A Physics Based Model of the Ionization of Samarium by the MOSC Chemical Releases in the Upper Atmosphere

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ABSTRACT

The release of Samarium vapor into the upper atmosphere was studied using during the Air Force Research Laboratory sponsored Metal Oxide Space Cloud (MOSC) rocket launches in May 2009. The Naval Research Laboratory supported these experiments with 3-D photochemical modeling of the artificial plasma cloud including (1) reactions with atomic oxygen, (2) photo excitation, (3) photoionization, (4) dissociative recombination, and (5) ion and neutral diffusion. NRL provided an experimental diagnostic instrument on the rocket with a dual frequency radio beacon on the rocket to measure changes in total electron content. The AFRL provided ground based diagnostics of incoherent scatter radar and optical spectroscopy and imagery. The NRL Chemical Release Model (CRM) has over 600 excited states of atomic Samarium neutrals, atomic ions, along with Samarium Oxide Ions and electrons. Diffusive transport of neutrals in cylindrical geometry and ions along magnetic field lines is computed along with the reactive flow to predict the concentrations of Sm, Sm-Ion, Sm0, and SmO Ion. Comparison of the CRM with observations demonstrates that Sm release into the upper atmosphere initially produces enhanced electron densities and SmO-Ions. The diatomic ions recombine with electrons to yield neutral Sm and O. Only the photo ionization of Sm yields a stable atomic ion that does not substantially recombine. The MOSC releases in sunlight yielded long duration ion clouds that can be replicated with the CRM. The CRM predicts that Sm releases in darkness would produce a lower density plasma cloud because of the lack of photo excitation and photoionization.

1. INTRODUCTION

Chemical releases may increase the electron density in the upper atmosphere to produce artificial plasma clouds. Previously studied materials such as barium, strontium, xenon, lithium, or cesium have required solar photons or particle collisions for ionization [Bernhardt, 1987]. The plasma-producing efficiency of these materials is often measured remotely with HF sounders, UHF radars or in situ with plasma probes and radio propagation beacons. Since the neutral and/or ionized forms of these materials fluoresce, optical instruments are also often used for their detection.

Another process for formation of enhanced ionization region is auto-ionization where the released material, usually in an atomic state, reacts spontaneously with atomic oxygen to form a molecular ion and electron pair. The AFRL Metal Oxide Space Cloud (MOSC) experiment was conducted to test the efficiency of electron production by the auto-ionization reaction involving samarium. The MOSC experiment used the release of vaporized samarium near 170-180 km altitude in sunlight to produce enhanced electron densities. The proposed production of the artificial plasma cloud was autoionization by the reaction

$$Sm + O \rightarrow SmO^+ + e^- + \Delta E \qquad (1)$$

where ΔE is the dissociation energy minus the ionization potential for SmO. For the reaction to proceed, ΔE must be positive so that the reaction is exothermic. With the previously accepted values of the dissociation/binding energy of neutral SmO 5.856±0.135 eV [Pedley and Marshall, 1983] and the ionization energy of SmO to yield SmO^+ is 5.55 eV [Ackermann, Rauh, and Thorn, 1976] the reaction energy was estimated to be ΔE = 0.3 eV. Paulovic et al. [2004] quote values for dissociation and ionization near these values and ΔE = 0.22 eV.

Recent measurements by the University of Utah in Collaboration with the Air Force Research Laboratory, however, indicates that the ionization potential for samarium monoxide is substantially greater than previously published and that reaction (1) may be energy neutral or even endothermic. The steps for determining the auto-ionization reaction energy are given in Figure 1. This energy could be based on the dissociation energy (D_1) for SmO and the ionization potential (I_1) of Sm or could be determined from the dissociation energy (D_2) of SmO^+ and the ionization potential (I_2) of SmO. The most recent measurements of these parameters are D_1 = 5.86 eV, I_1 = 5.64 eV, D_2 = 5.76 ± 0.09 eV, I_2 = 5.74 ± 0.20 eV yielding ΔE = 0.12 ± 0.20 eV. If reaction (1) is endothermic then it will not proceed in darkness.

The MOSC experiment, however, was conducted using a samarium release in direct sunlight and the atomic samarium can be pumped by the suns radiation to form metastable states. The auto-ionization from the metastable states proceeds by the reaction

$$Sm_\alpha + O \rightarrow SmO^+ + e^- + \Delta E_\alpha \qquad (2)$$

where $\Delta E_\alpha = 0.12 \pm 0.20 + E_\alpha$ eV and E_α is the energy of metastable level α above the ground state.

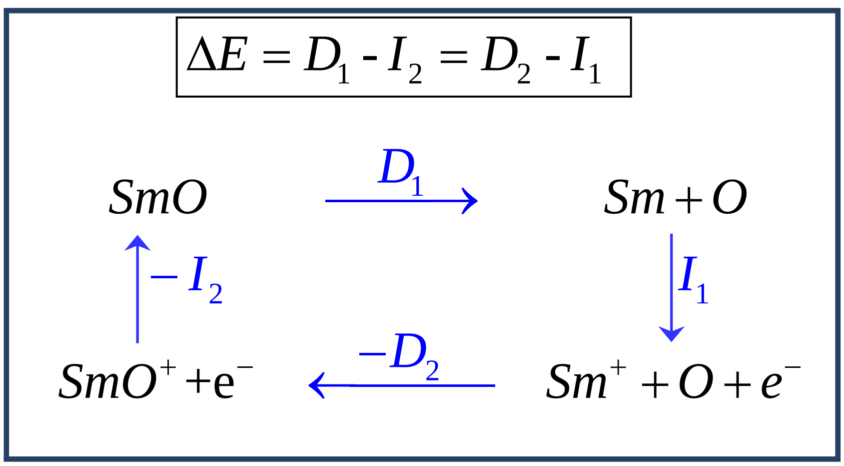

Figure 1. Dissociation and ionization processes that determine the reaction energy for Sm + O auto-ionization.

The four species involved in a chemical release of atomic samarium into the upper atmosphere are Sm atoms, Sm^+ ions, SmO diatomic molecules, and SmO^+ diatomic ions. The interactions between these species, ambient oxygen atoms and molecules, and sunlight are illustrated by the diagram in Figure 2. The presence of excited species can be identified with optical line spectra excited by solar resonance fluorescence. The electron density enhancements are detected using radio beacon and ground radar scatter.

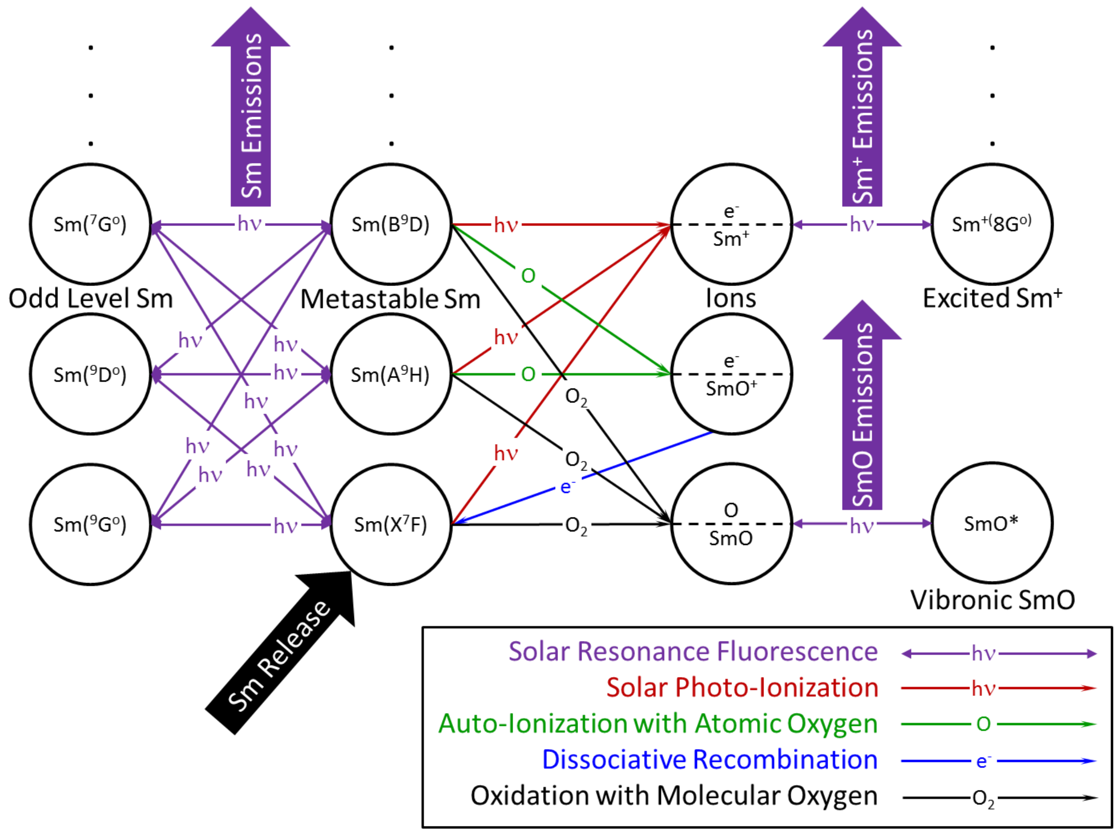

Figure 2. Atoms, Molecules, Ions and Optical Emissions resulting from the release of atomic samarium into the solar-illuminated upper atmosphere composed of atomic and molecular oxygen. Resonance fluorescence excites visible line emissions in Sm, Sm^+ and SmO that can be viewed from the ground.

2. CHEMICAL RELEASE MODEL

The time dependent chemistry for production of electrons from a samarium release is combined with transport for determination of the electron production for a Sm release in sunlight including the autoionization reaction with O. The solar photoionization reaction with the rate is given as

$$Sm + h\nu_{Sun} \xrightarrow{k_{SmSun}} Sm^+ + e^- \text{ rate: } k_{SmSun} = 0.00442\ s^{-1} \tag{3}$$

The metastable state autoionization reaction for a release at 171 km altitude described by

$$Sm^* + O \xrightarrow{k_{Sm+O}} SmO^+ + e^- + \Delta E_\alpha \text{ rate: } k_{Sm+O} = f_{SmExo}\,\overline{\sigma_{Sm+O}\text{v}} \tag{4}$$

where the fraction of exited exothermic states, $f_{SmExo} = 1$. The reaction cross section is assumed to have a constant value of

$$\sigma_{Sm+O} \simeq 5\times10^{-15} cm^2 \tag{5}$$

based on the exothermic reaction data of Fite, Patterson and Siefel [1976] for a number of atoms. The oxygen thermal speed is taken to be $v = (kT_O/m_O)^{1/2} = 718$ m/s for $T_O = 1000$ K giving $k_{Sm+O} = 3.73\ 10^{-10}\ cm^3/s$. At 180 km with atomic oxygen density $n_O = 6.8\ 10^9\ cm^{-3}$, the reaction (4) proceeds at a rate $k_{Sm+O}\ n_O = 2.54\ s^{-1}$ and a time constant of about 0.4 seconds. Autoionization will initially proceed at much faster than the photoionization given by (3).

Because the autoionization reaction (1) is only slightly exothermic, the dissociative recombination (DR) of electrons and the molecular ions must be considered. The DR reaction is

$$SmO^+[^6\Gamma] + e^- \xrightarrow{k_{SmO^+e^-}} Sm[^7F] + O[^3P] \text{ rate: } k_{SmO^+e^-} \approx 10^{-7}\ \text{cm}^3 s^{-1}$$

(6)

where the reactive species are produced in their ground electronic states and the rate constant is estimated using similar reactions from Larsson and Orel [2008].

The factors of photoionization, autoionization and dissociative recombination are combined into the rate equations for the ionized species and electrons.

$$\begin{aligned}
\frac{dN_{Sm}}{dt} &= -(k_{SmSun} + k_{Sm+O}n_O)N_{Sm} + k_{SmO^+e^-}N_{SmO^+}N_e \\
\frac{dN_{Sm^+}}{dt} &= k_{SmSun}N_{Sm} \\
\frac{dN_{SmO^+}}{dt} &= k_{Sm+O}n_O N_{Sm} - k_{SmO^+e^-}N_{SmO^+}N_e \\
N_e &= N_{Sm^+} + N_{SmO^+}
\end{aligned} \qquad (7)$$

These equations are solved for the initial conditions of $N_{Sm} = N_0$ and all initial ion densities are set to zero.

The expansion of a vapor cloud from a chemical release can proceed in three phases with transitions between self-collision-dominated fluid motion, free-molecular flow and diffusive expansion in the background atmosphere. These phases may be modeled using particle collisions with a Direct Simulation Monte Carlo (DSMC) method [Kaplan and Bernhardt, 2010, and Bernhardt et al. 2012]. Here, a simplified model is used to estimate the effect of transport on the electron density at the center of the MOSC samarium cloud.

Initially, the cloud is dense enough that the neutral mean-free-path inside the cloud is smaller than the cloud itself. At this point, the expansion is described by fluid equations of continuity, momentum and temperature/heat flow. As the expansion proceeds and if the background density is low enough, the expansion can enter a phase of free molecular flow. The neutral density expands with a radial velocity $v_r = r/t$ around the release point at distance r and time t. This expansion is self-similar with the density and velocity given in terms of the initial velocity distribution $F_{Sm}(v_r)$ by the function

$$n(r,t) = F_{Sm}\left(\frac{r}{t}\right)/t^3, \quad \mathbf{v} = \frac{r}{t}\mathbf{r} \qquad (8)$$

The continuity equation for this free-atomic expansion is

$$\frac{\partial n}{\partial t} = -\nabla \bullet (n\mathbf{v}) - \beta n = -n\frac{3}{t} + \frac{\partial n}{\partial r}\frac{r^3}{t} - \beta n \qquad (9)$$

where β represents loss by photoionization, autoionization or other processes. At the center of release where $\partial n/\partial r = 0$,

$$\left.\frac{\partial n}{\partial r}\right|_{r=0} = 0 \text{ and } \frac{\partial n(0)}{\partial t} - n(0)\frac{3}{t} - \beta n(0) \qquad (10)$$

and the first equation in (7) becomes

$$\frac{dN_{Sm}}{dt} = -3\frac{N_{Sm}}{t} - (k_{SmSun} + k_{Sm+O}n_O)N_{Sm} + k_{SmO^+e^-}N_{SmO^+}N_e \qquad (11)$$

For the MOSC samarium release at 180 km, it is more likely that the cloud never enters the diffusive state but expands by collisional diffusion. The three-dimensional diffusion equation is

$$\frac{\partial n}{\partial t} = -\nabla \bullet (n\mathbf{v}) - \beta n = \nabla \bullet (D\nabla n) - \beta n = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial n}{\partial r}\right) - \beta n \qquad (12)$$

where D is the atomic-molecular diffusion coefficient given by the formula

$$D_{Sm} = \left(\sum_{j \neq Sm} 1/D_{Smj} \right)^{-1} \text{ where } D_{Smj} = \frac{3}{32\, f r_{Smj}^2 n_j} \left(1 + \frac{m_{Sm}}{m_j} \right)^{1/2} \left(\frac{8kT_{Sm}}{\pi m_{Sm}} \right)^{1/2} \quad (13)$$

and j represents O, N_2 or O_2. The altitude profiles of the background neutral concentrations and the samarium diffusion coefficient are given in Figure 3. The diffusion coefficient at the release point is estimated to be 5.83 x 10^8 cm^2/s.

The neutral density solution for a point release for diffusion in a uniform atmosphere is given by

$$n(r,t) = \frac{N_0}{(4\pi D t)^{3/2}} \exp\left(-\frac{r^2}{4Dt} - \beta t \right) \quad (14)$$

Substitution of (14) into and evaluation at r=0 gives the continuity equation

$$\frac{\partial n(0,t)}{\partial t} = 3D \frac{\partial^2 n(0,t)}{\partial^2 t} - \beta n(0,t) = -\frac{3}{2}\frac{n(0,t)}{t} - \beta n(0,t) \quad (15)$$

which has ½ the transport dissipation of the free expansion continuity equation (9). For diffusive expansion, the first equation in (7) becomes

$$\frac{dN_{Sm}}{dt} = -\frac{3}{2}\frac{N_{Sm}}{t} - (k_{SmSun} + k_{Sm+O} n_O) N_{Sm} + k_{SmO^+e^-} N_{SmO^+} N_e \quad (16)$$

The ions are transported along the magnetic field lines by one-dimensional, ambipolar diffusion.

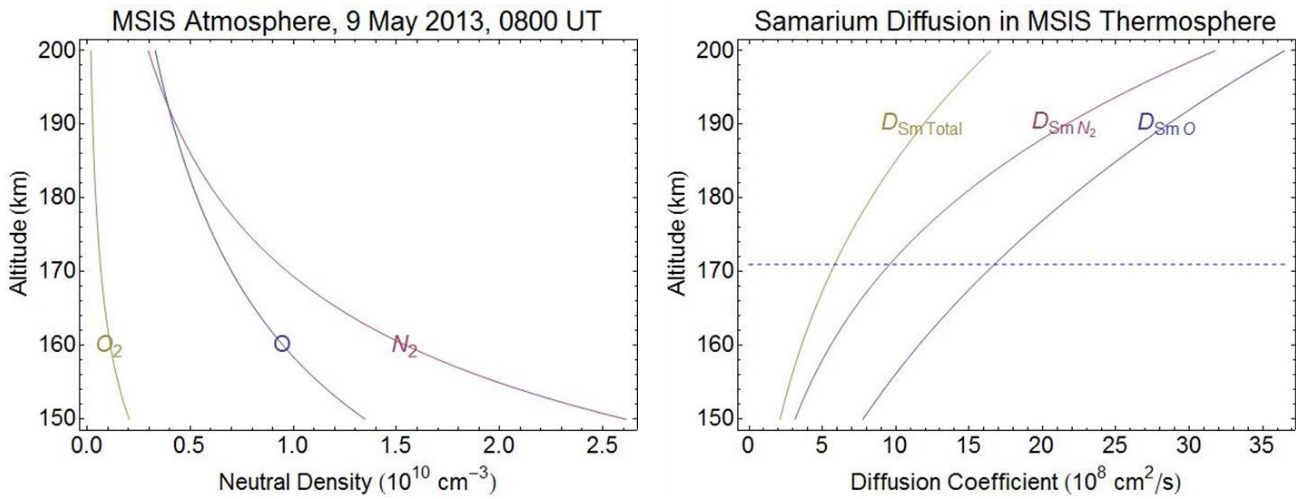

Figure 3. Upper atmosphere densities (right) of molecular nitrogen, atomic oxygen, and molecular oxygen for the MOSC release over Kwajalein on 9 May 2013. The samarium vapor diffusion coefficients (left) have contributions primarily by collisions with O and N_2.

The full three-dimensional expansions with photo-chemistry are written in 2-D cylindrical geometry with the radial coordinate R and the axial coordinate z along the direction of the horizontal magnetic field. The time dependent diffusion equations are

$$\begin{aligned}
\frac{\partial N_{Sm}}{dt} &= \frac{D_1}{R}\frac{\partial}{\partial R}\left(R \frac{\partial N_{Sm}}{\partial R} \right) + D_1 \frac{\partial^2 N_{Sm}}{\partial z^2} - \beta_{Sm} N_{Sm} + k_{SmO^+e^-} N_{SmO^+} N_e \\
\frac{\partial N_{SmO^+}}{dt} &= D_1 \frac{\partial^2 N_{SmO^+}}{\partial z^2} + \beta_{Sm+O} N_{Sm} - k_{SmO^+e^-} N_{SmO^+} N_e, \; \beta_{Sm+O} = k_{Sm+O} n_O \\
\frac{\partial N_{Sm^+}}{dt} &= D_1 \frac{\partial^2 N_{Sm^+}}{\partial z^2} + \beta_{SmSun} N_{Sm} \\
\frac{\partial N_{SmO}}{dt} &= \frac{D_1}{R}\frac{\partial}{\partial R}\left(R \frac{\partial N_{SmO}}{\partial R} \right) + D_1 \frac{\partial^2 N_{SmO}}{\partial z^2} + \beta_{Sm+O_2} N_{Sm}, \; \beta_{Sm+O_2} = k_{Sm+O_2} n_{O_2} \\
N_e &= N_{Sm^+} + N_{SmO^+}, \; \beta_{Sm} \equiv \beta_{SmSun} + \beta_{Sm+O} + \beta_{Sm+O_2}
\end{aligned} \quad (17)$$

where the gravity force has been neglected to maintain two-dimensional symmetry. The initial samarium cloud is initialized with the spherical distribution given by (25). For the Sm release in full sunlight $\beta_{SmSun} = 0.00442\ s^{-1}$, $\beta_{Sm+0} = 2.54\ s^{-1}$, and $\beta_{Sm+02} = 6.37\ 10^{-4}\ s^{-1}$. These equations comprise the NRL Chemical Release Code (CRC) used to study the MOSC experiments.

3. SIMULATIONS OF ION AND ELECTRON PRODUCTION WITH THE MOSC SAMARIUM RELEASE

The original concept for ion cloud production from a samarium release was that the auto-ionization reaction (1) was exothermic and a stable molecular ion plasma cloud would be produced. To simulate this scenario, the dissociative recombination rate in (7) is set to zero ($k_{SmO^+e^-} = 0$) and the equations in (7) and (16) are solved numerically for a 2 kg Sm vapor release. The resulting time dependence for the artificial plasma cloud is illustrated in Figure 4. Under these recombination-free conditions, the predominant ion is SmO+ and the electron density reaches 9 x 10^6 cm^{-3}.

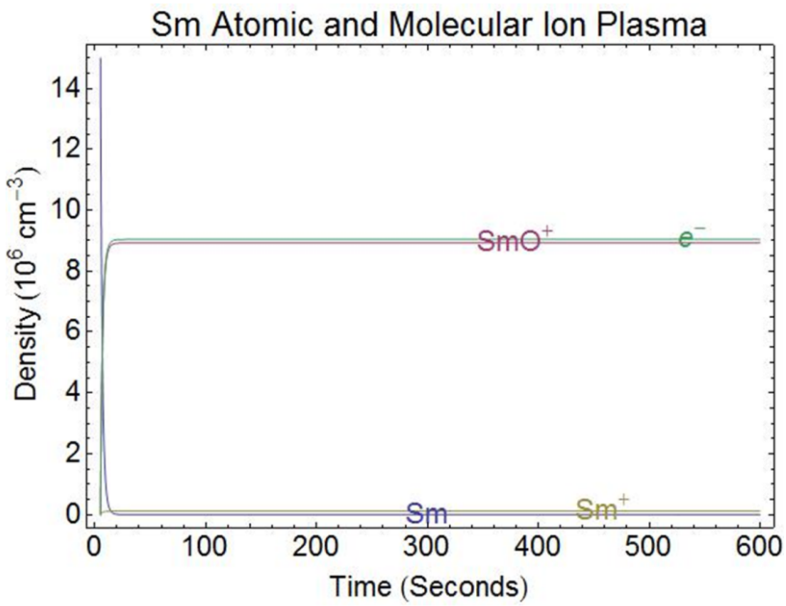

Figure 4. Samarium release ion production *neglecting* (SmO^+ , e^-) *recombination*. Uniform 3-D diffusion is assumed for the neutrals. No transport is used with the ions and electron computations. The solution is started 5 seconds after the release with an initial Sm density N_0 = 1.5 x 10^7 cm^{-3}.

For a more realistic simulation, the dissociation recombination term in the equations (7) and (16) is turned on using $k_{SmO^+e^-} = 10^{-7}\ cm^3s^{-1}$. The computed plasma densities at the center of the plasma cloud are given in Figure 16 for the same release conditions as Figure 5. Initially, SmO^+ dominates the ion population reaching a maximum of 4.38 10^6 cm^{-3} at release time 2.5 s. After the samarium oxide ion recombines with electrons, the dominant ion is Sm^+ which is stable to recombination. The electron density reaches a steady state density of 1.37 10^6 cm^{-3} after 600 seconds. The plasma density will eventually dissipate by diffusion along magnetic field lines.

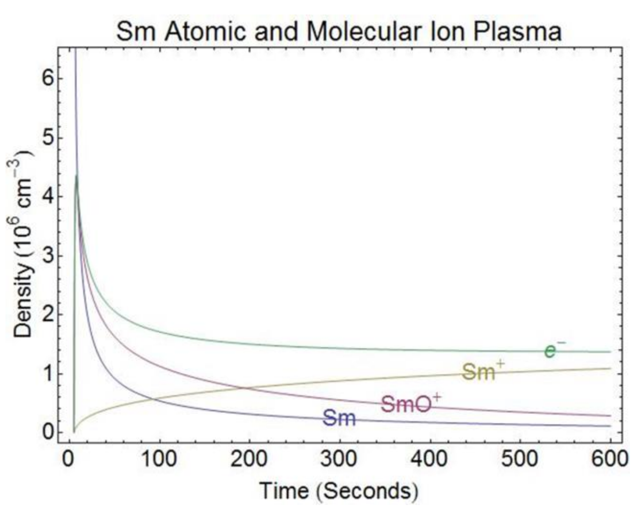

Figure 5. Simulation of the MOSC samarium release with full computation of ion production including (SmO^+ , e^-) recombination.

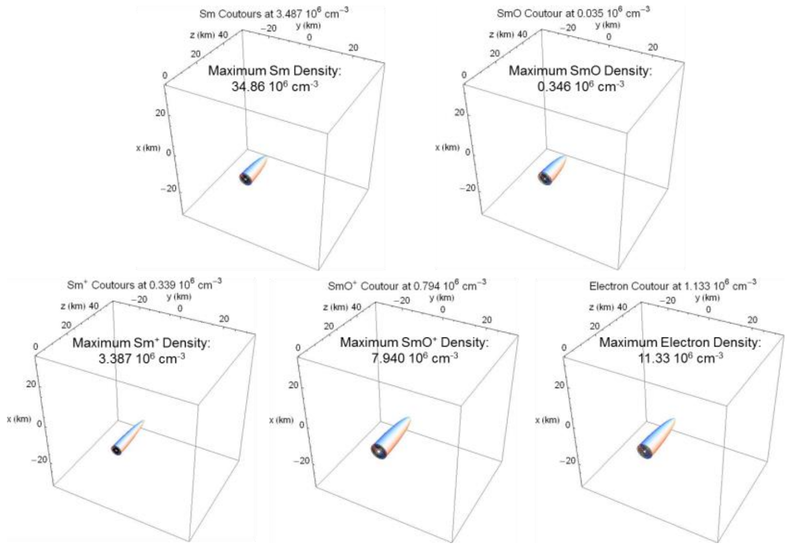

Figure 6. Samarium derived neutrals and ions calculated for the MOSC samarium release into the upper atmosphere for production of a dense electron cloud 20 seconds after the release. The plasma is primarily composed of samarium oxide ions and electrons. The SmO neutral is only 1% of the total neutral density in the cloud. The ion cloud is stretched along the direction of the horizontal magnetic fields.

The geometric distributions of the samarium derived species are computed with a full 3-D CRC simulation of the gas expansion in the upper atmosphere. The set of equations (17) are solved numerically with diffusive expansion of neutrals computed in cylindrical coordinates and the field aligned diffusion computed along horizontal magnetic field lines. To initialize the simulation, the neutral samarium cloud is allowed to expand for 5 seconds without reaction with the background environment. This represents free expansion and displacement of the ambient atmosphere. For the next 15 seconds, the neutral cloud reacts with atomic and molecular oxygen, is excited and ionization by sunlight, and starts to recombine with electrons. Figure 6 illustrates constituents of the dense plasma cloud 20 seconds after the release. The neutral cloud is made up of atomic samarium with negligible amounts of samarium monoxide. The diatomic ion SmO^+ dominates the plasma composition over the atomic ion Sm^+. The electron density is over 10^7 cm^{-3} and is much greater than observed in the natural ionosphere.

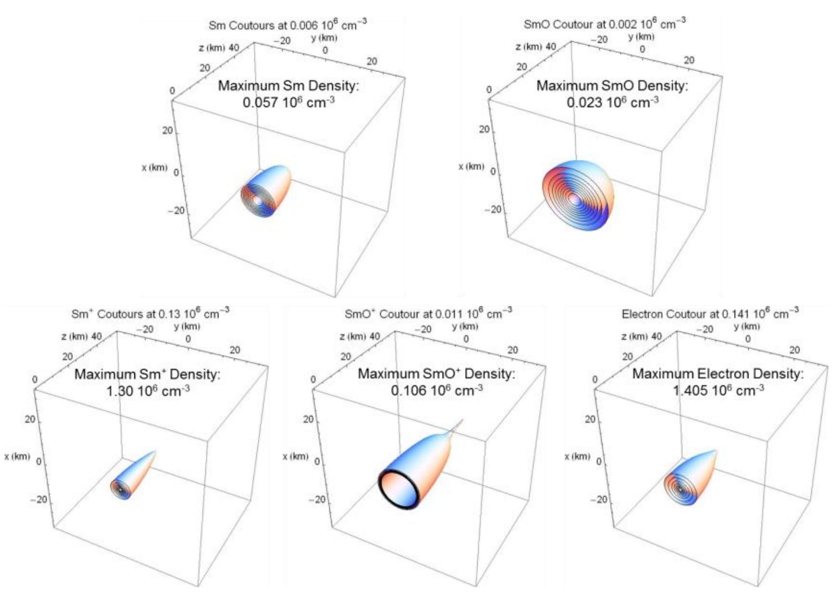

Figure 7. State of the samarium related clouds 550 seconds after release. In the long term, most of the ions are atomic Sm^+ balanced with an equal density of number of electrons.

After 550 seconds (Figure 7), most of the molecular ions computed with the CRC model have recombined only Sm^+ remains with a density of 1.3 x 10^6 cm^{-3}. The lifetime of the samarium ion cloud will be determined by field aligned diffusion and cross-B convection electric fields. At this density, it is unlikely that field aligned irregularities will form. The neutral samarium density has been reduced by photoionization, diffusion and chemical reactions to a twice that of the samarium oxide SmO density. The Sm cloud is more elongated in the magnetic field direction indicating that it has been generated in part by the dissociative recombination of the SmO^+ ion. The SmO cloud is spherical around the release point. Ground-based imagery of the plasma at this time should be able to isolate the different components.

This CRC model study shows that initially, a dense SmO^+ cloud will be produced by a samarium release into upper atmosphere. This cloud will be detected using radio beacon propagation from the chemical release rocket to ground receivers, by ground based ionosonde and incoherent scatter radar, and by optical spectroscopy. As the molecular ions start to recombine with electrons, the population of the atomic samarium ions builds up until at about 100 seconds after release, they start to dominate the center of the plasma cloud. The optical spectra will shift from being dominated by atomic Sm and molecular SmO^+ lines to atomic Sm+ and molecular SmO emission lines at this point. The nature of this composition shift is shown by the numerically computed integral of the ion and electron densities through the center of the plasma cloud. The change in the line intensities will follow the volume emission rate dependence on composition illustrated in Figure 5. This optical emission time history will be explored in a future paper.

ACKNOWLEDGMENTS

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REFERENCES

R. J. Ackermann, E. G. Rauh, and R. J. Thorn, The thermodynamics of ionization of gaseous oxides; the first ionization potentials of the lanthanide metals and monoxides, The Journal of Chemical Physics, Vol. 65, No.3, 1 August 1976.

Bernhardt, P.A., "A critical comparison of ionospheric depletion chemicals," **J. Geophys. Res.**, 92, 4617, 1987.

P. A. Bernhardt et al., Ground and Space-Based Measurement of Rocket Engine Burns in the Ionosphere, IEEE Transactions On Plasma Science, 40, 1267-1286, 2012.

G. Bujin and C. Linton, High Resolution Analysis of Transitions to the Five Lowest Electronic States of Samarium Monoxide, J. Molecular Spectroscopy, 137, 114-126, 1989.

W.L. Fite, T.A. Petterson, M.W. Siegel, Cross Sections for Thermal Reactions Between Uranium Atoms and Atmospheric Species, AFGL-TR-77=0030, 31 December 1976.

Kaplan, C.R. and Bernhardt, P.A., "The Effect of an Altitude-Dependent Background Atmosphere on Space Shuttle Engine Burn Plumes," *Journal of Spacecraft and Rockets*, **47**, 700 (2010).

M. Larsson and A.E. Orel, Dissociative Recombination of Molecular Ions, Cambridge University Press, 2008

Jozef Paulovic, Laura Gagliardi, John M. Dyke, Kimihiko Hiraoa, The gas-phase chemi-ionization reaction between samarium and oxygen atoms: A theoretical study, Journal of Chemical Physics Volume 120, Number 21, 9998-10001, 2004

J B. Pedley, and E.M. Marshall, Theromochemical Data for Gaseous Monoxides, J. Phys. Chem. Ref. Data, 12, 967-1031, 1983.