Reactivity of nano-particles in cementitious systems

VANDERBILT SCHOOL OF ENGINEERING

THE UNIVERSITY OF TENNESSEE MARTIN

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INTRODUCTION

Background:

Nano-particles (NP's) have been added to cement products to improve mechanical and durability properties[1]. This contribution has been attributed to the NP's high surface area to volume ratio[1]. However, previous studies have yet to define the specific chemical reaction between NP's and cementitious systems.

Objectives:

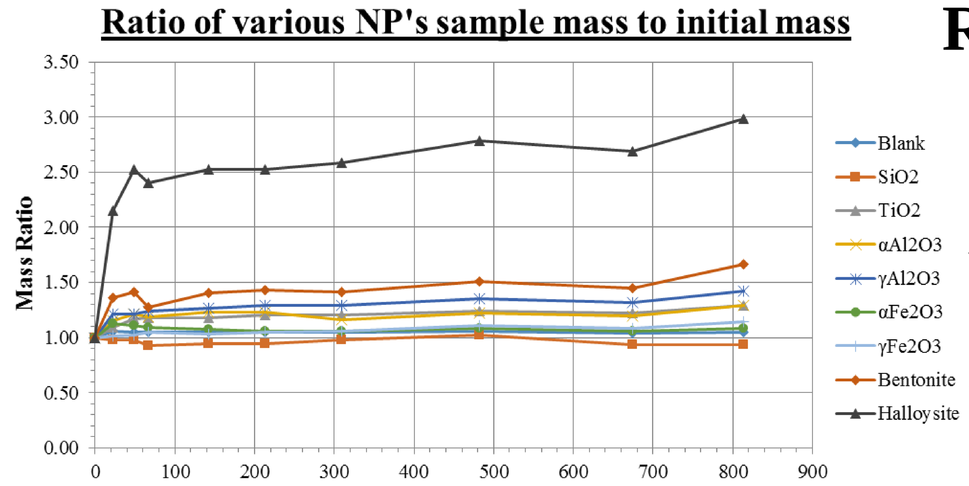
- Characterize intrinsic and catalytic reactivity of NP's in cement-based systems
- Distinguish the effect of cement chemistry on the agglomeration of nano-TiO_2

NP'S REACTIVITY

Methods:

- Reaction of solid phases with dissolved $Ca(OH)_2$ for the formation of new binding phases (i.e. pozzolanic reaction) in the cement system[2], monitored by sample mass change.
- NP's (nano- SiO_2, TiO_2, α-Al_2O_3, γ-Al_2O_3, α-Fe_2O_3, γ-Fe_2O_3, bentonite and halloysite) immersed in $Ca(OH)_2$, to study the pozzolanic reactivity of NP's alone.
- Fly ash (FA) containing NP's immersed in $Ca(OH)_2$, to study effect of NP's on pozzolanic reaction of FA.

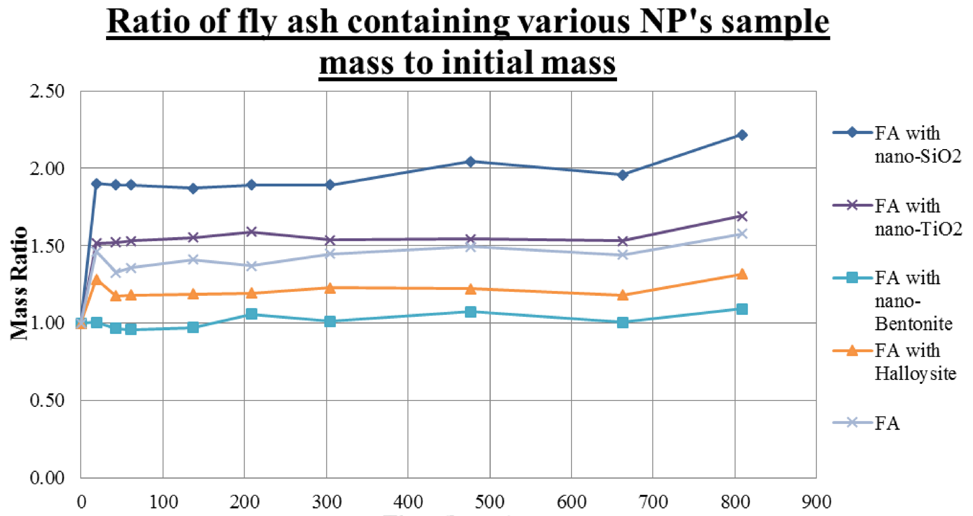
Ratio of various NP's sample mass to initial mass



Results and Discussion:

Halloysite appeared to be the most pozzolanically reactive.

Ratio of fly ash containing various NP's sample mass to initial mass



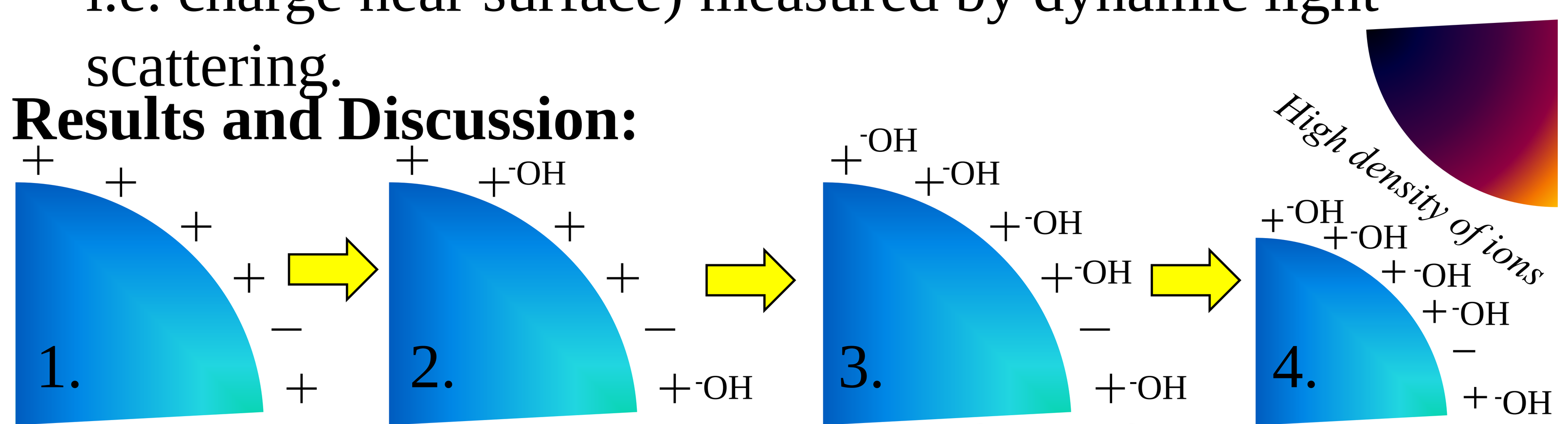
SiO_2 appeared to be the most catalytic for the hydration of FA.

AGGLOMERATION OF NP'S

Methods:

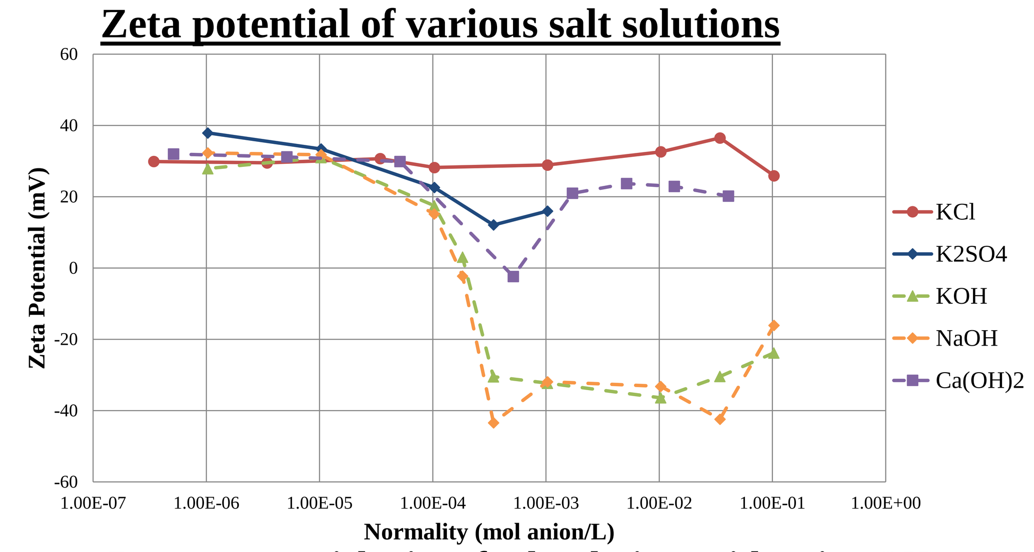
- Dispersion of nano-anatase-TiO_2 by probe sonicator for 40 minutes (steady state for particle size)
- Solution chemistry modified by salts ($Ca(OH)_2$, NaOH, KOH, KCl, and K_2SO_4)
- Particle size (i.e. agglomerate size) and zeta potential (ZP i.e. charge near surface) measured by dynamic light scattering.

Results and Discussion:



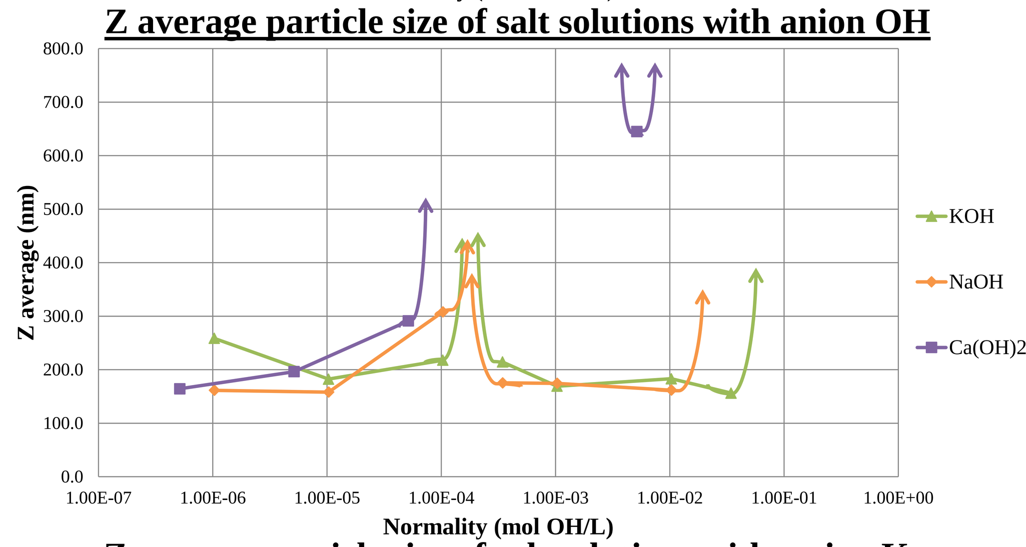
1. Mostly positive sites near outer surface of NP
2. OH^- attach to positive sites of NP; ZP decreases
3. OH^- cover the positive sites; ZP is ~0 mV; charge balancing
4. Higher concentration of ions between NP's; charge screening

Zeta potential of various salt solutions



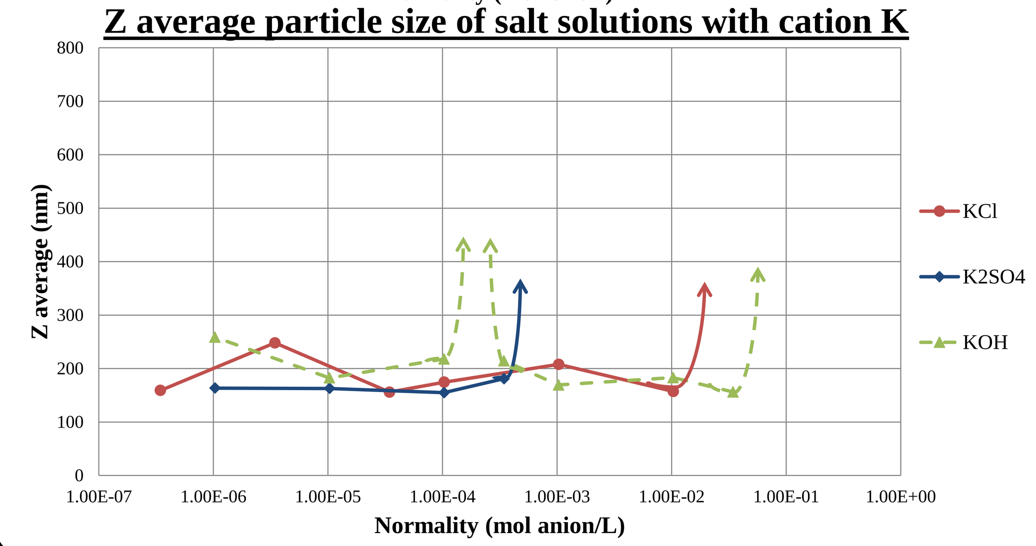
OH^- salts reach ~0 mV (point of zero electrostatic repulsion). KCl and K_2SO_4 remain positive.

Z average particle size of salt solutions with anion OH



Two points of agglomeration due to surface charge balancing (~10^{-4} mol/L) and charge screening (~10^{-2} mol/L).

Z average particle size of salt solutions with cation K



Agglomeration for Cl^- and SO_4^{2-} anions occurs only for charge screening.

CONCLUSIONS

- NP's and fly ash reacted pozzolanically as observed by mass gain; steady state has yet to be achieved.
- Nano-TiO_2 largely agglomerated even in deionized water.
- Ions found in cement porewater caused further agglomeration by a combination of balancing surface charge and screening charges through the solution. Agglomeration was observed at significantly lower concentrations than in cement porewater.

FUTURE STUDIES

- Analyze nano-TiO_2/cement pastes with SEM/EDS
- Examine the NP's/cement pastes using DSC-TGA
- Evaluate the effects of the various NP's on the hydration of cement
- Study the effects of polycarboxylates utilized as ligands

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REFERENCES

[1] F. Sanchez and K. Sobolev, "Nanotechnology in concrete-A review," *Construction and Building Materials*, vol. 24, pp. 2060-2071, 2010.

[2] F. Massazza, "Pozzolana and Pozzolanic Cements, "*Lea's Chemistry of Cement and Concrete,"* edi. 4, pp.471-635, 1998.

SEM background image provided by Yonathan Reches