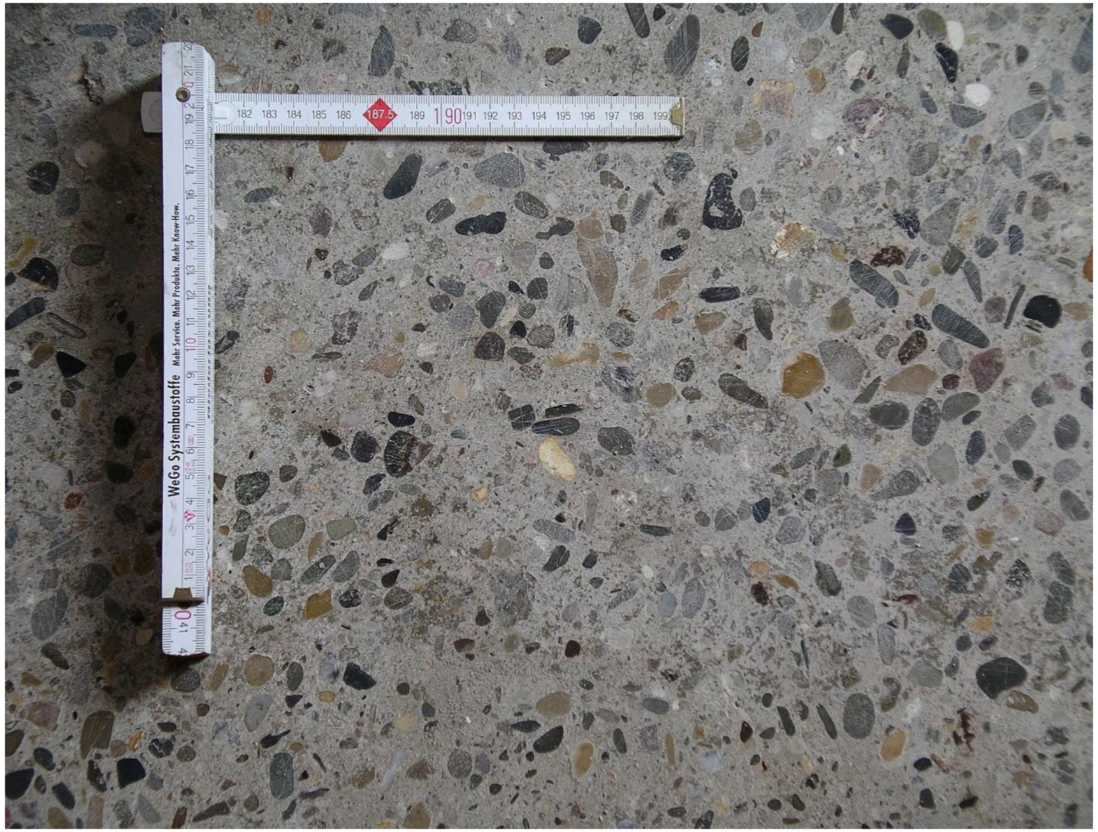
8. Infrastructural and Environmental Nanostructures

Repetition from the Last Lecture

- Diamond and graphite – which of these materials is a conductor?
- What is the name of the carbon-bonding orbital in the graphene plane and what is the name of the orbital perpendicular to the graphene plane.
- What are spherical carbon molecules called?
- What is the name of the vector that determines the type of electrical conductivity of nanotubes?
- Name at least 3 applications of graphene.

The Most Commonly Used Material in Infrastructure – Concrete

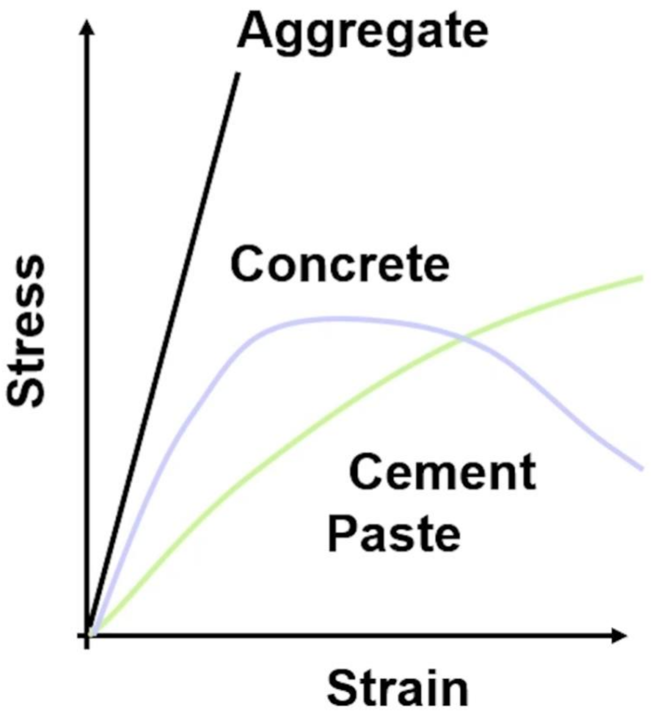
- Concrete – a composite material consisting of aggregate, binder, water and various additives and admixtures
- When cured, it forms a solid artificial conglomerate/composite.
- The most common is cement concrete – the binder is cement and the filler is aggregate, all bonded together using water.
- Another option is asphalt concrete used for road construction.
- The first use of cement concrete is in ancient Rome – the binder is pucolán – volcanic cement.

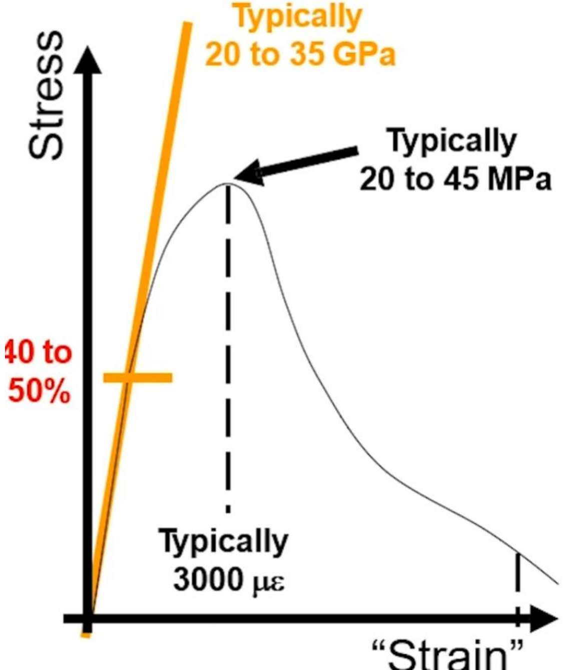


https://cs.wikipedia.org/wiki/Beton

Concrete Strength

- Concrete is a very strong material in compression
- Composite – very brittle and non-deformable filler (stone, sand) and easily deformable binder (cement paste – cement, water, air)
- The result is a composite that is also very brittle – linear and very rapidly increasing stress/strain curve





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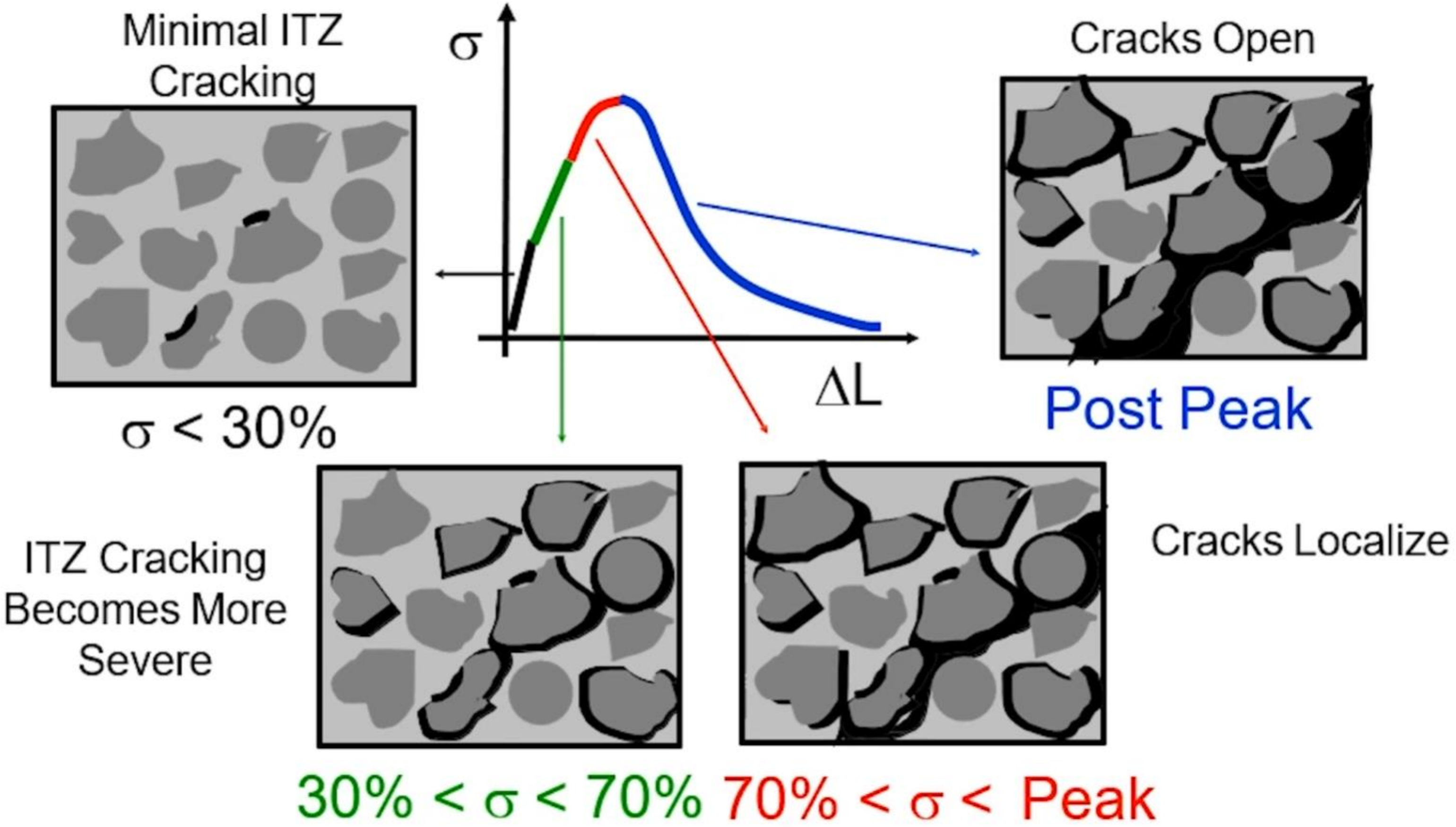
Load - Tension



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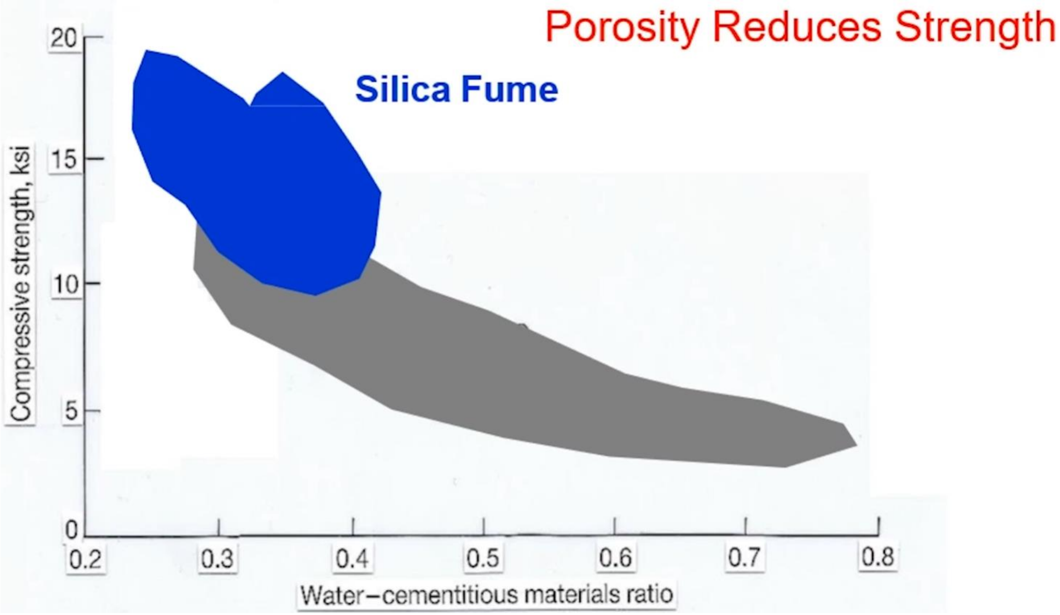
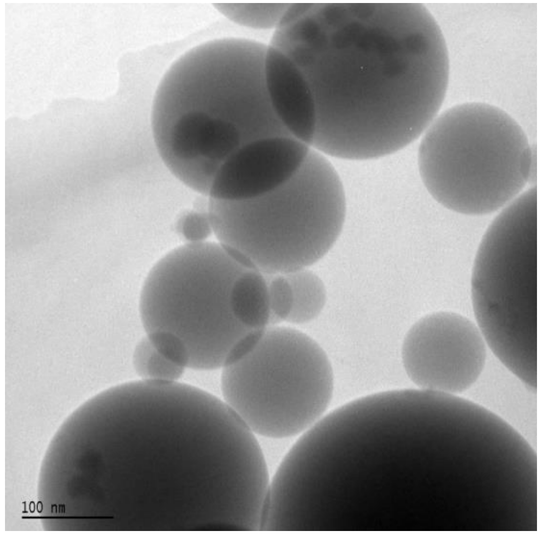
Porosity

- Porosity makes crack propagation easier; we want to get rid of it
- An important characteristic of concrete is the ratio of water to cement, typically 0.35
- At a given water ratio, we can significantly increase the strength of concrete by adding silica fume (microsilica) to reduce porosity, thicken the concrete + SiO_2 + CaOH reaction which leads to further cement paste formation





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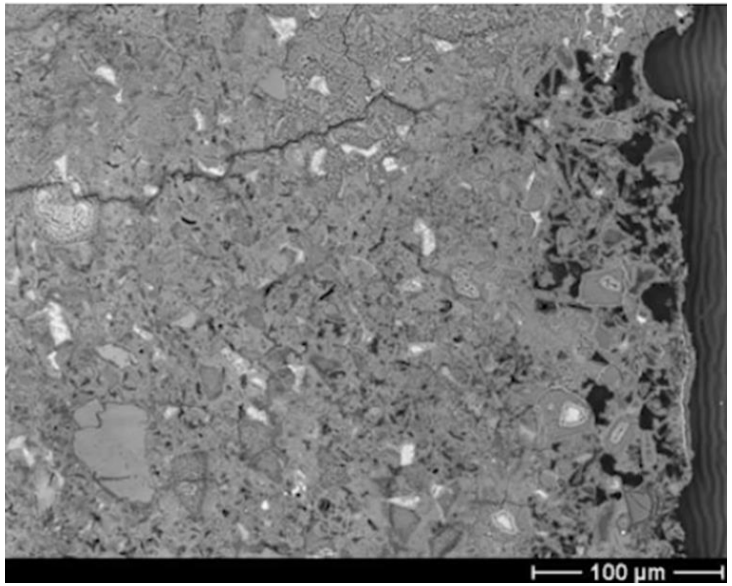
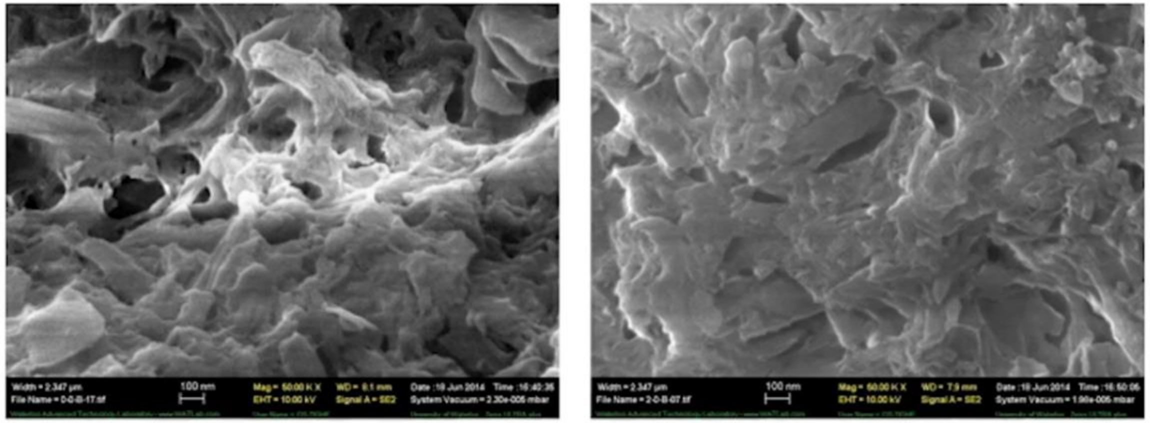
https://en.wikipedia.org/wiki/Silica_fume

Aggregate and Binder Interfaces

- The interface between aggregate and binder is the weakest link in concrete
- It is highly porous and permeable
- Contains CaOH, which can be a by-product of the hydration reaction
- Nanoscale silica fume both fills the pores and prevents the formation of CaOH (Pozzolanic reaction)





(a) Control

(b) 2% nano silica

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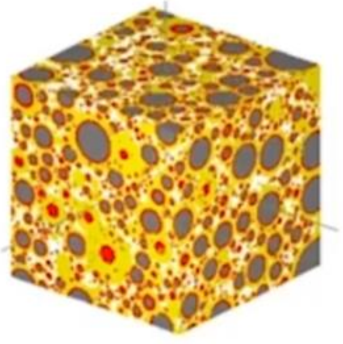
Additional Nano-Additives to Improve the Interface

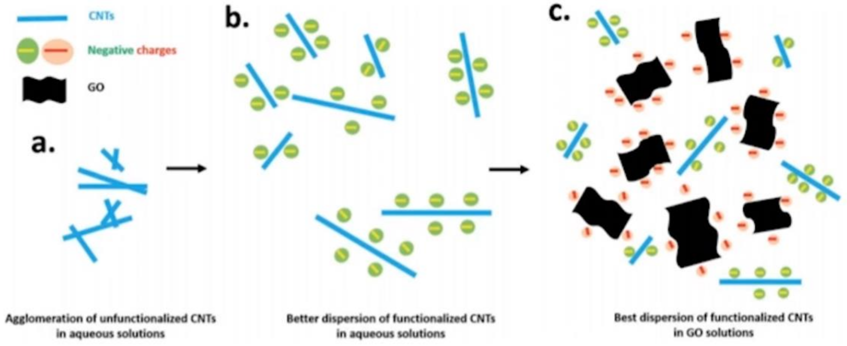
- Nano TiO2
  - Serves as a nucleating core for cement hydration products
  - Improves volumetric hydration and hardens the bonding matrix, ideal concentration 1%

(i) Reference-90 days



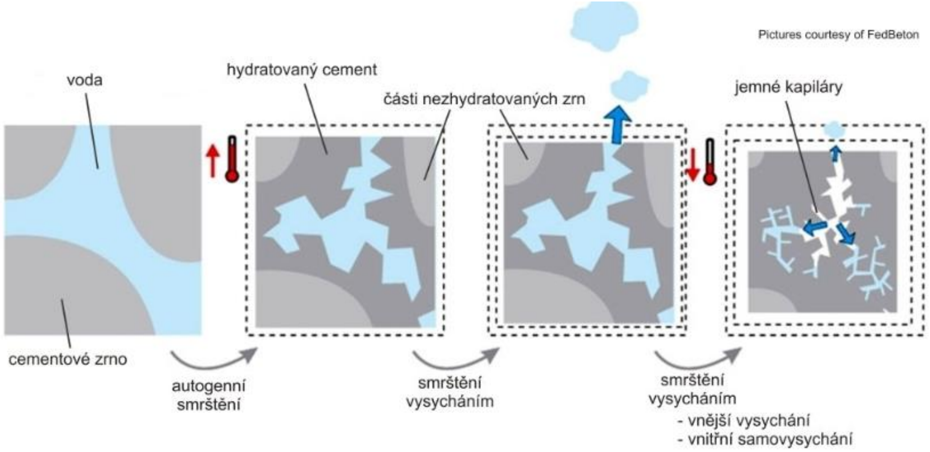
(j) 1% TiO_2-90 days

- Carbon nanotubes and graphene oxide
  - Matrix reinforcement and improved material bending properties
  - Uniform dispersion is key, which is complicated



Effect of Nanomaterials in Concrete Drying

- As the cement cures and dries, its volume decreases – cracks form
  - Chemical shrinkage – reduction of chemical reaction products of cement, water and aggregates
  - Autogenous shrinkage (self-decomposition) – evaporation of water during hardening
  - Drying shrinkage – drying after the concrete has finished hydrating
  - Shrinkage by reaction with carbon (CO_2) from the external atmosphere



Pictures courtesy of FedBeton

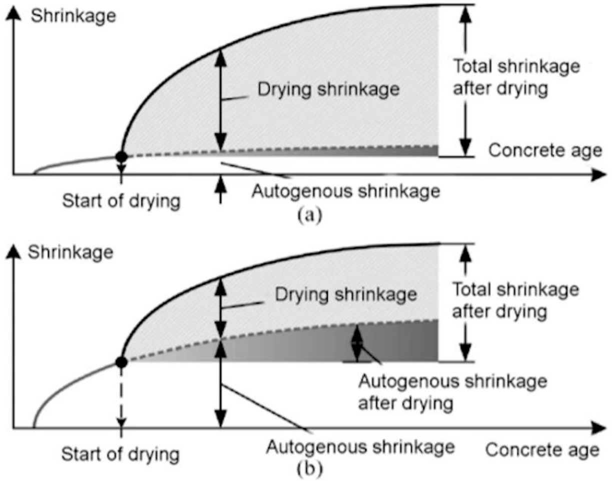


Fig. 1. Shrinkage strain components in normal (a) and high-strength (b) concrete (Sakata & Shimomura 2004)

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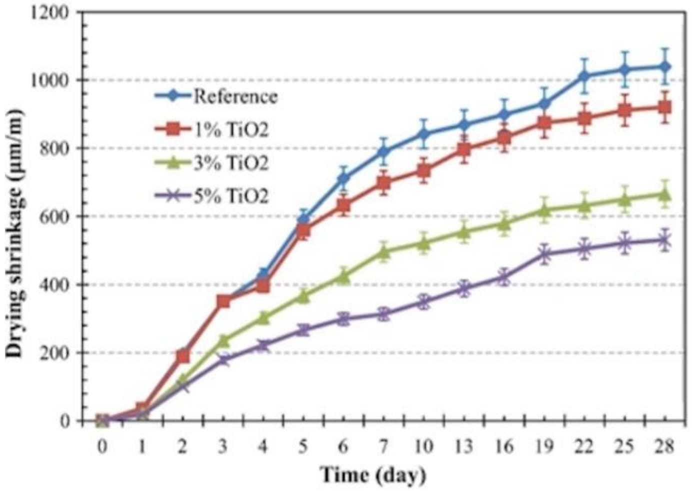
https://www.ebeton.cz/pojmy/smrstovani-betonu/

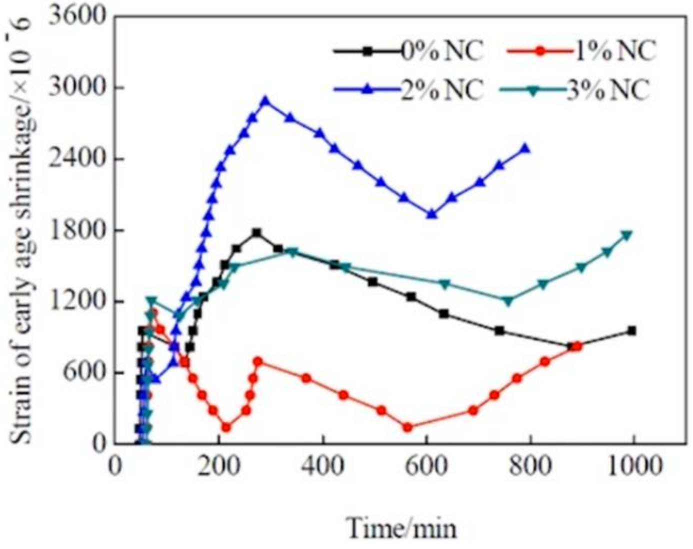
Adding Nanomaterials Can Significantly Prevent Shrinkage

n-TiO_2



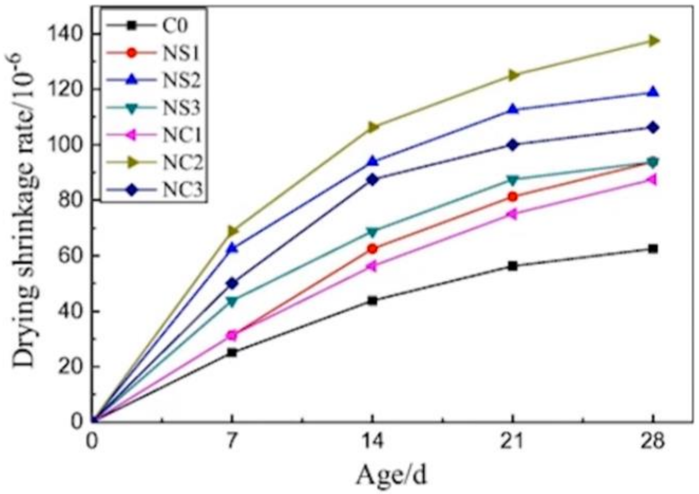
P. Duan et al, Effects of adding nano-TiO2 on compressive strength, drying shrinkage, carbonation and microstructure of fluidized bed fly ash based geopolymer paste, Construction and Building Materials,106,(2016)

n-$CaCO_3$



X. Liu et al, Effect of Nano-CaCO3 on Properties of Cement Paste,Energy Procedia, 16 (Part B), (2012)

n-SiO_2 and n-SiC



Y. Gao et al, Effects of nano-particles on improvement in wear resistance and drying shrinkage of road fly ash concrete,Construction and Building Materials,151 (2017)

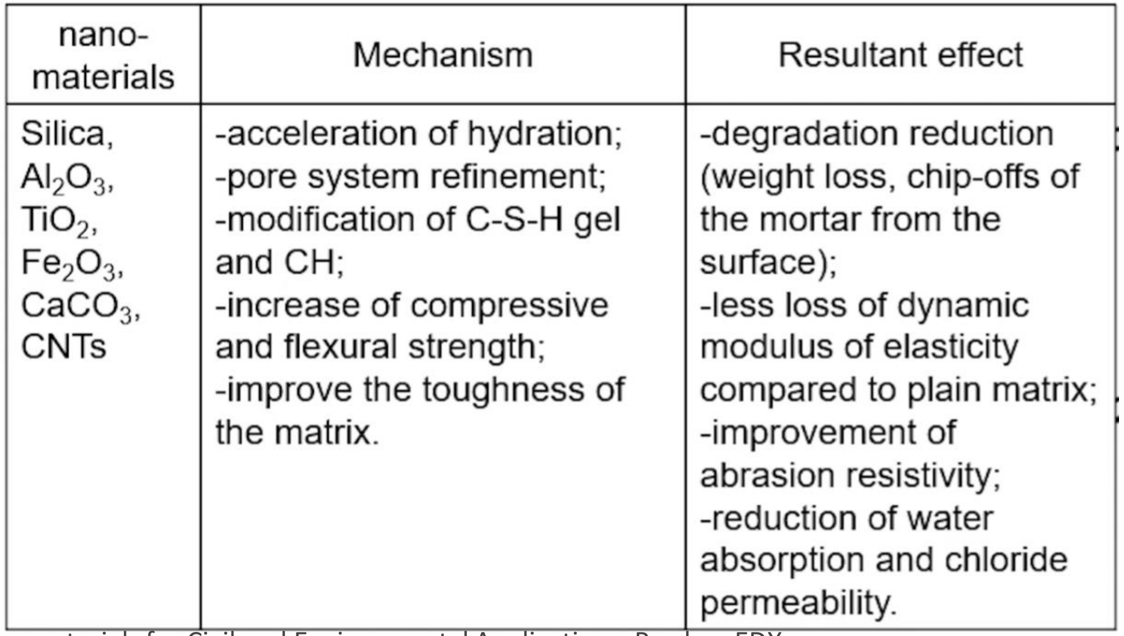
Long-Term Durability of Concrete – Problems

- Corrosion of steel rods in reinforced concrete
- Corrosion due to depassivation of the natural passivation oxide layer on the steel due to lower pH of salt, acidic rainwater, etc. (pH of concrete 12-14)
- Red rust has approximately 3 times the volume of iron – expansion and significant cracking of reinforced concrete
- Cracks are then further enlarged by freeze-thaw cycles
- Other problems – flaking, aggregate strength, alkaline reactions of aggregates, sulfate corrosion

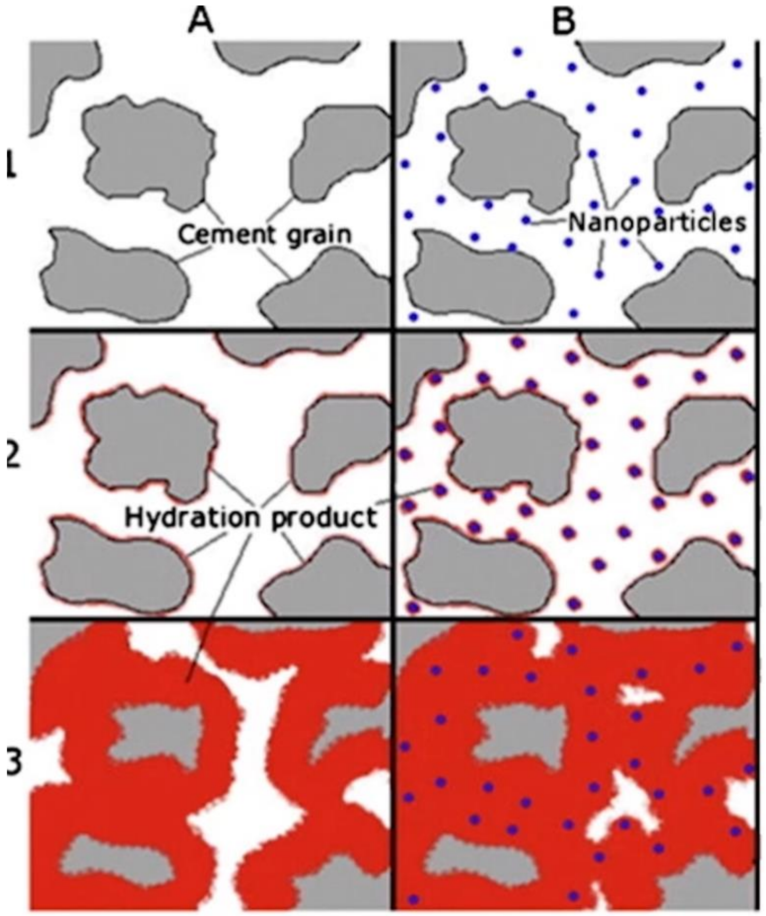
http://www.sanacninoviny.cz/wp-content/themes/generous/noviny/2014_27.pdf

Long-Term Durability of Concrete – Problem Solving

- Reinforcement corrosion
  - Anti-corrosion coatings for steel reinforcement
  - Cement matrix thickening with nanoparticles



nano-materials	Mechanism	Resultant effect
Silica, Al_2O_3, TiO_2, Fe_2O_3, $CaCO_3$, CNTs	-acceleration of hydration; -pore system refinement; -modification of C-S-H gel and CH; -increase of compressive and flexural strength; -improve the toughness of the matrix.	-degradation reduction (weight loss, chip-offs of the mortar from the surface); -less loss of dynamic modulus of elasticity compared to plain matrix; -improvement of abrasion resistivity; -reduction of water absorption and chloride permeability.



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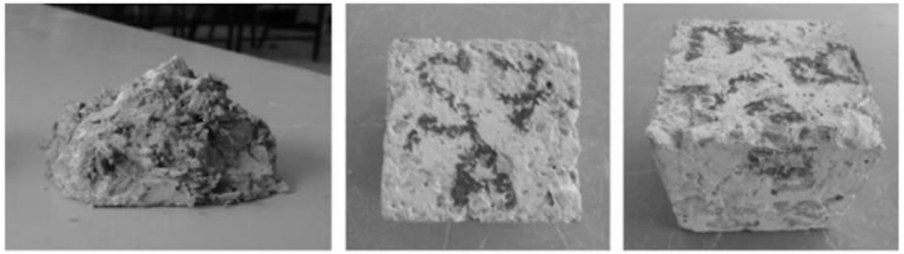
Long-Term Durability of Concrete – Problem Solving 2

- Freezing/melting
  - n-SiO2, n-Al2O3 – nucleation sites, Pozzolanic reaction

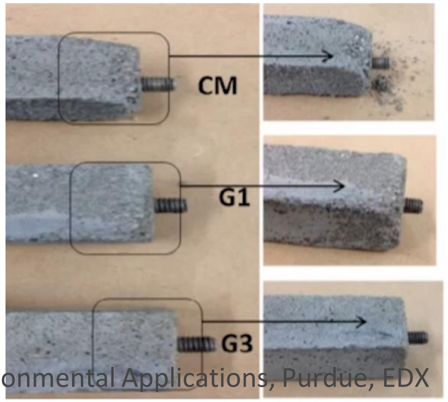


Control

5% Nano-silica

3% Nano-alumina

  - Graphene oxide



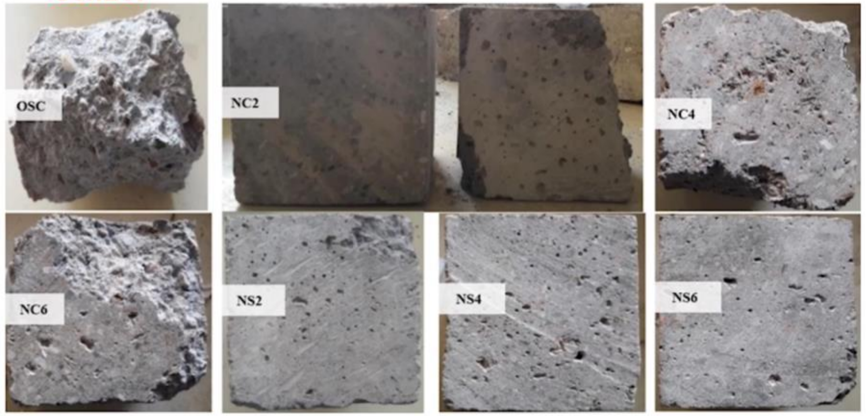
Control

0.01% Graphene oxide

0.06% Graphene oxide

- Nanoclay (cheap and available)

Control



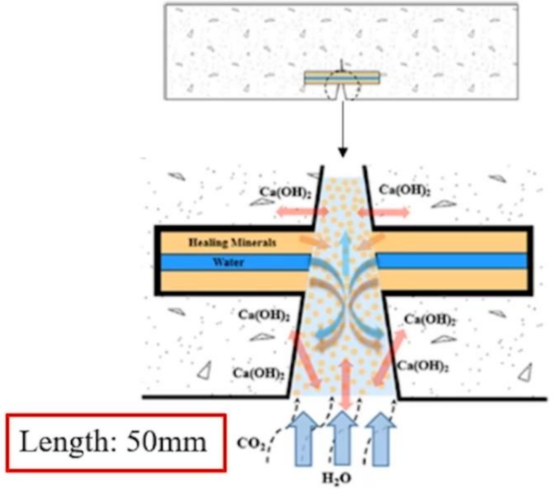
- Scaling
  - n-SiO2, fly ash

Control

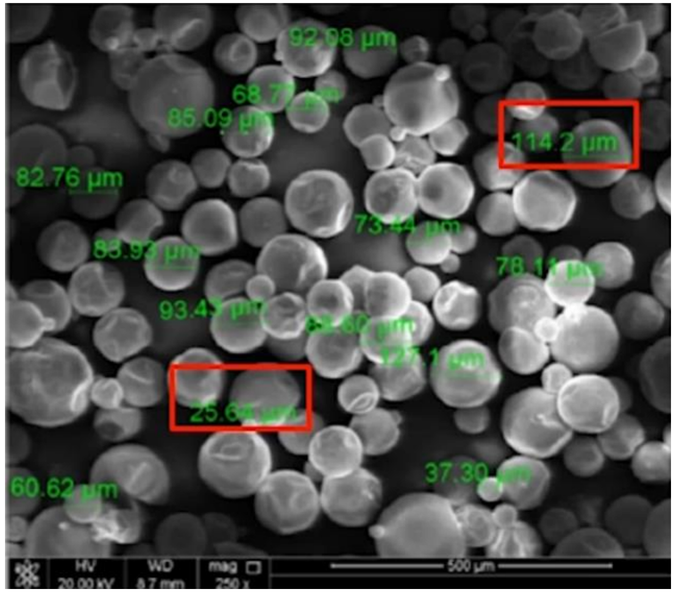
With nano-silica

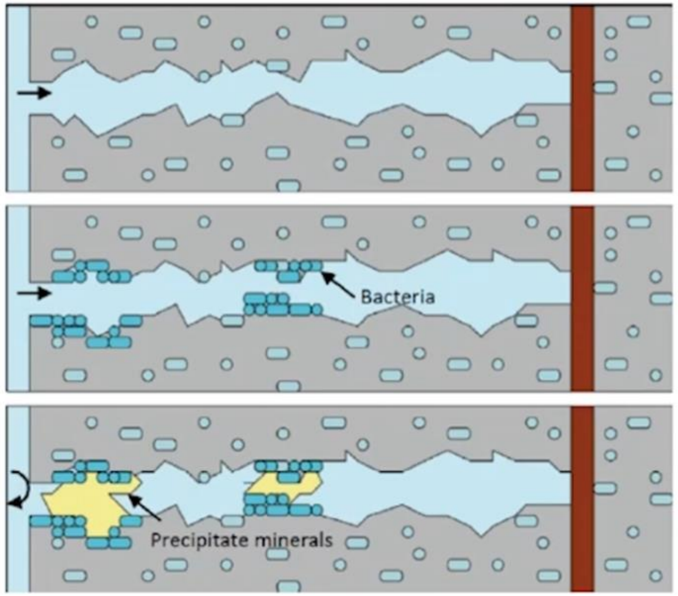
Self-Healing Concrete

- Autonomous repairs
  - External force leads to the release of encapsulated material that repairs the crack
  - One-time use and costly



Concentric glass capsules





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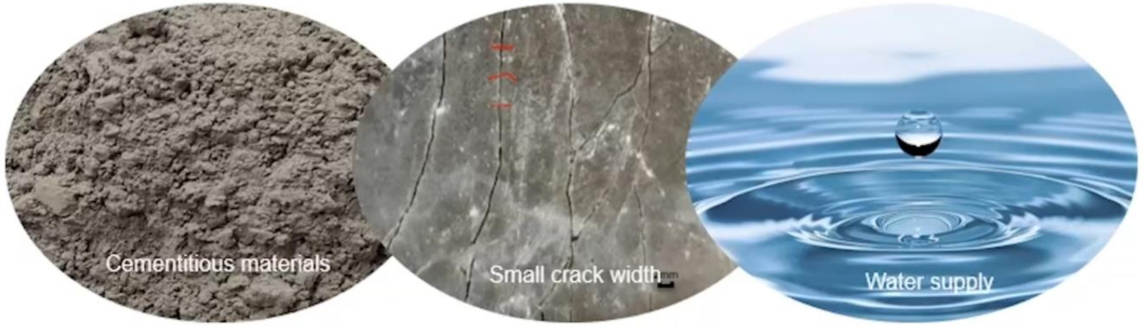
Self-Healing Concrete 2

- Autogenous repairs
  - Concrete repairs itself, no foreign material is added
  - The repair cycle can be repeated

  - (1) Additional hydration of unhydrated cement
  - (2) Formation of calcite CaCO3
  - (3) Recrystallization of portlandite from cement paste (dissolution of $Ca(OH)_2$ and recrystallization)

- For a good function you need
  - Unhydrated cement
  - Water
  - Relatively small crack (< 150 μm) – cracks are reduced by the presence of (nano)fibres



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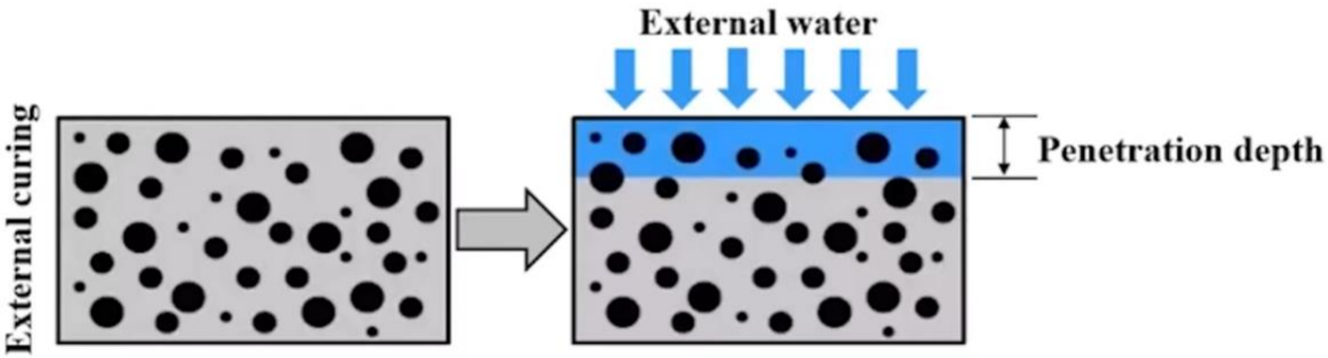
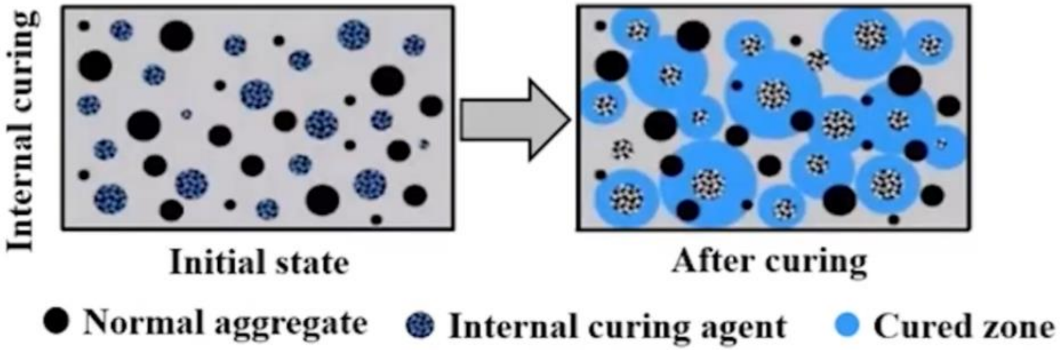
External and Internal Healing

- External healing
  - The source of water is only on the outside of the material, only the surface layer is healed and cracks can spread inside, for example when the concrete dries

- Internal healing
  - The source of water are the particles inside the material that have bound water to themselves. There is high internal moisture in the concrete.





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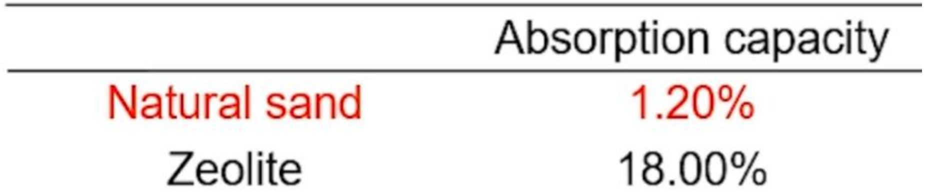
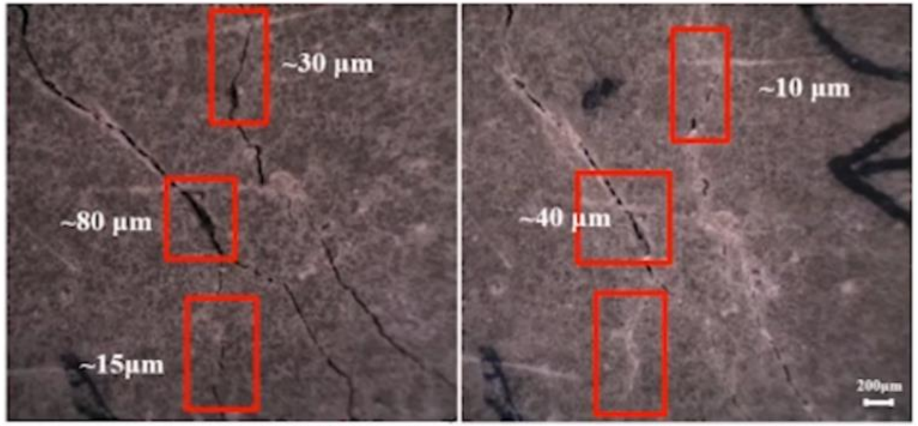
Zeolite – Moisture Carrying Particles

- Zeolites are used as water carriers
- They have many small nanometre-size pores and therefore a large surface area – high water binding capacity



	Absorption capacity
Natural sand	1.20%
Zeolite	18.00%



Microcracks in SHCC before and after self-healing

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Environmental Nanotechnology

- Environmental nanotechnologies are those applied to prevent or reduce damage to an already damaged environment
- Damage
    - Air
    - Water
    - Soil

https://www.eadarsha.com/eng/environment-damage-behind-1-in-4-global-deaths-disease-un/

Water Protection Technology

- Wastewater is generated
  - From agriculture
  - Residential
  - Industry
- They can have a very negative impact on human health, as well as the health of animals and plants in the environment

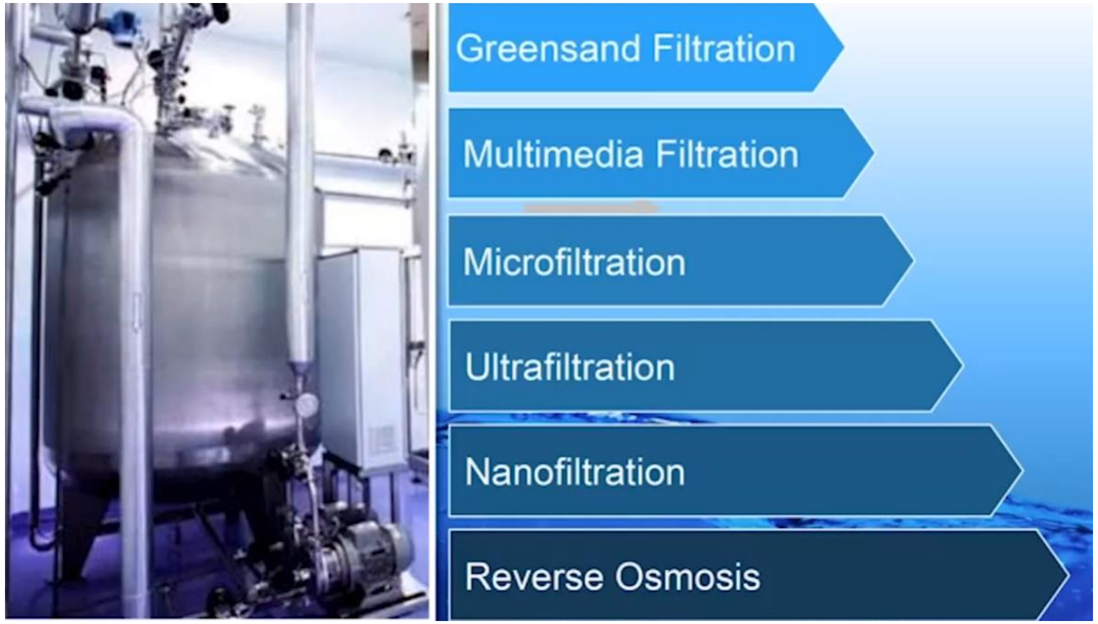
Worldwide, the majority of wastewater is neither collected nor treated. Wastewater is a valuable resource, but it is often seen as a burden to be disposed of. This perception needs to change.

80% of global wastewater is released to the environment without adequate treatment

https://blogs.worldbank.org/water/wastewater-treatment-critical-component-circular-economy

Water Purification Options

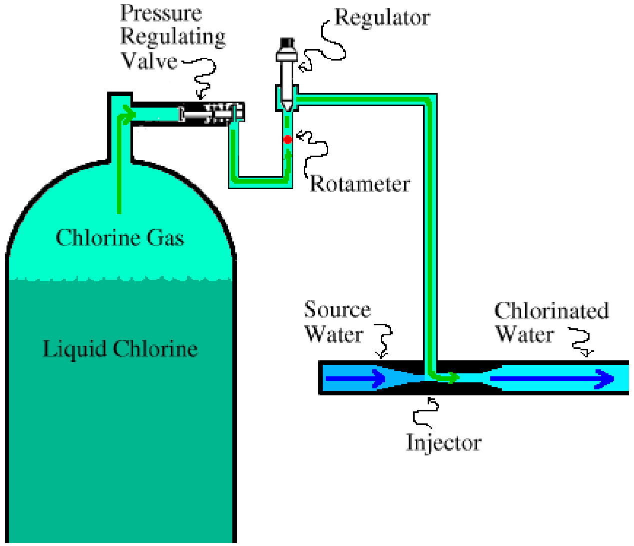
- Physical
  - Do not use any chemicals



- Greensand Filtration
- Multimedia Filtration
- Microfiltration
- Ultrafiltration
- Nanofiltration
- Reverse Osmosis

- Chemical

Chemicals are added to the water, e.g. for coagulation, neutralisation, absorption and disinfection (chlorine, O_3)



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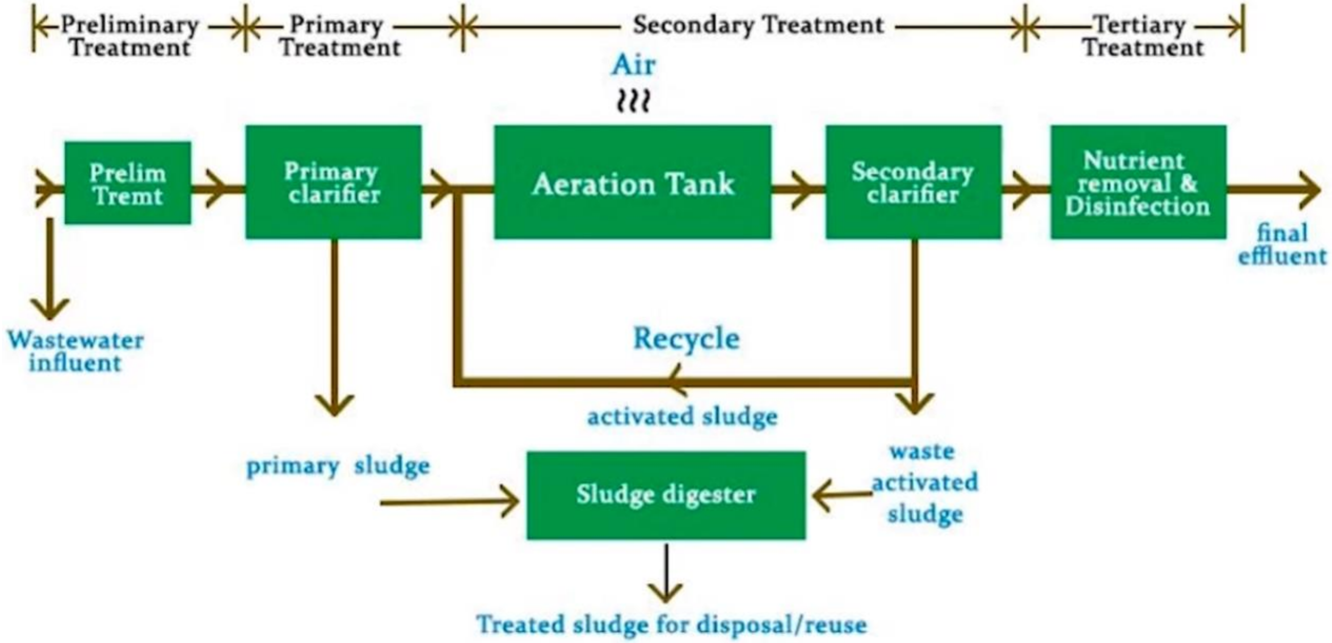
https://www.thewatertreatments.com/disinfection/chlorinators/

Water Purification Options 2

- Biological
  - Based on bacteria and other microorganisms that break down organic contaminants through standard cellular processes
  - Options: Aerobic (normal decomposition), anaerobic (fermentation), anoxic (composting)



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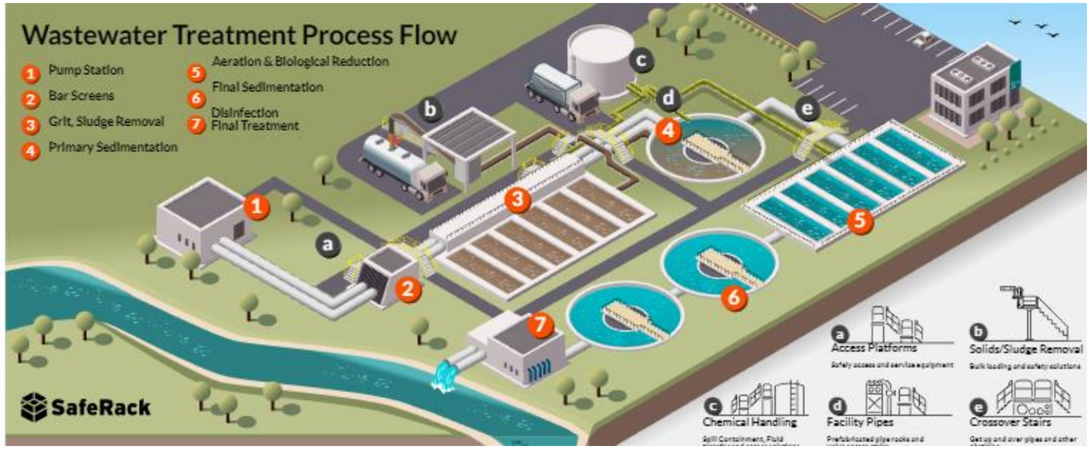
Standard Wastewater Treatment Plant

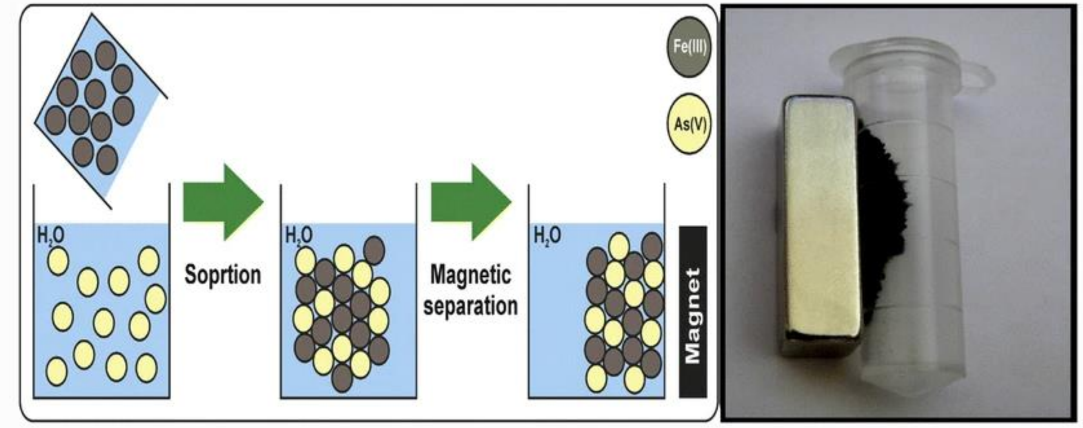
- Stirring and clarification of water (coagulation) in tanks
- Sedimentation – settling of sludge flakes at the bottom of the tank
- Filtration through layers of sand or charcoal
- (Aeration and biological processes)
- Sterilization and disinfection – chlorine, ozone, UV radiation



https://www.saferack.com/wastewater-treatment-plant/wastewater-treatment-process-illustrationv2/

Nanotechnology in Water Purification

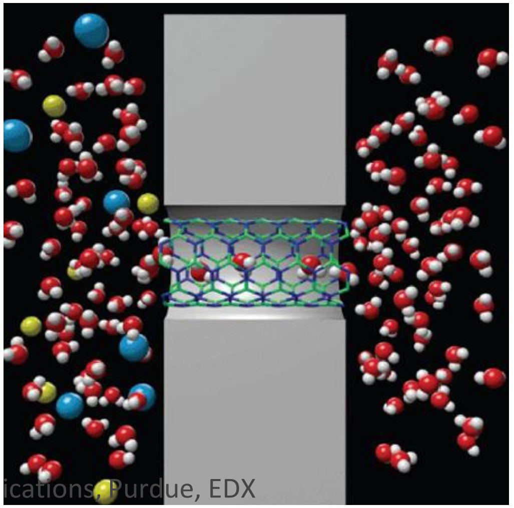
- Adsorbents
  - High reactivity and chemical specificity
  - Functionalized carbon nanotubes (MnO_2, Fe_3O_4, Al, Ag,…) for binding organic pollutants and heavy metals (Cd, Ni, Zn, Pb, ...)
  - Magnetic nanoparticles for the binding of heavy metals

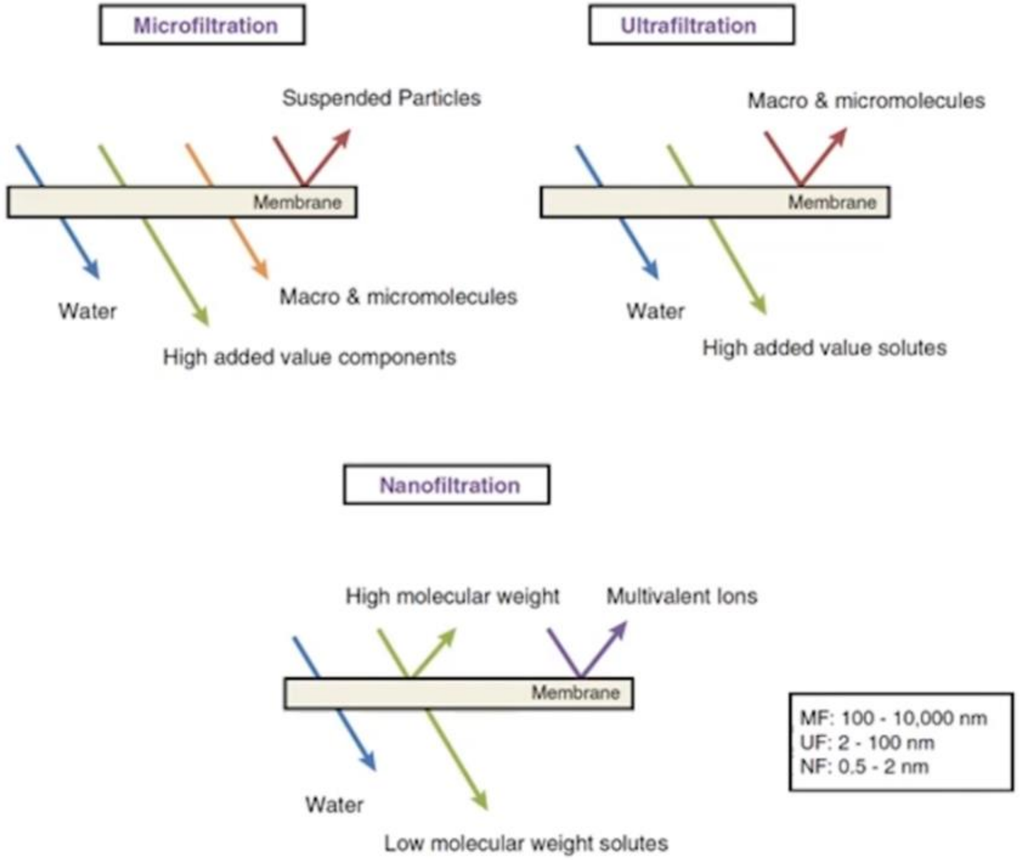


https://link.springer.com/article/10.1007/s11356-016-6457-z

Nanotechnology in Water Purification 2

- Membranes for filtration
    - - nanofibre, nanocomposite, ...
- Ideal of carbon nanotubes
    - Water flows through the hydrophobic interior of the CNT without friction (nanofluidic transport)





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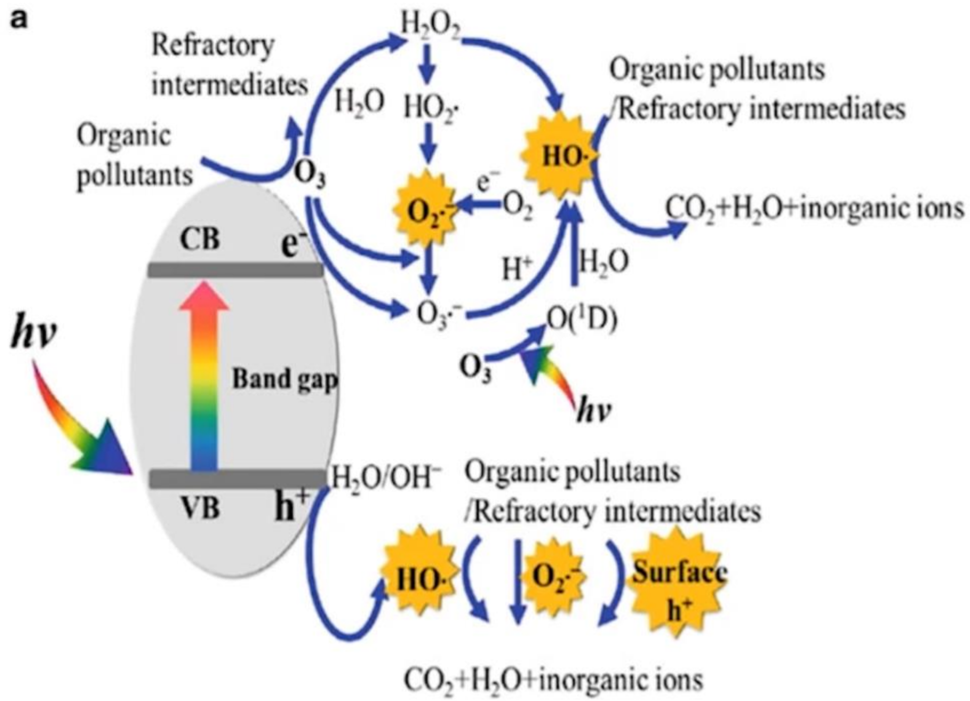
https://www.sciencedirect.com/science/article/abs/pii/S1226086X1200144X

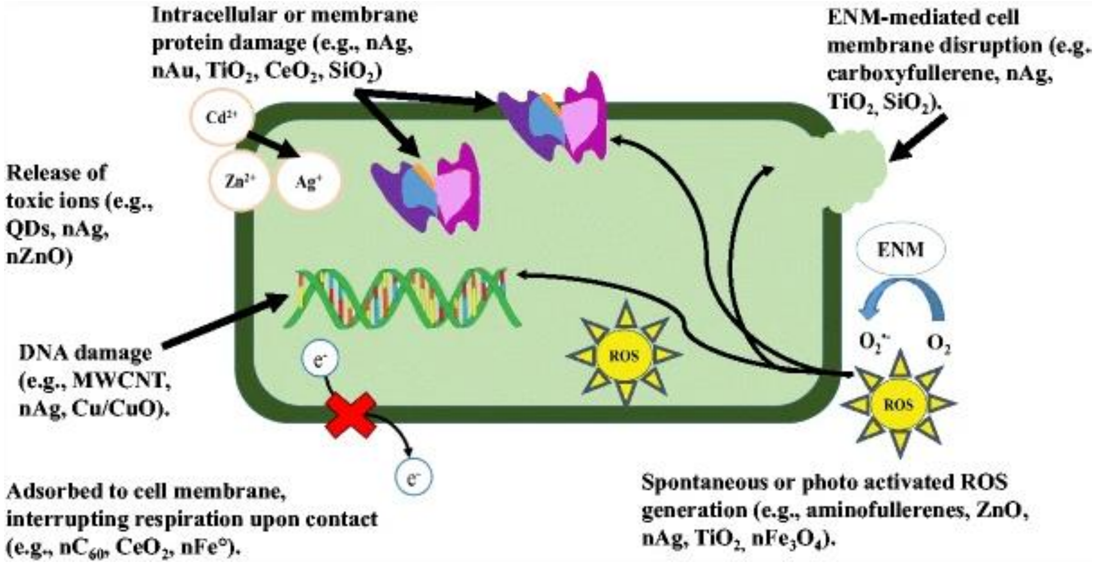
Water Photocatalysis

- Radicals generated by photocatalyte illumination decompose typically organic impurities
- TiO_2, ZnO_x



Disinfection and Pathogen Control

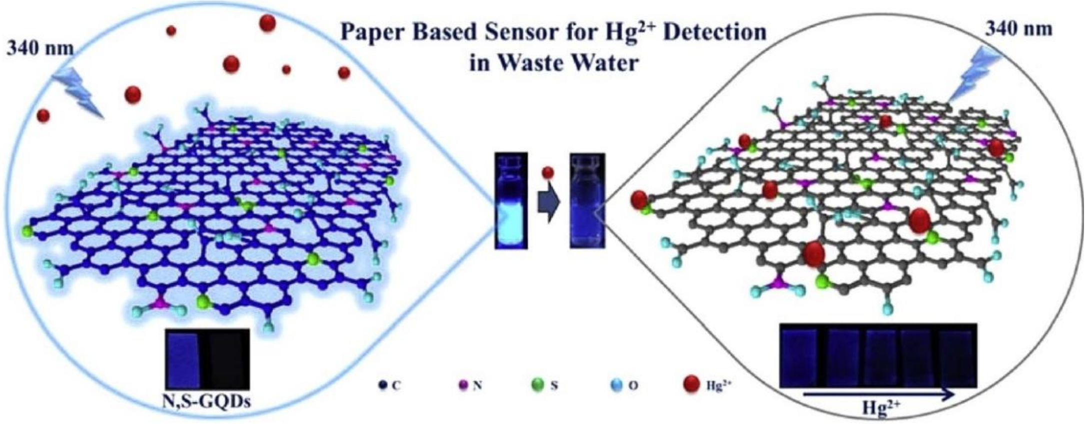
- For inactivation of various types of microbial pathogens – viruses, bacteria, protozoa, other microorganisms
- Current disinfectants such as chlorine, ozone, chlorine dioxide and others work, but have a short reactivity time and produce toxic waste products (about 600 of these are known so far and most are carcinogenic)
- Therefore, the use of nanoparticles and nanomaterials is being explored



https://link.springer.com/article/10.1007/s11356-016-6457-z

Pollution Detection

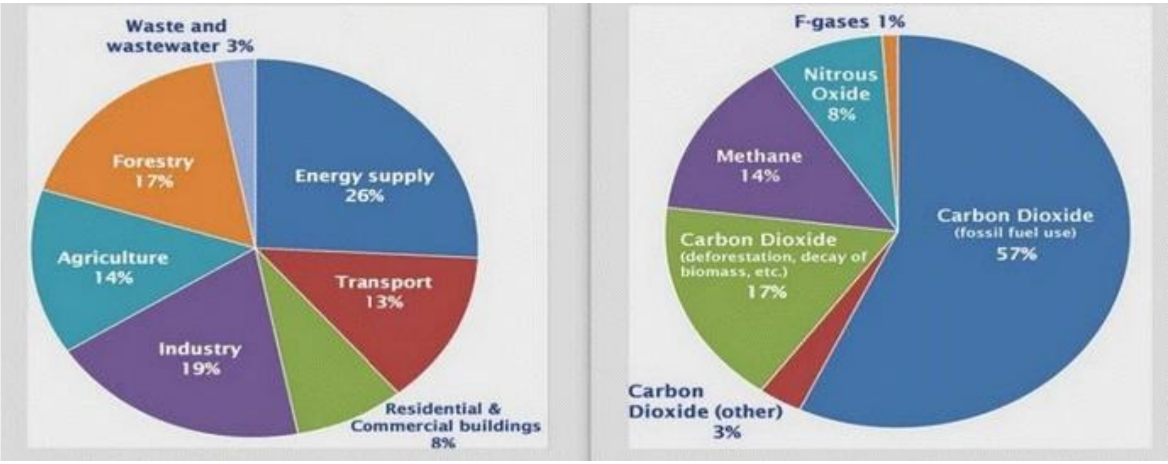
- Pollution detection using nanostructures – high surface area – high reactivity; functionalization – chemical selectivity
- Quantum dots, CNTs, gold nanoparticles,...



https://www.sciencedirect.com/science/article/abs/pii/S0925400517313916

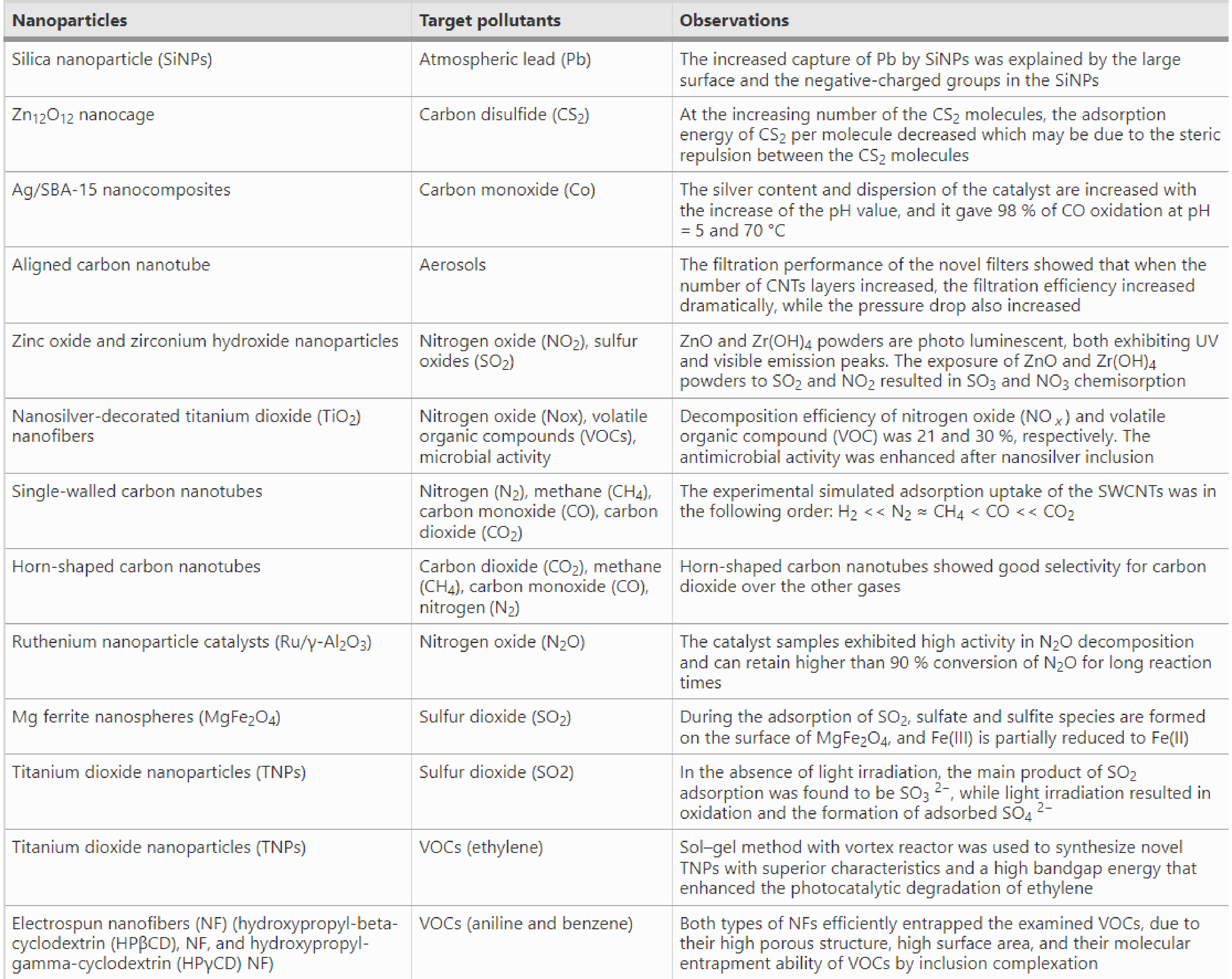
Air Pollution

- Air pollution means the spread of pollutants that are harmful to human health and the planet as a whole.



- The top ten most important pollutants:
  - SO_2
  - CO
  - CO_2
  - NO_x
  - Volatile organic compounds
  - Particulates
  - O_3
  - Chlorinated fluorocarbons
  - Unburned hydrocarbons
  - Lead and heavy metals

https://link.springer.com/article/10.1007/s11356-016-6457-z



Nanoparticles	Target pollutants	Observations
Silica nanoparticle (SiNPs)	Atmospheric lead (Pb)	The increased capture of Pb by SiNPs was explained by the large surface and the negative-charged groups in the SiNPs
$Zn_{12}O_{12}$ nanocage	Carbon disulfide (CS_2)	At the increasing number of the CS_2 molecules, the adsorption energy of CS_2 per molecule decreased which may be due to the steric repulsion between the CS_2 molecules
Ag/SBA-15 nanocomposites	Carbon monoxide (Co)	The silver content and dispersion of the catalyst are increased with the increase of the pH value, and it gave 98 % of CO oxidation at pH = 5 and 70 °C
Aligned carbon nanotube	Aerosols	The filtration performance of the novel filters showed that when the number of CNTs layers increased, the filtration efficiency increased dramatically, while the pressure drop also increased
Zinc oxide and zirconium hydroxide nanoparticles	Nitrogen oxide (NO_2), sulfur oxides (SO_2)	ZnO and $Zr(OH)_4$ powders are photo luminescent, both exhibiting UV and visible emission peaks. The exposure of ZnO and $Zr(OH)_4$ powders to SO_2 and NO_2 resulted in SO_3 and NO_3 chemisorption
Nanosilver-decorated titanium dioxide (TiO_2) nanofibers	Nitrogen oxide (Nox), volatile organic compounds (VOCs), microbial activity	Decomposition efficiency of nitrogen oxide (NO_x) and volatile organic compound (VOC) was 21 and 30 %, respectively. The antimicrobial activity was enhanced after nanosilver inclusion
Single-walled carbon nanotubes	Nitrogen (N_2), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2)	The experimental simulated adsorption uptake of the SWCNTs was in the following order: $H_2 << N_2 \approx CH_4 < CO << CO_2$
Horn-shaped carbon nanotubes	Carbon dioxide (CO_2), methane (CH_4), carbon monoxide (CO), nitrogen (N_2)	Horn-shaped carbon nanotubes showed good selectivity for carbon dioxide over the other gases
Ruthenium nanoparticle catalysts ($Ru/\gamma\text{-}Al_2O_3$)	Nitrogen oxide (N_2O)	The catalyst samples exhibited high activity in N_2O decomposition and can retain higher than 90 % conversion of N_2O for long reaction times
Mg ferrite nanospheres ($MgFe_2O_4$)	Sulfur dioxide (SO_2)	During the adsorption of SO_2, sulfate and sulfite species are formed on the surface of $MgFe_2O_4$, and Fe(III) is partially reduced to Fe(II)
Titanium dioxide nanoparticles (TNPs)	Sulfur dioxide (SO2)	In the absence of light irradiation, the main product of SO_2 adsorption was found to be $SO_3{}^{2-}$, while light irradiation resulted in oxidation and the formation of adsorbed $SO_4{}^{2-}$
Titanium dioxide nanoparticles (TNPs)	VOCs (ethylene)	Sol–gel method with vortex reactor was used to synthesize novel TNPs with superior characteristics and a high bandgap energy that enhanced the photocatalytic degradation of ethylene
Electrospun nanofibers (NF) (hydroxypropyl-beta-cyclodextrin (HPβCD), NF, and hydroxypropyl-gamma-cyclodextrin (HPγCD) NF)	VOCs (aniline and benzene)	Both types of NFs efficiently entrapped the examined VOCs, due to their high porous structure, high surface area, and their molecular entrapment ability of VOCs by inclusion complexation

https://link.springer.com/article/10.1007/s11356-016-6457-z

Soil Pollution

- Contamination by oil, oils, heavy metals or pesticides
- Leads to
  - Climate change
  - Loss of soil fertility
  - Damage to human health
- Sources of pollution :
  - Industrial waste – the worst source of pollution. Chemicals in liquid and solid form.
  - Deforestation – leaves the land open to environmental influences, plus erosion.
  - Excessive use of fertilizers and pesticides – killing beneficial microorganisms in the soil, contaminating subsurface water
  - Landfilling of waste

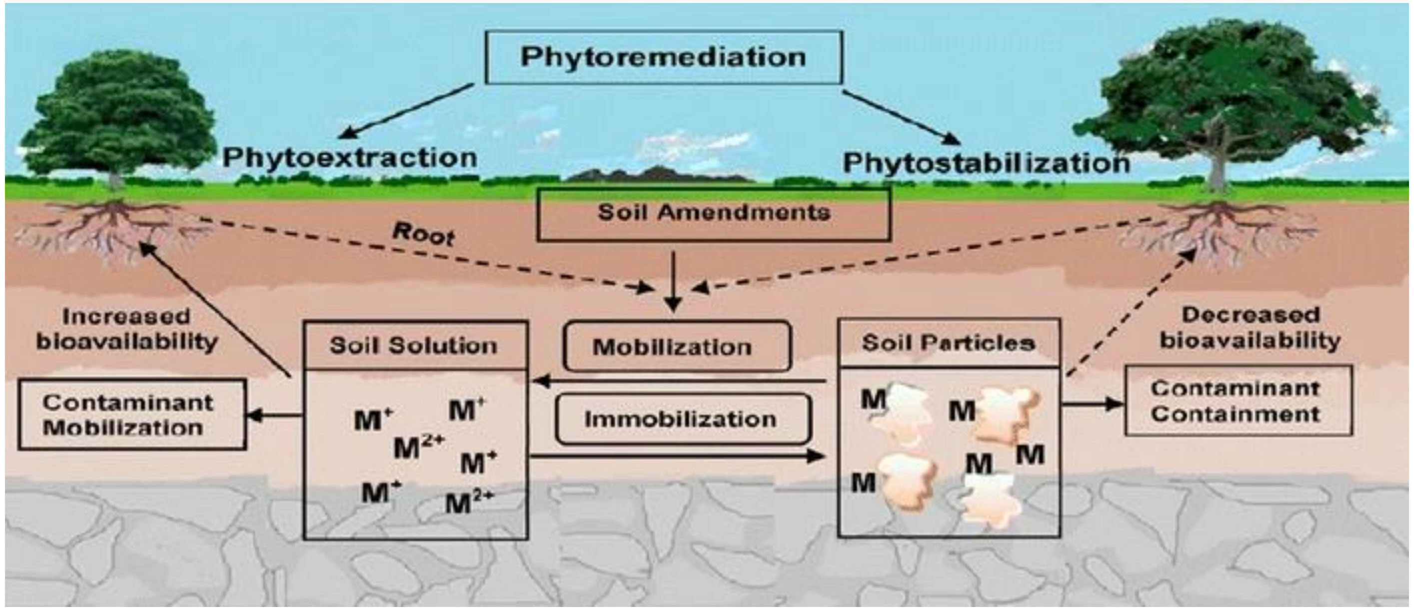
Strategies for Soil Protection

- Standard soil treatment technologies are extremely expensive.
- The best way is to prevent contamination of the soil with pollutants or at least to prevent their spread by immobilisation.

https://www.chacompanies.com/projects/contaminated-soil-remediation-and-management/

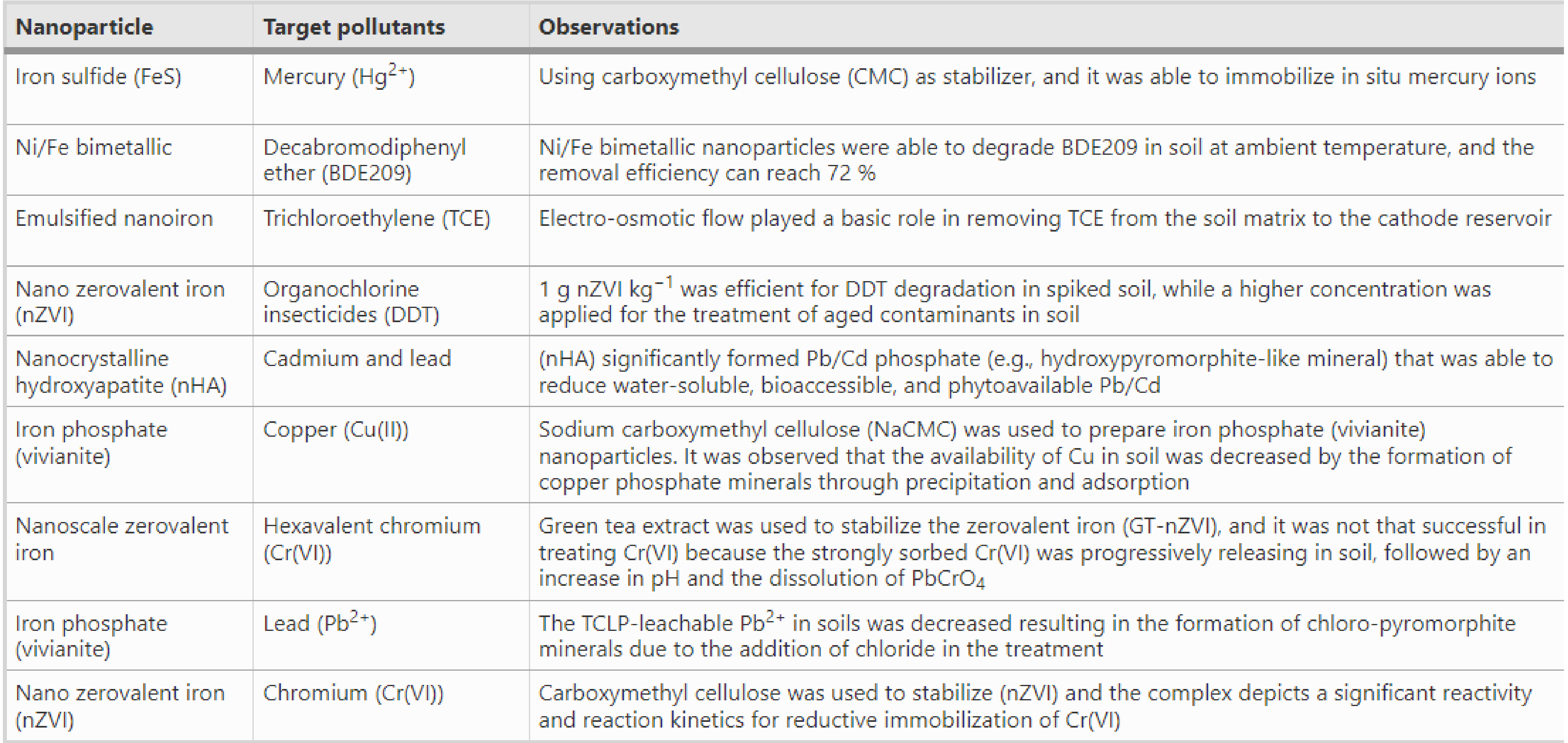
Strategies for Soil Protection 2

- Soil remediation – adding nanoparticles to the soil
  - Phytoextraction – mobilization of pollutants for better adsorption in plant roots and their removal from the soil
  - Phytostabilization – immobilization of pollutants to keep them out of the food chain and groundwater



https://link.springer.com/article/10.1007/s11356-016-6457-z

Heavy Metal Remediation



Nanoparticle	Target pollutants	Observations
Iron sulfide (FeS)	Mercury (Hg^{2+})	Using carboxymethyl cellulose (CMC) as stabilizer, and it was able to immobilize in situ mercury ions
Ni/Fe bimetallic	Decabromodiphenyl ether (BDE209)	Ni/Fe bimetallic nanoparticles were able to degrade BDE209 in soil at ambient temperature, and the removal efficiency can reach 72 %
Emulsified nanoiron	Trichloroethylene (TCE)	Electro-osmotic flow played a basic role in removing TCE from the soil matrix to the cathode reservoir
Nano zerovalent iron (nZVI)	Organochlorine insecticides (DDT)	1 g nZVI kg^{-1} was efficient for DDT degradation in spiked soil, while a higher concentration was applied for the treatment of aged contaminants in soil
Nanocrystalline hydroxyapatite (nHA)	Cadmium and lead	(nHA) significantly formed Pb/Cd phosphate (e.g., hydroxypyromorphite-like mineral) that was able to reduce water-soluble, bioaccessible, and phytoavailable Pb/Cd
Iron phosphate (vivianite)	Copper (Cu(II))	Sodium carboxymethyl cellulose (NaCMC) was used to prepare iron phosphate (vivianite) nanoparticles. It was observed that the availability of Cu in soil was decreased by the formation of copper phosphate minerals through precipitation and adsorption
Nanoscale zerovalent iron	Hexavalent chromium (Cr(VI))	Green tea extract was used to stabilize the zerovalent iron (GT-nZVI), and it was not that successful in treating Cr(VI) because the strongly sorbed Cr(VI) was progressively releasing in soil, followed by an increase in pH and the dissolution of $PbCrO_4$
Iron phosphate (vivianite)	Lead (Pb^{2+})	The TCLP-leachable Pb^{2+} in soils was decreased resulting in the formation of chloro-pyromorphite minerals due to the addition of chloride in the treatment
Nano zerovalent iron (nZVI)	Chromium (Cr(VI))	Carboxymethyl cellulose was used to stabilize (nZVI) and the complex depicts a significant reactivity and reaction kinetics for reductive immobilization of Cr(VI)

https://link.springer.com/article/10.1007/s11356-016-6457-z

Conclusion

- Infrastructure
  - Structure, mechanical properties and crack propagation in concrete
  - Cracks in concrete during drying
  - Nanomaterial admixtures for improved mechanical properties
  - Long-term stability of concrete – reinforcement corrosion as a major problem in Czechia
  - Self-repairing concrete
- Environmental technologies
  - Water
  - Air
  - Soil