Georgia Tech Institute for Electronics and Nanotechnology

National Nanotechnology Coordinated Infrastructure

NSF

Toward a Cleaner Future: NO_X Binding and Conversion in Individual Cement Phases

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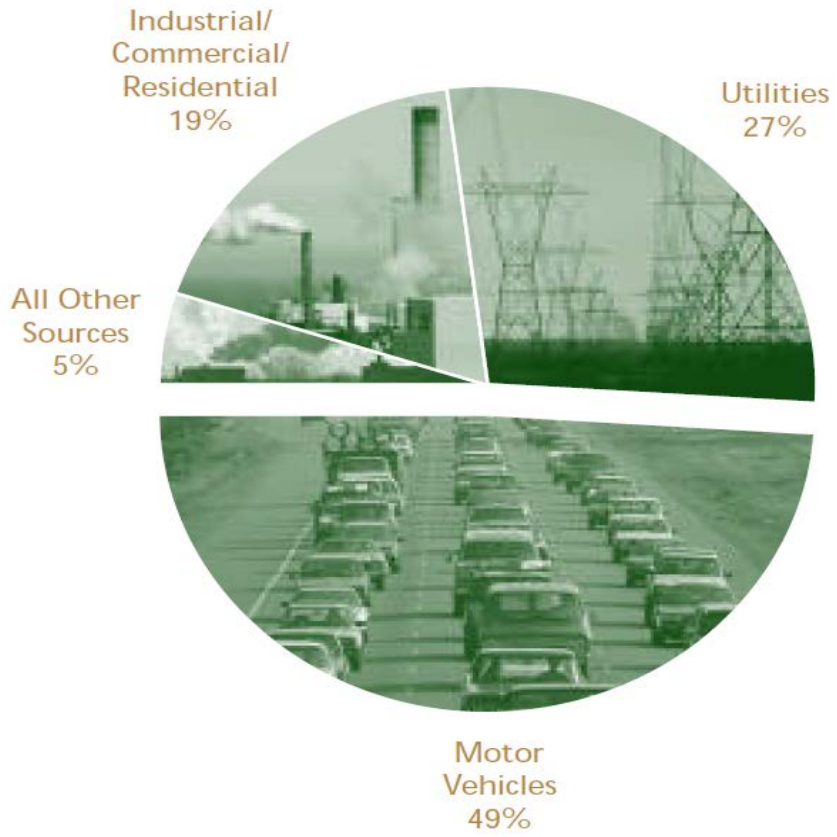
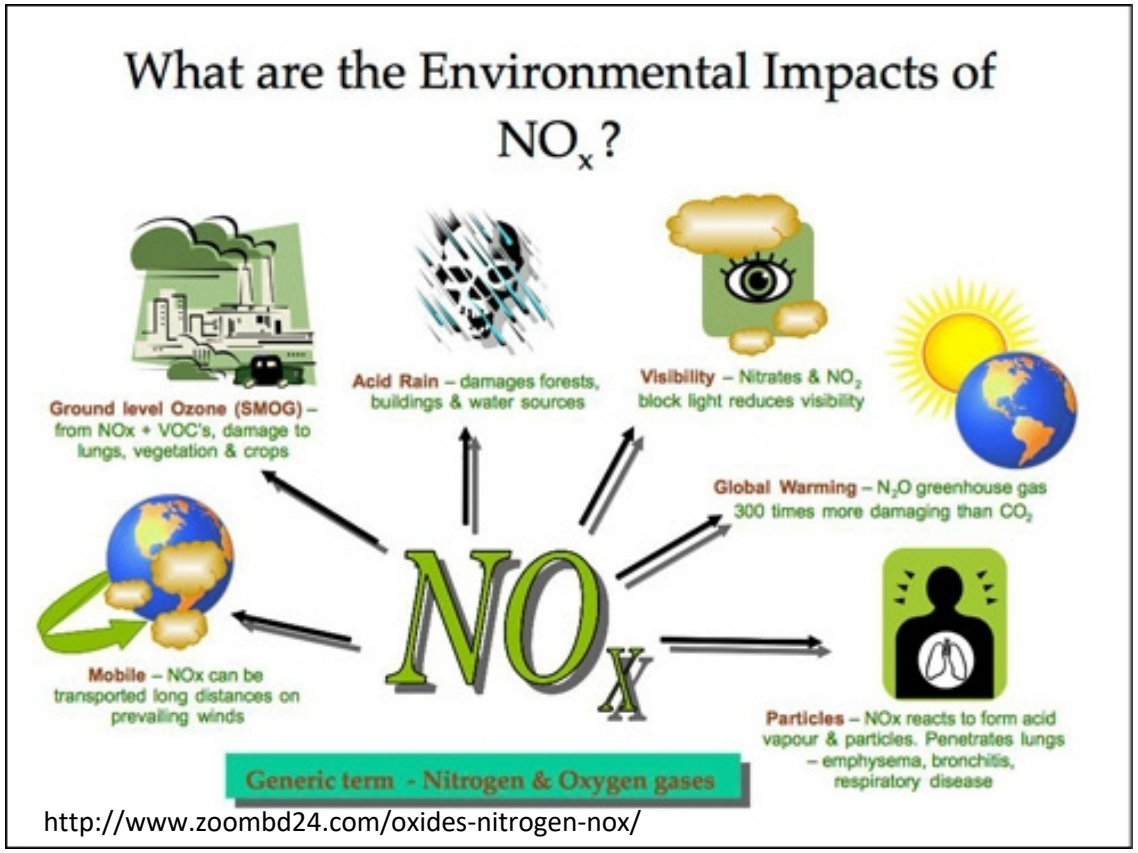
What's the big deal about NO_X?

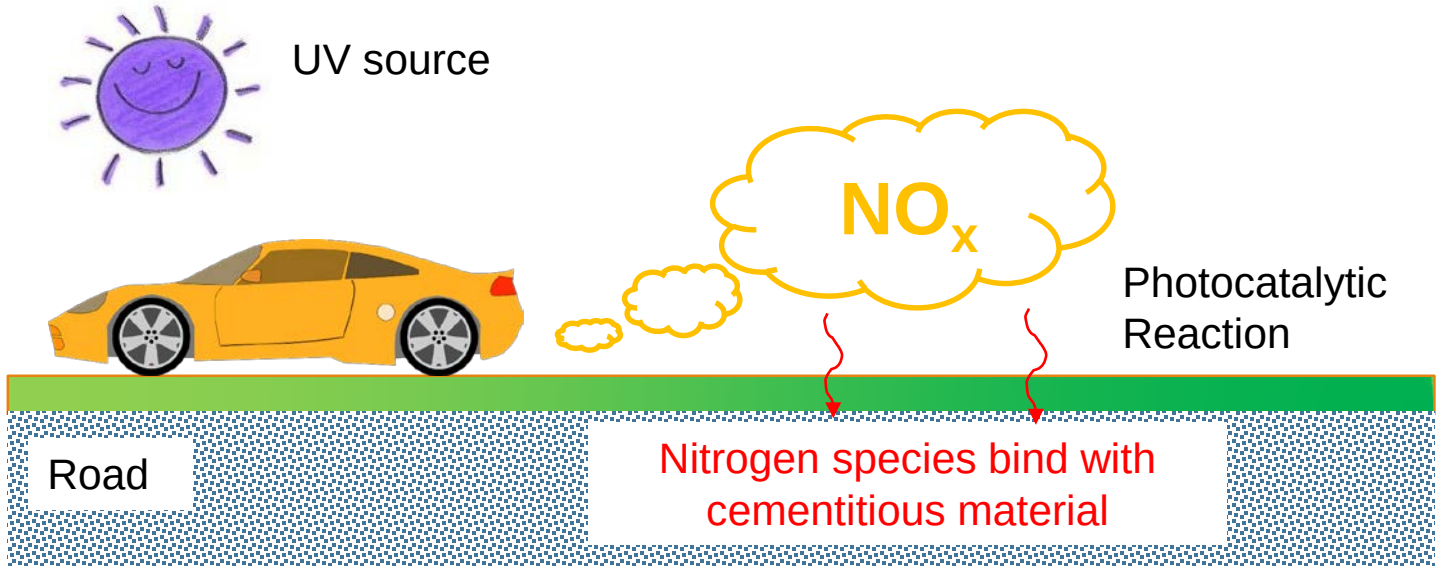




http://www.zoombd24.com/oxides-nitrogen-nox/

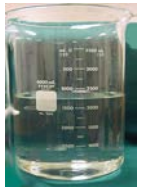
Why cement?

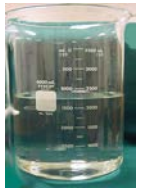
- Nearly 4 million miles of roads in the United States alone
- An estimated 3 trillion vehicle miles traveled per year
- Cement can uptake NO_X!
  - Some innate capacity
  - Through photocatalytic reactions



What exactly is cement?

- Different types of cements:
  - Portland cement (OPC, calcium silicate based)
  - Calcium aluminate cement
  - Magnesium-based (hydroxyapatite)
  - Gypsum
  - Calcium sulfoaluminate
  - Aluminosilicate

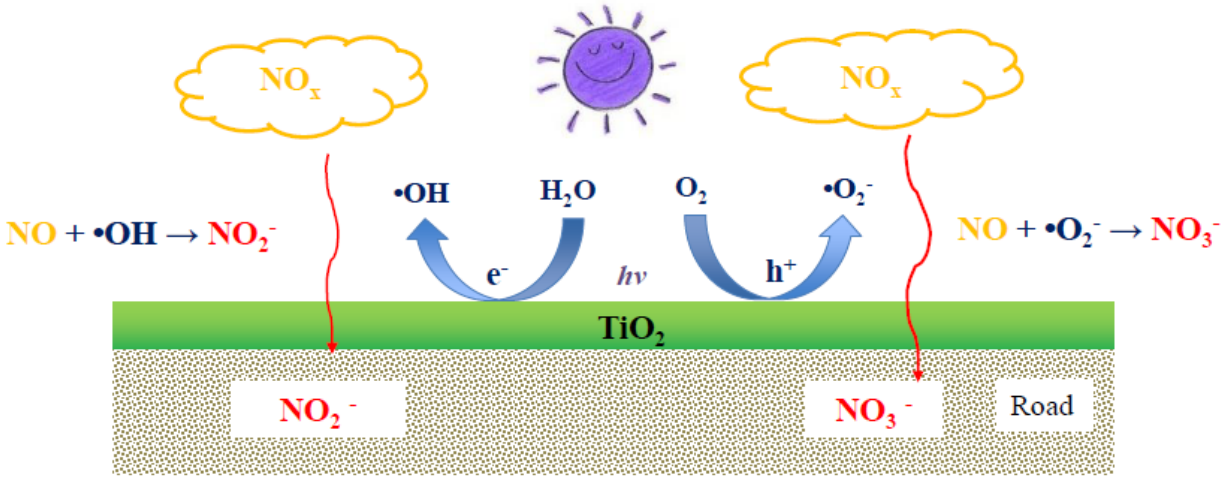
Cement paste =  + 

Mortar =  +  + 

Concrete =  +  +  + 

What are we trying to determine?

1. $TiO_2 \xrightarrow{h\nu} TiO_2 + e^- + h^+$
2. $h^+ + H_2O \rightarrow H^+ + OH^\bullet$
3. $e^- + O_2 \rightarrow O_2^{\bullet-}$
4. $NO + O_2^{\bullet-} \rightarrow NO_3^-$
5. $NO + OH^\bullet \rightarrow NO_2^- + H^+$
6. $NO + OH^\bullet \rightarrow HNO_2 + OH^\bullet \rightarrow NO_2 + H_2O$
7. $NO_2 + OH^\bullet \rightarrow NO_3^- + H^+$



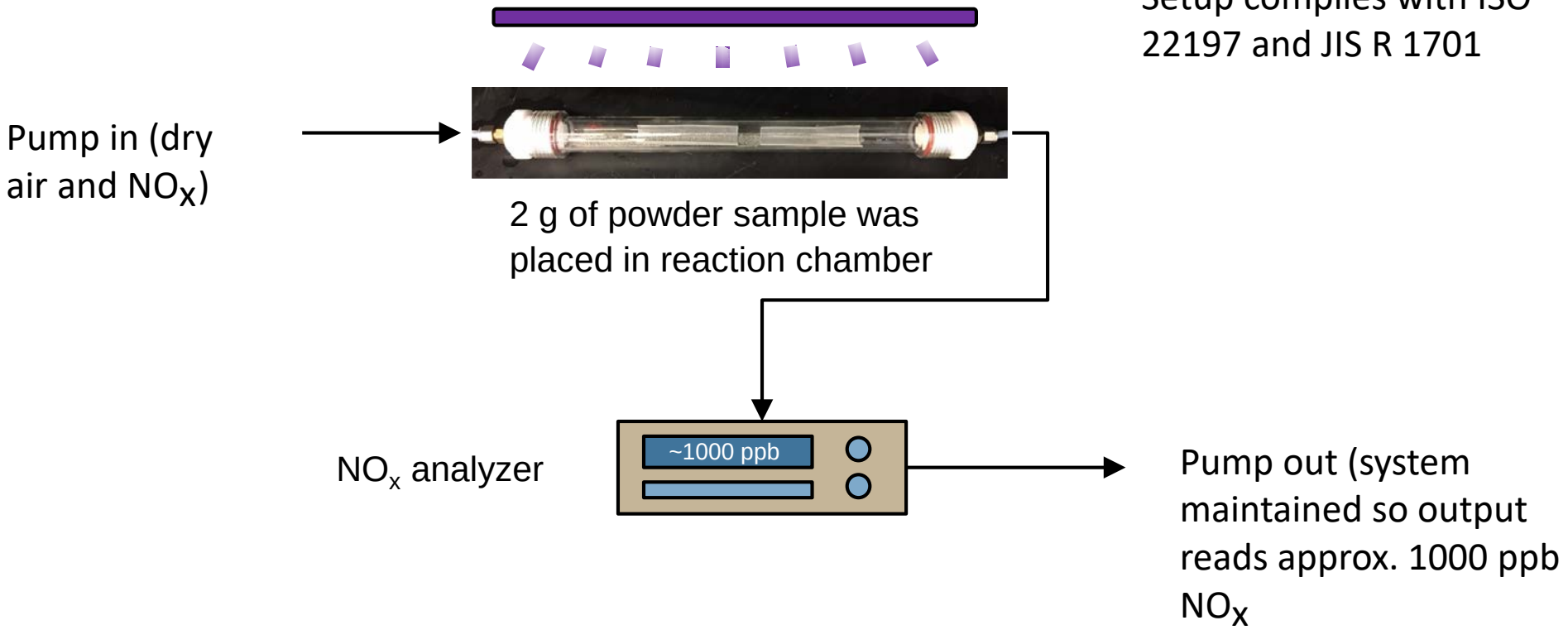
1. Why is unmodified cement capable of binding NO_X?
2. How much NO_X is converted to nitrate and how much is converted to nitrite in individual cement phases?
3. How is NO_X bound in the cement phases (e.g., physically vs. chemically)

Why does that matter?

- Increased NO_X binding efficiency → increased real-world practicability

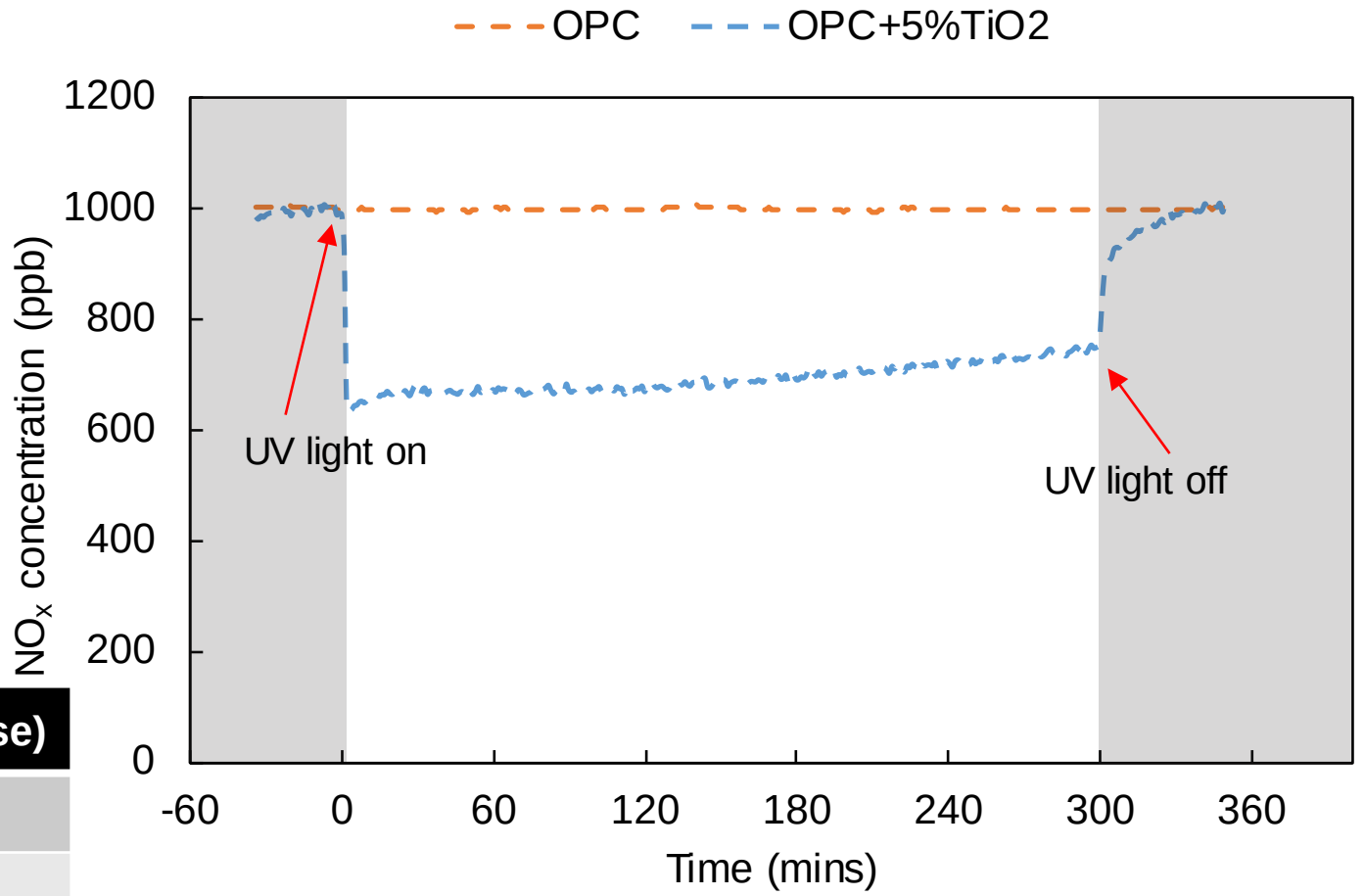
How do we test this?

Setup complies with ISO 22197 and JIS R 1701



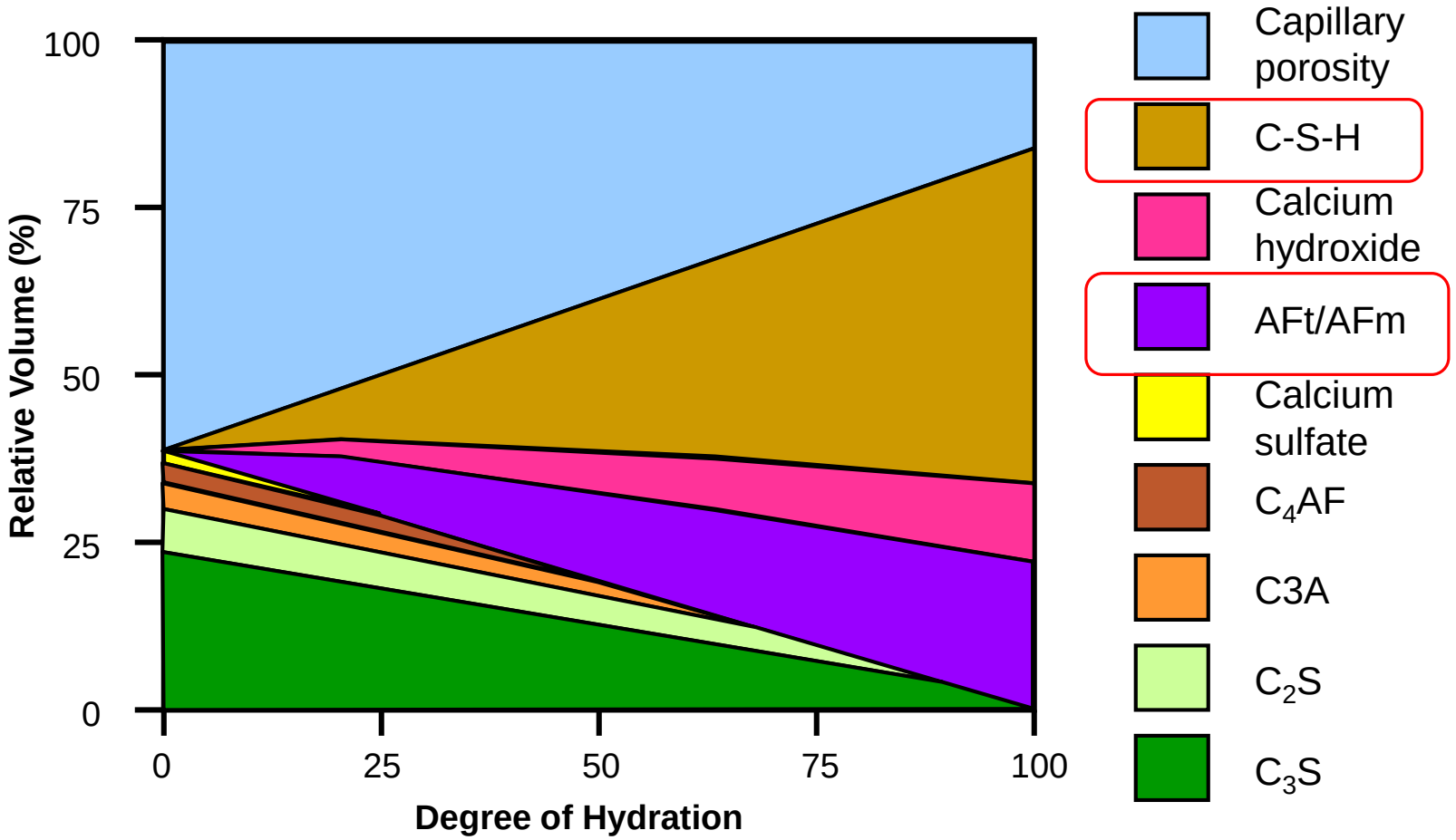
With added UV, NO_X concentration drops

- For unmodified samples, NO_X remains constant for the duration
- In all photocatalyst + UV cases, a similar drop occurs



Mix	OPC	w/c	TiO_2 (anatase)
OPC	1.0	0.4	0
OPC+5%TiO_2	0.95	0.4	0.05

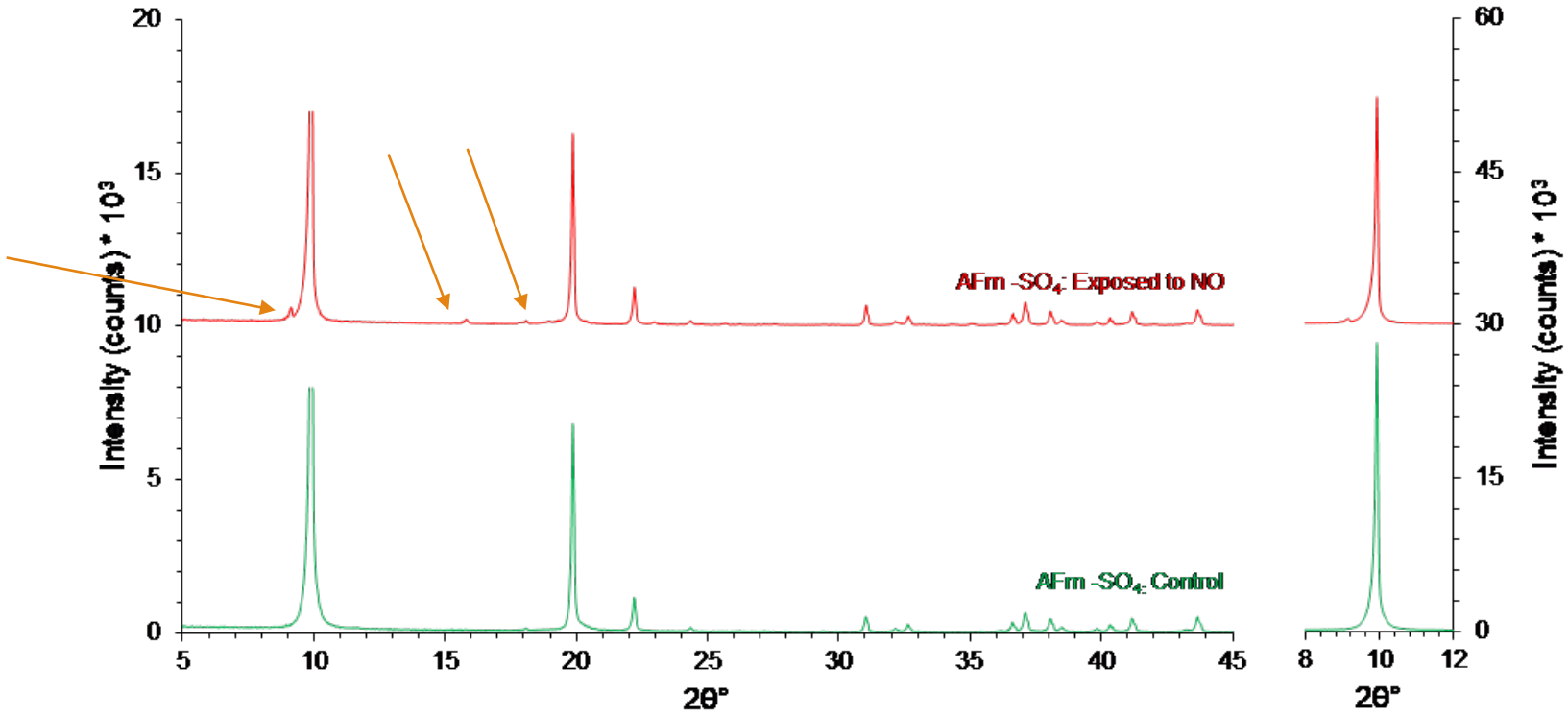
What is in the cement?



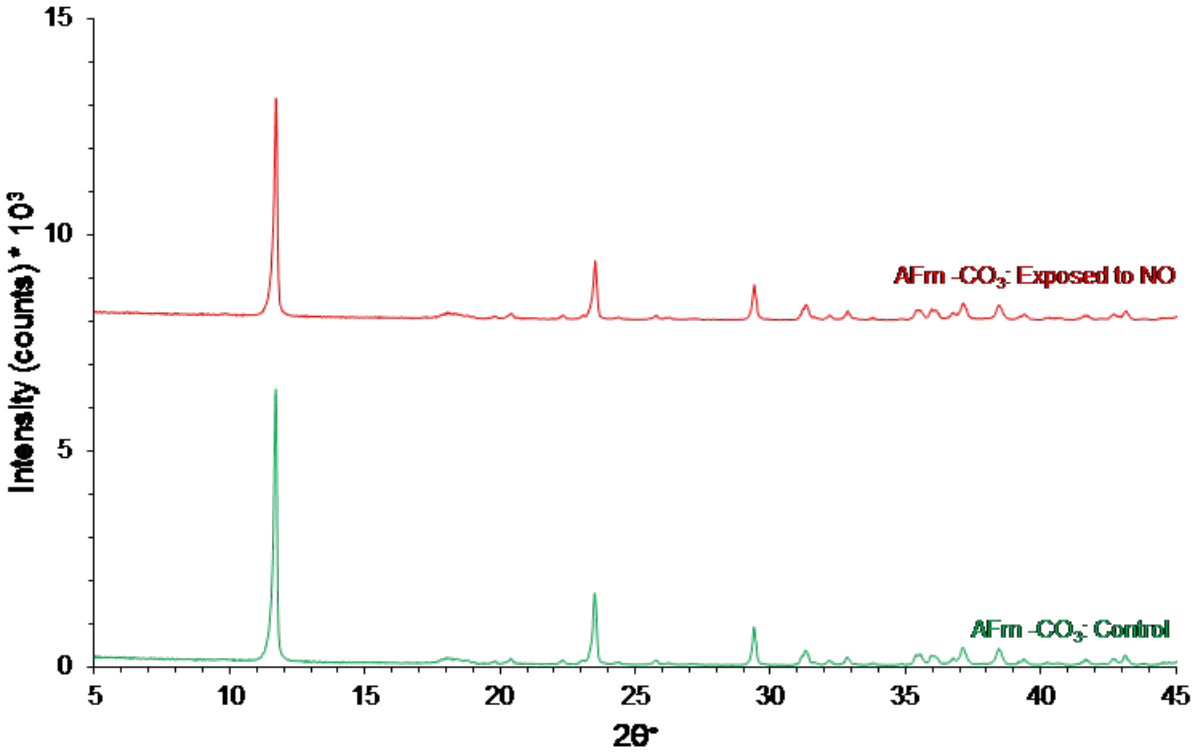
What is X-Ray Diffraction?

X-Ray Diffraction (XRD) is a characterization tool for determining qualitative information about crystalline substances

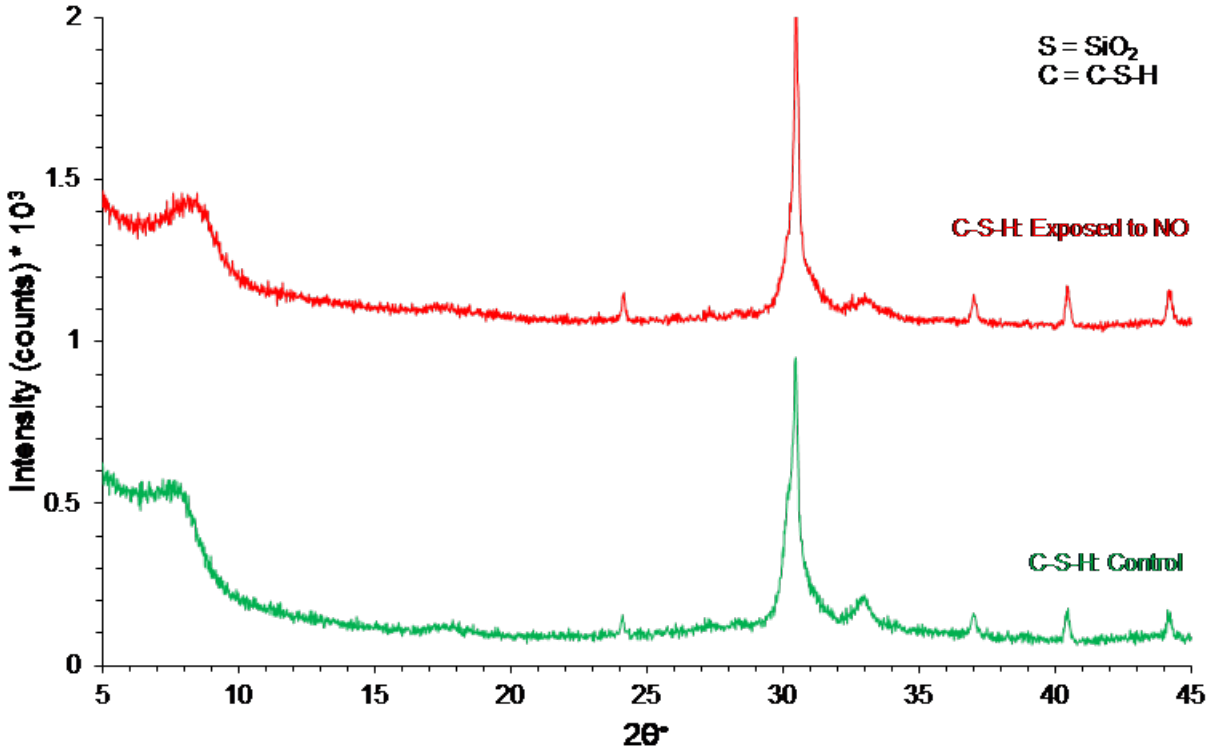
XRD of AFm-sulfate indicates the presence of nitrogen ion species



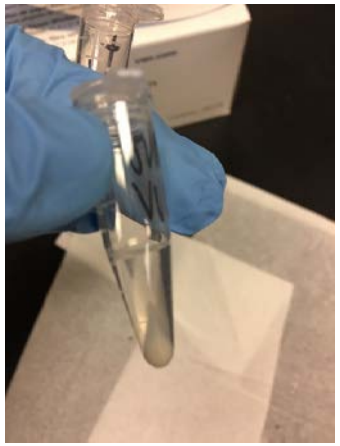
However, XRD of AFm-carbonate shows no sign of nitrogen ion species

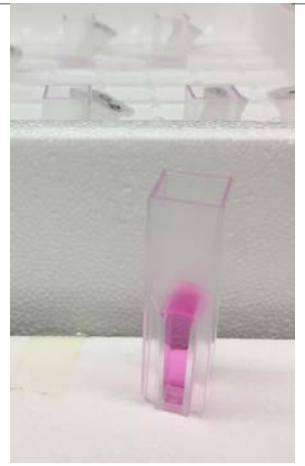


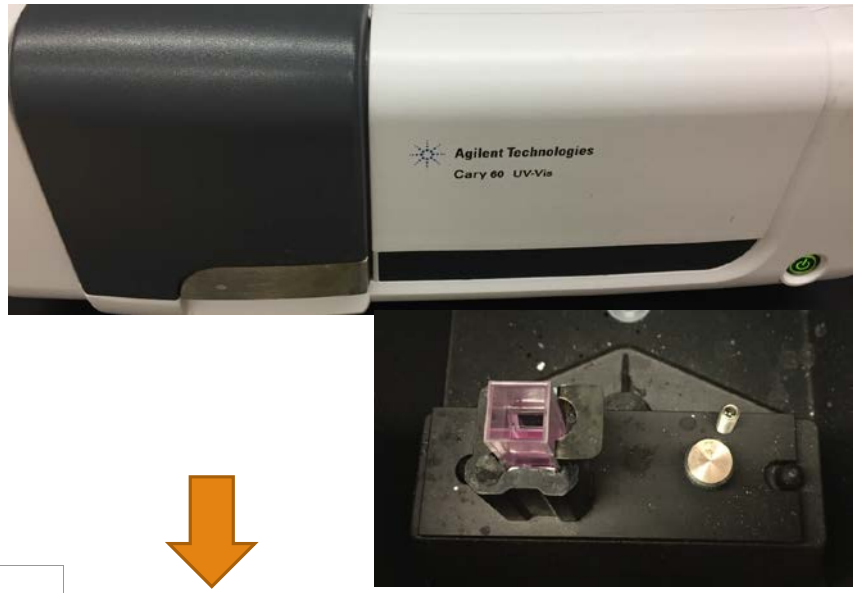
And neither does XRD of C-S-H



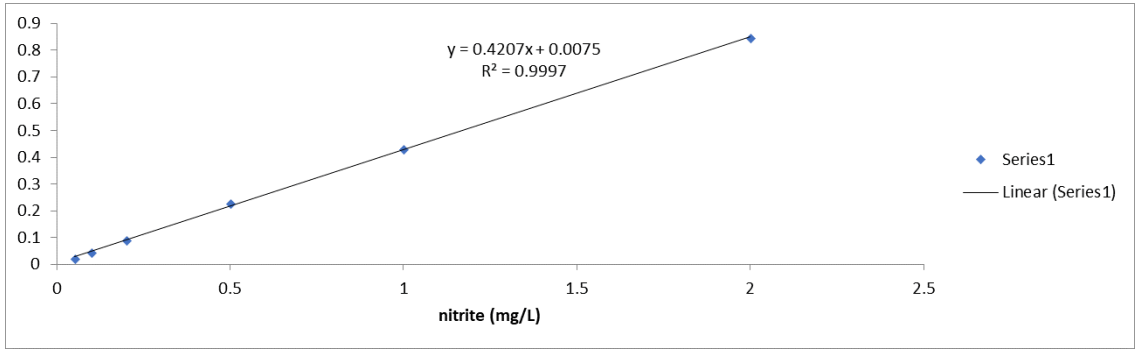
What is UV-visible spectrophotometry?



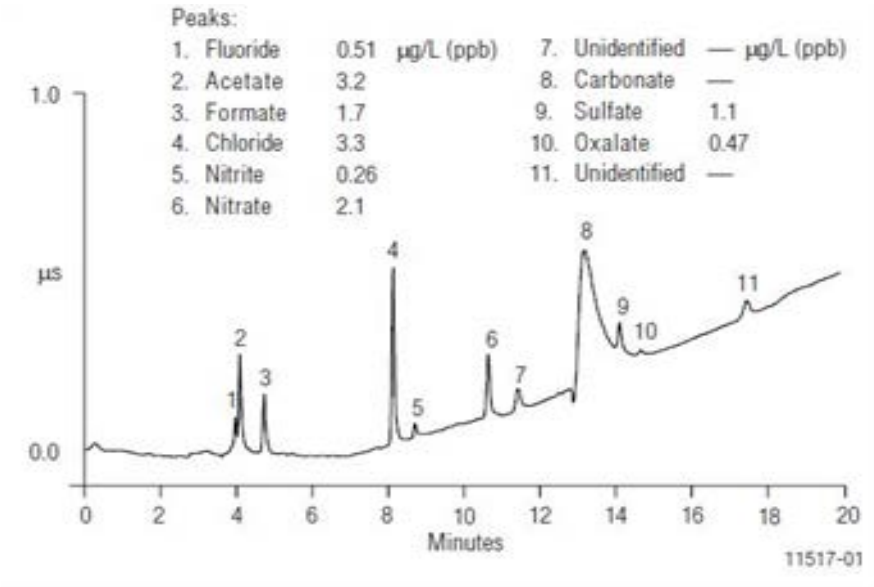


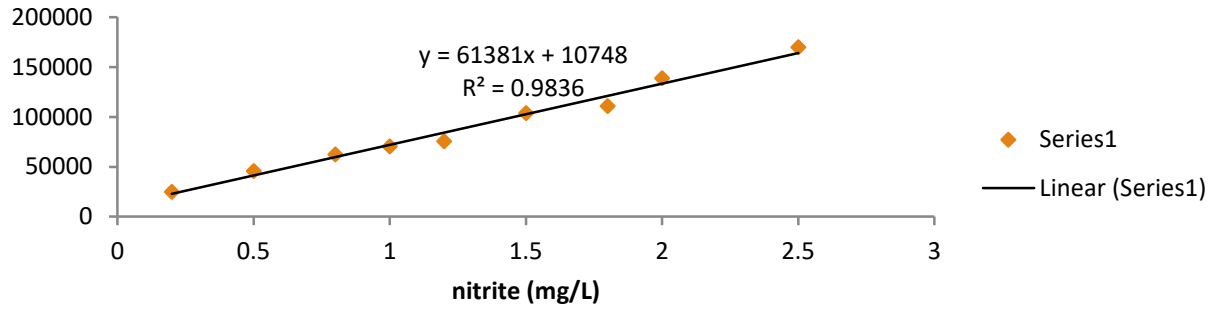


Results in terms of absorbance (Au) measured at 540 nm



What is ion chromatography?





Results in terms of peak area, measured under the portion of the curve representing nitrate

These methods quantify NO_X conversion!

Group ID	Materials	Exposure Condition		N mass (mg kg $^{-1}$ hr $^{-1}$)	
		UV	NO	$m_{N\ from\ NO_2^-}$	$m_{N\ from\ NO_3^-}$
1	AFm-SO_4	×	√	0.097 ± 0.0004	BDL
2	AFm-SO_4 + 20% TiO_2	√	√	2.319 ± 0.385	11.918 ± 3.452
3	AFm-CO_3	×	√	2.042 ± 0.179	BDL
4	AFm-CO_3 + 20% TiO_2	√	√	1.684 ± 0.352	9.017 ± 1.650
5	C-S-H	×	√	3.997 ± 0.141	1.638 ± 0.488
6	C-S-H + 20% TiO_2	√	√	3.352 ± 0.172	17.282 ± 2.203

Note: BDL (below detection limit)

Nitrite produced nearly 2400 times greater in modified than plain AFm-sulfate, massive increase in nitrate production as well

Roughly 18% decrease in nitrite produced in modified AFm-carbonate, still massive increase in nitrate production

Roughly 17% decrease in nitrite produced in modified C-S-H, nearly 1000 times greater amount of nitrate produced

Conclusions

- The presence of relatively high amounts of C-S-H in cements is likely responsible for much of cement's innate NO_X binding ability
- The presence of TiO_2 promotes a greatly increased nitrate formation
- AFm-sulfate has a minimal physical NO_X binding capacity, but may still have the ability to chemically bind NO_X via substitution
- AFm-carbonate has some capacity to bind NO_X despite carbonation, which ordinarily hinders NO_X binding
- UV-visible spectrophotometry and ion chromatography are the only tools we have found to date that are capable of consistent and accurate nitrate and nitrite detection and quantification,

Future Work

- Complete analysis of nitrogen dioxide-exposed materials
- Perform and analyze exposures of pure TiO_2 crystals to determine whether TiO_2 plays a role not just in the reaction but also in the binding of NO_X
- Perform and analyze exposures of both individual phases and OPC with different replacement percentages of TiO_2 to determine why TiO_2 so dramatically increases nitrate formation
- Determine whether chemical bonding occurs in the AFm phase (i.e. whether the sulfate is substituted for a nitrite or nitrate)

Questions?

Citations

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Additional Information

OPC Composition

Table 1. Composition (% by mass) and loss on ignition (LOI) of cement

C_3S	C_2S	C_3A	C_4AF	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	LOI
62.9	7.6	6.9	9.2	19.2	4.5	3	62.8	3.6	3.1	0.5	2.6

Photocatalyst Characteristics

Table 2. Characteristics of TiO_2 photocatalyst (provided by producer)

TiO_2 content	Form	Density	Bulk Density	SSA
>85%	anatase	3.9 g/cm^3	300 g/l	>225 m^2/g