October 2019


TIME FOR QUESTIONS
12
1
2
3
4