Nano-geoengineering: Nano on a Global Scale

There is growing concern within the scientific community that significant reductions in anthropogenic greenhouse gas (GHG) emissions will not materialize before climate change reaches crisis level. An ineffective international response to climate change coupled with resistance to changing the energy infrastructure and advances in technology have all contributed to a recent surge in interest in geoengineering [Crutzen, 2006]. Geoengineering is the global-scale manipulation of climate with the objective of mitigating climate change. There have increasingly been references to nanotechnology in geoengineering literature [Hollenkamp, 2010] although, to date, these references remain primarily speculative. Nevertheless, there are early indications that the emerging field of nano-geoengineering holds enormous potential.

Geoengineering technologies are broadly divided into two categories: solar radiation management (SRM) and carbon dioxide removal (CDR). SRM technologies have attracted the most attention due to their relative simplicity, rapid deployment and low cost while CDR continues to present significant cost and technological challenges [Wigley, 2007]. The aim of SRM-based geoengineering is to produce a negative radiative forcing by increasing atmospheric albedo. This forcing would offset – or, in an ideal scenario, balance the positive radiative forcing due to rising GHG concentrations in the atmosphere. Climate models predict that a reduction in insolation of 1.7% to 2.1% would be required to balance the radiative forcing of + 4 W/m^2 corresponding to a doubling of CO2 concentrations [Crutzen, 2006; Royal Society, 2009]. This reduction would require increasing the average planetary albedo from roughly 0.31 to 0.32 [Royal Society, 2009].

Nanotechnology has clear applications for one SRM scheme in particular: stratospheric aerosol injections (SAI). The idea of manipulating the climate using aerosols injected into the stratosphere was first proposed by Soviet scientist M. I. Budyko in the 1970s [Izrael et al*.,* 2010]. SAI involves the dispersal of aerosols or their precursors, commonly sulfates, in the upper stratosphere using a variety of delivery mechanisms including airplanes, artillery shells, balloons [Robock et al., 2009], ground-level gas release [Crutzen, 2006] or photophoretic levitation [Keith, 2010]. Sulfate aerosols are a natural choice for SAI as they are already found in the stratosphere and have been well-studied. Background levels originate primarily from the combustion of fossil fuels. Periodically, volcanic eruptions produce higher concentrations, as in the 1991 Mount Pinatubo eruption that caused a peak global cooling of 0.5°C [Royal Society, 2009]. Aerosols backscatter solar radiation into space creating a net positive radiative forcing which cools the planet. Particle sizes on the order of 0.1µm are ideal as the backscattering cross section per unit mass is nearly maximized and the particles would be small enough to remain suspended in the rarefied stratospheric air for months [Rasch et al*.,* 2008]. An alternate approach to sulfur aerosol-based SAI is the use of nano-engineered particles. Keith [2010] suggests that aerosols could be engineered to have specific properties enabling the manipulation of particle distribution, lifetime and radiative forcing in addition to fewer side effects. Both approaches to nano-geoengineering via SAI will be examined in this report.

A Nano Solution to Geoengineering

Thermal gradient forces arise due to temperature inhomogeneities across a particle due to irradiation [Orr et al., 1964]. Upon interacting with aerosol particles, gas molecules reflect from the surface with an energy that is proportional to the temperature of the aerosol particle. As momentum must be conserved, the aerosol particles are given an impulse in the direction of the cooler side of the particle.

The thermal accommodation coefficient is the probability that a molecule will reach thermal equilibrium with its surroundings. Particles may have a thermal accommodation coefficient that varies from one side of the particle to the other. As a result, there will be a thermal gradient across the particle causing an impulse in the direction of the cooler side of the particle. By designing aerosols to be oriented so that their cooler side faces upward due to the net gravitational torque acting on them, the thermal gradient forces would cause the particle to levitate [Rohatschek, 1996]. This is known as gravitophotophoresis. By precisely tailoring the properties of aerosols to exploit this force, they could be levitated above the stratosphere [Keith, 2010], which would minimize environmental side effects of aerosols on our climate. Sulfate aerosols in the stratosphere are known to promote ozone depletion as they accelerate chemical reactions in the ozone. If aerosols were to be levitated above the stratosphere, they would experience longer lifetimes, and would therefore need to be replenished less often than sulfate aerosols.

Aerosols that have a permanent electric or magnetic dipole moment may exhibit levitation due to a force similar to gravitophotophoresis. These particles have a specific equilibrium orientation due to a torque experienced that is parallel to the electromagnetic field, and may levitate due to thermal gradient forces. These forces are called electro- or magnetophotoretic forces and are much greater than gravitational torques for smaller particles. This would enable the possibility to levitate smaller particles (spherical particles with a radius <0.1µm) [Keith, 2010] in the atmosphere.

Despite the fact that natural sulfate aerosols are spherical, particles may be engineered to have different geometries. The most mass-efficient scatterer would be a thin disk with a radius that is much larger than the wavelength of light incident [Keith, 2010]. A proposed nanoparticle use for SRM show in *Figure 1* [Keith, 2010].

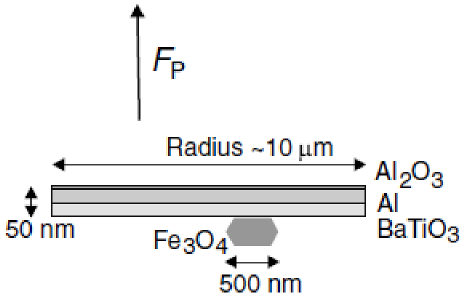

Figure 1: Example of a thin disk that could be used for SRM. The disk contains 5 nm aluminum oxide, 30 nm metallic aluminum and 15 nm barium titanate. The Al layer reflects a large amount of light to cool the top of the disk to levitate the disk using photophoretic forces. The Al_2O_3 layer prevents oxidation from occurring in the Al layer. The $BaTiO_3$ layer exploits electrostatic torques to orient the disk horizontally.

Using a disk with a large radius as a mass scatterer results in significantly less diffusive radiation compared to sulfate aerosols. This reduction has proven to have a significant effect on ecosystems [Gu et al., 2003]. Injecting engineered particles into the atmosphere does have one main disadvantage over sulfate aerosols; sulfate aerosols have proven to be successful through natural injection into the atmosphere through volcanic eruptions. Unnatural climate engineering solutions may have severe side-effects that are only evident upon large-scale implementation [Keith, 2010]. Furthermore, designing scatterers that have a long lifetime may be considered a disadvantage as the side effects of SRM are not well-known; it would be less easily reversible than using scatterers with a shorter lifetime.

Physics of Fabrication

There are two primary challenges in the use of nanoparticles for albedo enhancement: ensuring that the particles do not agglomerate and fabricating the particles.

The most efficient spherical bulk density scatters have radii of approximately 1000Å, about a tenth of the wavelength of scattered radiation. This type of scattering is called Mie scattering. For diameters much less than the wavelength, the scattering efficiency is proportional to d^3/λ^4 – thus extremely small particles are ineffective. In addition, for wavelengths that are much greater than particle diameter, efficiency is inversely proportional; thus extremely large particles are also ineffective. Therefore, a balance in between must be found in the nanometer range around 1000Å. In conjunction with the size of the particles, the aerosols should have minimal absorption (thermal infrared radiation), minimal mass, minimal vapor pressure, and must be chemically stable in the oxidizing atmosphere [Katz, 2009]. The options currently considered are oxides of boron, silicon, phosphorus and sulfur. These make excellent choices as they have volatile hydrides that can oxidize to the oxides in the stratosphere [Katz, 2009]. The hydrides also minimize coagulation by delaying oxidation until after they are well diluted in the stratosphere. This reduces the mass that must be lofted [Katz, 2009].

The second concern with these nanoparticles is their tendency to agglomerate. The physics behind aerosol injections relies on Brownian motion of these aerosol particles. The Brownian mean free path of a spherical particle is described equation 1.

$$mfp_{part} = \frac{4}{3C_D}\frac{\rho}{\rho_a} r \approx 5 \times 10^4 r \tag{1}$$

where ρ is the particle density, r is the radius, ρ_a is the density of air, C_D the drag coefficient is 1. Equation 1 only applies when the mean free path of air molecules is much greater than the particle radius, known as Knudsen flow. This is the type of flow that occurs in the stratosphere with the aerosol particles. The uncharged monodisperse particles also undergo some coagulation effects which can be described using equation 2.

$$t_{coag} = \frac{2}{nK} \tag{2}$$

where n is the particle number density and the K is the coagulation coefficient. K is described below in equation 3.

$$K = A\sqrt{\frac{24\pi k_B T r}{\rho}} \approx A\,4 \times 10^{-9}\ cm^3/sec \tag{3}$$

where A is the accommodation coefficient. The aforementioned theory has shown to match aerosols models made by other researchers such as Rasch and Tilmes [Rasch et al., 2008].

Many researchers are looking to integrated circuit fabrication techniques as a means of fabricating these aerosol particles. The ability to control the size and shape of these particles makes these fabrication techniques extremely compatible with aerosol injection.

The process starts with a silicon wafer substrate 100mm in diameter, and 0.5mm thickness also with 1-micrometer thick layers of aluminum, silicon dioxide and a photoresist. The aluminum is deposited using Ar sputtering from an aluminum target. The silicon dioxide is then deposited with a low temperature; plasma enhanced chemical vapor deposition process using SiH_4 and N_2O as the source gases. The wafers are then placed in a positive photoresist bath that removes the exposed photoresist. The resulting silicon dioxide region is then plasma etched down to the underlying aluminum film using O_2 as the source gas. The remaining aluminum layer is then dissolved to free the particles from the silicon substrate [Hoover, 1990]. Subsequently the wafers are then placed in bath of HCl to dissolve the aluminum sublayer and release the particles which can now be aerosolized. The problem with this method is the generation efficiency is only around 3% for a 2µm disc. This generation efficiency is drastically lower than that of spherical particles which are at 50% [Hoover, 1990].

The cost of production is around $300 (1990 dollars) per 10^8 particles. Furthermore, this process can used to create particles as small as 20 nm. Other methods such as ultrasonic methods are being investigated to improve the application of the mono disperse non spherical particles [Hoover, 1990]. Although the work of Hoover is now over two decades old, it remains the most relevant article detailing fabrication techniques for engineered aerosol particles. Recent advances in nanofabrication could potentially improve both the efficacy and cost of manufacturing techniques, although these benefits have yet to be realized.

Social, Political and Ethical Considerations

Nanotechnology could be applied to overcome many of the technical barriers to SRM; it could increase the technology's effectiveness, facilitate a highly targeted approach, limit adverse environmental impacts and provide superior aerosol fabrication methods. However, the application of nanotechnology would not address the social, political and ethical issues associated with SRM.

Continued research and discussion of SRM are controversial on the international stage [Boyd, 2008], as evidenced by the 2008 international moratorium on geoengineering at the 2008 UN Convention on Biological Diversity [Horton, 2011]. An obvious political issue stemming from SRM is the allocation of control. The question of who should be responsible for geoengineering decisions and oversight has not been addressed [Robock et al., 2009]. Implementation of a SRM scheme would have direct effects not only on the implementing nation, but the global community [Robock, 2008]. There is currently no international governing body for geoengineering and national development efforts have been largely unilateral. Blackstock and Long [2010] note that developing nations—many of which are particularly vulnerable to climate change—have largely been absent from SRM discussions and deserve an active role in the political process. Another major impediment to the development of SRM technologies is the absence of international norms, standards and best practices for research. The lack of global standards is problematic given the increasing prospect of field tests.

Another form of unilateral action is military use of the technology. In fact, the weaponization of geoengineering is not unprecedented; the United States artificially induced rain to cause flooding during the Vietnam War [Robock, 2008]. The issue of weaponization has since been addressed by the U.N. Convention on the Prohibition of Military or Any Other Hostile Use of Environmental Modification Techniques which has 85 signatory nations [Robock, 2008]. Engineered nanoparticles would be desirable from a military standpoint since particle characteristics like atmospheric lifetime could be tailored to suit weapons applications. Nanoscientists would be faced with the possibility that their work could be misappropriated for military use.

The level of public understanding will also influence perception and support of SAI. In democratic societies, the public will be the ultimate arbiter of the decision to pursue geoengineering. An informed public will hold policy-makers accountable for the timely and efficient implementation of geoengineering, should it be deemed necessary. Conversely, a misinformed or uninformed public could prevent or significantly impede geoengineering development, notwithstanding the actual benefits and costs. At present, public familiarity with geoengineering is disconcertingly low. Only 8% of Canadian, American and English respondents to a 2011 survey were able to correctly define “geoengineering” [Mercer et al., 2011]. Despite the poor level of understanding, Mercer et al. found a clear division in public opinion; most people readily identify as supporters or detractors of the technology. Their results also suggest that support for SRM is strongly driven by optimism about research and characterization of potential risks. This finding supports the notion that SAI’s technical and social issues are mutually dependent; public support can foster research and development while increased research and development may allay concerns and uncertainties thereby increasing public support. Integrating nanotechnology into geoengineering would add a level of complexity, potentially making the technology even more incomprehensible to the public.

An additional concern is that effective SRM could limit the incentive to reduce greenhouse gas emissions as their consequences would be less severe [Robock et al., 2009]. Since SRM does not address the cause of climate change—merely its effects—other impacts of climate change will persist. Without the pressure that rising temperatures provides, nations may maintain the status quo of unfettered greenhouse gas emissions. Furthermore, there is significant uncertainty related to potential environmental side effects including ozone layer depletion, acid rain and hydrological cycle perturbation [Robock, 2008]. Robock [2008] also notes that current models are often woefully incomplete. Given that the understanding of sulfate aerosols is incomplete at best, nanoparticle-based SRM may prove even more challenging to accurately model.

As field testing of SAI becomes a reality, geoengineering is no longer a hypothetical prospect. This development brings some ethical issues to the fore. There is the issue of moral authority [Robock, 2008]; given the technological means to manipulate the climate, do humans have the right? Referring to geoengineering, Lovelock [2008] invokes his famous Gaia Hypothesis, the notion of a living Earth, observing that “our contract with Gaia is not about human rights alone, but includes human obligations.” In this sense, geoengineering could be viewed as a form of planetary stewardship. Another point is that, if geoengineering has known environmental impacts, should it proceed regardless? Do human needs transcend all other components of the ecosphere? Unlike the unresolved technical problems with SAI, these are obviously questions without definite answers. Although every individual has a unique perspective on these ethical questions, geoengineering will affect everyone on Earth.

Nanotechnology has the potential to revolutionize geoengineering. By increasing the effectiveness of SRM and minimizing some of the negative environmental impacts, nano could take the technology one step closer to reality. However, it is clear that SRM-based geoengineering is not a cure-all. Given its many issues, the scientific community must decide whether it is worth pursuing nano-geoengineering. With the aim of mitigating climate change, perhaps efforts are better spent researching nano applications for CDR or alternative energy technologies.

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