Supporting Information

Understanding the Behavior of Radioactive Cesium during the Incineration of Contaminated Municipal Solid Waste and Sewage Sludge by Thermodynamic Equilibrium Calculation

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S1. Formula to Calculate Thermodynamic Properties

S1.1. Estimation equation for molar heat capacity of solid metal oxides\textsuperscript{44,45}:

\[ C_P = A + BT + C/T \]  
\[ A = \frac{10^3 T_m [C_{P,298} + 4.7n] - 1.25n \times 10^5 (T_m)^{-2} - 9.05n}{10^{-3} T_m - 0.298} \]  
\[ 10^3 B = \frac{25.6n + 4.2n \times 10^5 (T_m)^{-2} - C_{P,298}}{10^{-3} T_m - 0.298} \]  
\[ 10^{-5} C = -4.2n \]

List of symbols:

- \( C_P \): molar heat capacity at constant pressure [J·mol\(^{-1}\)·K\(^{-1}\)]
- \( T \): absolute temperature [K]
- \( T_m \): melting point [K]
- \( C_{P,298} \): molar heat capacity at constant pressure at 298 K [J·mol\(^{-1}\)·K\(^{-1}\)]
- \( n \): number of atoms in a molecule or a unit (e.g., 10 for CsAlSi\(_2\)O\(_6\))

NOTE: This formula is Maier-Kelley type and known to have large estimation errors at higher temperatures. Because the heat capacities for other alkali aluminosilicates in the commercial database were expressed in this form, here we also employed this Maier-Kelley type estimation equation. \( C_P \)'s were calculated for a limited temperature range indicated in the Table 3 of the body text. At higher temperatures, \( C_P \)'s were set constant to prevent exceeding far from the Dulong-Petit limit.
Figure S1. Estimated molar heat capacities of Cs aluminosilicates together with the heat capacities of Na- and K-aluminosilicates having similar chemical formulae.
S1.2. Statistical formula for thermodynamic properties of ideal gas with rigid rotor-harmonic oscillator approximation\(^\text{49,50}\):

\[
C_p/R = \frac{5}{2} + \frac{1}{2} m + \sum_{i=1}^{3n-3-m} \left[ \frac{(\omega_i)^2}{(\omega_i^2)} \exp \left( -\frac{\omega_i^2}{RT} \right) \right]
\]

(S-5)

\[
S/R = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{elec}}
\]

(S-6)

\[
S_{\text{trans}}/R = \frac{3}{2} \ln \left( \frac{2\pi m kT}{h^2} \right) + \ln(kT) - \ln \left( \frac{p}{\rho_0} \right) + \frac{5}{2}
\]

(S-6-1)

\[
S_{\text{rot}}/R = \left( \frac{3}{2} \ln \left( \frac{2\pi m kT}{h^2} \right) + \frac{1}{2} \ln(I_A I_B I_C) + \ln \left( \frac{\pi}{\sigma_{\text{rot}}} \right) + \frac{3}{2} \right)^{m=3}, \quad m=2
\]

(S-6-2)

\[
S_{\text{vib}}/R = \ln \left( \frac{8\pi^2 kT}{h^2} \right) + 1
\]

(S-6-4)

\[
S_{\text{elec}}/R = \ln \left( \sum_i g_i \exp \left( -\frac{\epsilon_i}{kT} \right) \right) + \frac{\sum_i g_i (\epsilon_i / kT)^{1/2}}{\sum_i g_i \exp \left( -\frac{\epsilon_i}{kT} \right)}
\]

(S-6-5)

\[
\Delta f H_{298} = \Delta f H_0 + \sum_i c_i (H_{298} - H_0) i
\]

(S-7)

\[
(H_{298} - H_0)/RT = \frac{5}{2} + \frac{1}{2} m + \sum_{i=1}^{3n-3-m} \left[ \frac{(\omega_i)^2}{(\omega_i^2)} \exp \left( -\frac{\omega_i^2}{RT} \right) \right]
\]

(S-7-1)

\[
\Delta f H_0(\text{CsO}_2) = D_0(\text{CsO}_2=\text{Cs}+\text{O}_2) + \Delta f H_0(\text{Cs}) + \Delta f H_0(\text{O}_2)
\]

(S-7-2)

List of symbols:

- \(R\): the ideal gas constant
- \(m\): freedom of rotation (0 for atoms, 2 for linear molecules, and 3 for nonlinear polyatomic molecules)
- \(m_w\): molecular mass [kg·molecule\(^{-1}\)]
- \(n\): number of atoms in a molecule
- \(h\): the Planck constant (6.626·10\(^{-34}\) J·s)
- \(\nu_i\): i-th vibration frequency in s\(^{-1}\)
- \(S\): molar entropy [J·mol\(^{-1}·\)K\(^{-1}\)]
- \(p\): partial pressure [Pa]
- \(I_A, I_B, I_C\): moment of inertia [kg m\(^2\)]
- \(\sigma_{\text{rot}}\): rotational symmetry number
- \(\omega_i\): i-th vibrational frequency in cm\(^{-1}\), \(\omega_i=\nu_i/c\)
- \(g_i\): degeneracy of i-th electronic state
- \(\epsilon_i\): electronic energy of i-th electronic state [J·molecule\(^{-1}\)]
- \(\Delta H_{\text{sol}}\): standard enthalpy of formation [J·mol\(^{-1}\)]
- \(c_i\): 1 for the compound and \((-1 \times \text{number of } i\text{-th element in the compound})\) for the constituent elements (e.g., in the case of CsO\(_2\), 1 for Cs\(_2\)O, -1 for Cs and -1 for O\(_2\))

NOTE: In the calculation, we neglected the contribution from the excited electronic states. As these equations do not consider the effects due to the anharmonicity or vibration-rotation coupling in the heat capacities, the estimation errors may be not negligibly small at higher temperatures. The last term in eq. S-7 is the difference in \(H_{298}-H_0\) between the gas species and the constituent elements.
Table S1. Molecular constants employed in the calculation of thermodynamic properties of gases.

| formula (electronic state) | structure | Rotation constant $A$, $B$, $C$ / cm$^{-1}$ | wavenumber $\omega$ / cm$^{-1}$ | note |
|---------------------------|-----------|---------------------------------------------|--------------------------------|------|
| Cs$_2$O (X'1Σ$^+$)*      | Cs––O––Cs | $r_{GO}$=2.39 Å, $\theta_{GOO}$=180°       | $\Delta$$H_{298}$, $S_{298}$ by Badawi [51] |
| CsO (X 2Σ$^+$)           | Cs––O     | 0.0111                                     | 121, 68, 452                  |      |
| CsO$_2$ (X 2A$^2$)       | Cs=O=O=Cs | $r_{GO}$=2.651 Å, $r_{OO}$=1.345 Å         | $\Delta$$H_{298}$, $S_{298}$ by Lamoreaux [53] |
| CsO$_2$ (X 1A$_g$)**     | Cs=O=O=Cs | $r_{GO}$=4.37 Å, $r_{OO}$=1.50 Å           | $\Delta$$H_{298}$, $S_{298}$ by Lamoreaux [53] |

$A = h(8\pi^2 c I_A)$, $B = h(8\pi^2 c I_B)$, $C = h(8\pi^2 c I_C)$; $h$: the Planck constant, $I_A$, $I_B$, $I_C$: moment of inertia in kg m$^2$ s$^{-1}$

$\omega = 1/\lambda = \nu/c$, $\nu$: frequency in s$^{-1}$

* Electronic ground state of Cs$_2$O was not found in the literature. Other alkali oxides (M$_2$O, M=Li, Na, K) have ground state of '1Σ$^+$' [ST1-1].

** Electronic ground state of CsO$_2$ was not found in the literature. Other alkali oxides (M$_2$O$_2$, M=K by Tremblay et al.[ST1-2], K and Rb by Bravo and Blaisten-Barojas [ST1-3, ST1-4]) have the ground state of '3Δ$^+$'.

$\sigma$: molecular symmetry number

[ST1-1] Vasiliu, M.; Li, S.; Peterson, K. A.; Feller, D.; Gole, J. L.; Dixon, D. A. Structures and heats of formation of simple alkali metal compounds: Hydrides, chlorides, fluorides, hydroxides, and oxides for Li, Na, and K. *J. Phys. Chem. A* **2010**, *114*, 4272–4281.

[ST1-2] Tremblay, B.; Roy, P.; Manceron, L.; Pullumbi, P.; Bouteiller, Y.; Roy, D. Vibrational spectrum and structure of the K$_2$O$_2$ complex in solid argon: A far infrared and density functional theory study. *J. Chem. Phys.* **1995**, *103*, 1284–1291.

[ST1-3] Allavena, M.; Blaisten-Barojas, E.; Silvi, B. LCAO–MO–SCF calculation of the metal–oxygen bonding in the M$_2$O$_2$ series: M= Li, Na, and K. *J. Chem. Phys.* **1981**, *75*, 787–792.

[ST1-4] Bravo, G.; Blaisten-Barojas, E. Electronic structure and vibrational analysis of the alkali peroxides K$_2$O$_2$ and Rb$_2$O$_2$. *Chem. phys. Lett.* **1984**, *108*, 237–240.
S2. Calculated Phase Equilibrium Properties Using the Thermodynamic Data of Cs-Compounds

Figure S2. Calculated phase diagram for Cs-O system.

Thermodynamic data used in this figure are the solution data and solid pure compound data for Cs₂O, Cs₃O, Cs₄O, Cs₅O, Cs₂O₂, CsO₂, and CsO₃ (Guéneau and Flèche in 2015) [43] and estimated gas species data for Cs₂O, CsO, Cs₂O₂, and CsO₂ in Table 3.

Figure S3. Calculated phase diagram for Cs₂O-SiO₂ system.

In the cesium silicate systems, melting points and solid-liquid equilibria have been reported. S3-1,S3-2 The thermodynamic data used in this figure are solid and liquid Cs₂SiO₃, Cs₂Si₂O₅, and Cs₂Si₄O₉ data (Knacke 1991) [38] and solid and liquid SiO₂ pure compound data (FactPS) of FactSage 7.0 (GTT-technologies). The thermodynamic data of mixed liquid cesium silicate was estimated assuming that the three cesium silicates and liquid SiO₂ make ideal solution. No further thermodynamic assessment was attempted.

[S3-1] Kracek, F. C. The cristobalite liquidus in the alkali oxide-silica systems and the heat of fusion of cristobalite. J. Am. Chem. Soc. 1930, 52, 1436–1442. [S3-2] Boivin, P.; Berthelay, J. C.; Blanc, Y.; Coulet, A.; Castanet, R. Determination of temperature and enthalpy of melting alkali disilicates by differential calorimetric analysis. J. Mat. Sci. 1993, 28, 1834–1838.
Figure S4. Calculated phase diagrams for CsAlSiO₄-SiO₂ system. (trial calculation)

Model I: The $\Delta fH_{298}$ values of CsAlSiO₄ and CsAlSi₅O₁₂ were shifted from the literature values (listed in Table 3), and $C_p(T)$ of CsAlSi₅O₁₂ was estimated using the precipitation temperature of CsAlSi₅O₁₂ from a mixed molten oxide (1693 K) as the $T_m$ for eqs. S1-4. (listed in Table 3)

Model II: The $\Delta fH_{298}$ values of CsAlSiO₄ and CsAlSi₅O₁₂ were the shifted values (Table 3), and $C_p(T)$ of CsAlSi₅O₁₂ was estimated using the melting temperature of CsAlSiO₄ (2023 K) as the $T_m$ for eqs. S1-4.

Model III: The $\Delta fH_{298}$ value of CsAlSiO₄ was the original value by Taylor et al. (–2133 kJ mol⁻¹) The $\Delta fH_{298}$ value of CsAlSi₅O₁₂ was the shifted value (Table 3), and $C_p(T)$ of CsAlSi₅O₁₂ was the estimation from the precipitation temperature. (Table 3)

Model IV: The $\Delta fH_{298}$ value of CsAlSiO₄ was the shifted value (Table 3). The $\Delta fH_{298}$ value of CsAlSi₅O₁₂ was the original value, and $C_p(T)$ of CsAlSi₅O₁₂ was the estimation from the precipitation temperature. (Table 3)

According to the literature, the melting temperature of CsAlSiO₄ was above 2023 K.⁴⁶ The estimated standard state thermodynamic data were available,⁴¹,⁴² but the heat capacity at high temperature has not been reported for this material. CsAlSi₅O₆ (pollucite) has the similar crystal structure with analcime (NaAlSi₂O₆·H₂O), and natural pollucite are mostly the solid solution of pollucite and analcime.⁶⁰ Besides analcime, at least pollucite and leucite or pollucite and Rb-leucite produce single phase crystalline solid from hydrothermal reaction⁵⁵ or calcination,⁵⁶,⁵⁷ therefore it is probable that leucite and pollucite make solid solution at least at high temperatures such as the temperature of calcination. In heating, analcime dehydrate up to 700 K S⁴⁻¹ and natural pollucite also slightly dehydrate.³⁹ The melting temperature of pure stoichiometric pollucite was reported to be above 2173,⁴⁷ whereas the melting temperature of Cs-deficient pollucite or solid solutions may be much lower, because in a heating treatment on a Cs-deficient pollucite (Cs₈₋₉Al₁₀Si₂₆O₇O₆), the relative density decreased at 1773 K due to the formation of a glassy phase resulting from Cs components’ vaporization.⁵⁴,⁵¹ The thermodynamic properties of natural pollucite³⁹,⁶¹ and synthetic end-member pollucite⁴⁰ were available. We employed Semenov’s standard state thermodynamic data⁴⁰ cited in the Ogorodova et al.’s article.³⁹ CsAlSiO₄ has similar crystal structure with wairakite (CaAl₂Si₁₀O₂₄).⁶⁰ The melting temperature was at least above 1693 K,⁴⁸ which is the precipitation temperature of CsAlSiO₄ from a mixed molten oxide (initial composition: BaCO₃ 4.00 g, Cs₂CO₃ 4.91 g, H₂SiO₃ 3.60 g, Al₂O₃ 0.500 g, Fe₂O₃ 33.3 mg, and V₂O₃ 10 g), but the accurate melting temperature of CsAlSi₅O₁₂
has not been reported. The estimated standard state properties\textsuperscript{41,42} were available, but the heat capacity was not found in the literature. Cs\textsubscript{2}Al\textsubscript{2}O\textsubscript{5}Si\textsubscript{2}O\textsubscript{6} was synthesized from hydrothermal method\textsuperscript{62} and no thermodynamic data was available. For liquid cesium aluminosilicates, there was no assessed set of thermodynamic parameters. Thermodynamic data for Cs\textsubscript{2}O-Na\textsubscript{2}O-SiO\textsubscript{2} or Cs\textsubscript{2}O-SiO\textsubscript{2} systems S\textsuperscript{4-3,4-4} and Henry’s law constant for cesium in liquid CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} at the eutectic composition S\textsuperscript{4-5} have been reported.

The thermodynamic data used in the Figure S4 are solid Cs\textsubscript{2}SiO\textsubscript{4}, Cs\textsubscript{2}Al\textsubscript{2}O\textsubscript{5}Si\textsubscript{2}O\textsubscript{6} and Cs\textsubscript{2}SiO\textsubscript{12} (Table 3), solid SiO\textsubscript{2} pure compound data (FactPS, FToxic-slag A solution data of FactSage 7.0 (GT-Techologies), liquid Cs\textsubscript{2}O data\textsuperscript{43} and liquid Cs\textsubscript{2}Al\textsubscript{2}O\textsubscript{4} data (estimated as follows). Thermodynamic data of liquid cesium aluminosilicates was estimated assuming that Cs\textsubscript{2}O and CsAlO\textsubscript{2} dissolve into the aluminosilicate solution (FToxic-slagA) with activity coefficients of $\gamma_{\text{CsO}} = 10^{-10}$, $\gamma_{\text{CsAlO}_2} = 10^{-2.5}$. The thermodynamic data of liquid Cs\textsubscript{2}O was not reported, and we temporarily estimated the values as follows:

$$\Delta H_{298}^{\text{CsAlO}_2,\text{liq}} = \Delta H_{298}^{\text{KAI}_2\text{O}_2} + \left(\Delta H_{298}^{\text{KAIO}_2} - \Delta H_{298}^{\text{NaAI}_2\text{O}_2}\right)$$
$$S_{298}^{\text{CsAlO}_2,\text{liq}} = S_{298}^{\text{KAI}_2\text{O}_2} + \left(S_{298}^{\text{KAIO}_2} - S_{298}^{\text{NaAI}_2\text{O}_2}\right)$$

Thermodynamic data for the liquid NaAlO\textsubscript{2} and KAlO\textsubscript{2} were cited from ref. S4-6, and the temperature function of $C_p$ for liquid Cs\textsubscript{2}O\textsubscript{2} was assumed as the $C_p$ for solid Cs\textsubscript{2}O\textsubscript{2} cited from ref. S4-7.

The melting temperatures obtained in the phase diagram calculations (in Figure S4) and the literature values for the three cesium aluminosilicates were as follows:

| Model      | Cs\textsubscript{2}SiO\textsubscript{4} | Cs\textsubscript{2}Al\textsubscript{2}O\textsubscript{5}Si\textsubscript{2}O\textsubscript{6} | Cs\textsubscript{2}SiO\textsubscript{12} |
|------------|----------------------------------------|---------------------------------------------|-----------------------------------------|
| Model I    | 1940 K, Cs\textsubscript{2}SiO\textsubscript{4} | 2368 K, Cs\textsubscript{2}Al\textsubscript{2}O\textsubscript{5}Si\textsubscript{2}O\textsubscript{6} | 2597 K (used in this article)            |
| Model II   | 1940 K, Cs\textsubscript{2}SiO\textsubscript{4} | 2399 K, Cs\textsubscript{2}SiO\textsubscript{12} | 2350 K                                  |
| Model III  | 1473 K, Cs\textsubscript{2}SiO\textsubscript{4} | 2368 K, Cs\textsubscript{2}SiO\textsubscript{12} | 2597 K                                  |
| Model IV   | 1940 K, Cs\textsubscript{2}SiO\textsubscript{4} | 2399 K, Cs\textsubscript{2}SiO\textsubscript{12} | no melting temperature                  |
| Reported   | Cs\textsubscript{2}SiO\textsubscript{4}: above 2023 K\textsuperscript{46} Cs\textsubscript{2}Al\textsubscript{2}O\textsubscript{5}Si\textsubscript{2}O\textsubscript{6}: 2173 K\textsuperscript{47} and Cs\textsubscript{2}SiO\textsubscript{12}: above 1693 K\textsuperscript{48} |

The descriptions about the models are indicated below the Figure S4. In Model III, the melting temperature of Cs\textsubscript{2}SiO\textsubscript{4} obtained from the phase diagram calculation was 1473 K, which was far below the literature value. Therefore, we shifted the $\Delta H_{298}$ value of Cs\textsubscript{2}SiO\textsubscript{4} below the reported value to obtain better melting temperature. In Model IV, we had no Cs\textsubscript{2}SiO\textsubscript{12} phase in the calculated phase diagram, thus we shifted the $\Delta H_{298}$ value of Cs\textsubscript{2}SiO\textsubscript{12} to downwards to emerge this phase. After shifting the $\Delta H_{298}$ values, in Model I, we obtained too high melting temperature for Cs\textsubscript{2}SiO\textsubscript{12}, whereas in model II, we had better melting temperature for Cs\textsubscript{2}SiO\textsubscript{12}. The two models had different $C_p$ functions for the Cs\textsubscript{2}SiO\textsubscript{12}: in Model I, the precipitation temperature from a mixed molten oxide (1693 K\textsuperscript{48}) was employed as $T_m$ for eqs. S1-4 to obtain the temperature function of $C_p$ (listed in Table 3) while in Model II, the melting temperature of Cs\textsubscript{2}SiO\textsubscript{4} (2023 K) was used as a tentative $T_m$ value for eqs S1-4 for Cs\textsubscript{2}SiO\textsubscript{12}.

As we did not have accurate thermodynamic data for Cs\textsubscript{2}SiO\textsubscript{12}, thermodynamic equilibrium calculations for MSWI and SSI were also conducted using the Models II and IV as well as using the Model I. We obtained almost the same results from the Models I and II. In the results using Model IV, the fraction of Cs\textsubscript{2}SiO\textsubscript{12} was decreased (the fraction of this compound was approximately 50 % of the total Cs at 850 °C in the usual sewage sludge incineration condition (SS1 and SS2), whereas the same fractions were almost 100 % when the calculations were performed using Model I or Model II.) Because almost all of Na and K were obtained as crystalline aluminosilicates (feldspars) in the equilibrium calculation, from the observed similarity of leachability of Cs and other alkali species in the actual SSI ash, we employed the Model I in our discussion as it provided the similar fate for Cs and the other alkali metals.

NOTE: The phase diagram shown above includes many estimations, and especially the data for Cs\textsubscript{2}O\textsubscript{2} was fictive one. In our calculations for municipal waste incinerations, we did not use the thermodynamic data of Cs\textsubscript{2}O\textsubscript{2} (I) because the employed solution model (FToxic-slagH) did not require the data of aluminates. For further studies, it is necessary to obtain accurate thermodynamic data, especially the melting properties and heat capacities of cesium aluminosilicates, and the liquid phase thermodynamic data.

\[\text{[S4-1] Wang, J.; Neuhoff, P.S. Thermodynamics of dehydration in analcime: Absorption calorimetry and equilibrium observations.} \text{Am. Min.} \text{2008, 93, 1449–} 1459.\]
\[\text{[S4-2] Yanase, I.; Konakawa, J.; Kobayashi, H. Influence of Cesium Nitrile and Heating Rate on Densification and Microstructure of Cs-Deficient Pollucite} \text{Sintered Body.} \text{J. Am. Ceram. Soc.} \text{2006, 89, 184–188.}\]
\[\text{[S4-3] Bennour, F.; Chastel, R.; Mathieu, J.-C.; Coutures, J.-P.; Bergman, C. Determination of the excess thermodynamic functions in ternary Cs\textsubscript{2}O-SiO\textsubscript{2}-Na\textsubscript{2}O melts by Knudsen effusion mass spectrometry.} \text{Phys. Chem. Liq.} \text{1996, 33, 229–248.}\]
\[\text{[S4-4] Morishita, M.; Navrotsky, A.; Wilding, M. C. Direct measurement of relative partial molar enthalpy of SiO\textsubscript{2} in SiO\textsubscript{2}–M\textsubscript{2}O (M= Li, Na, K, Cs) binary and SiO\textsubscript{2}–CaO–Al\textsubscript{2}O\textsubscript{3} ternary melts.} \text{J. Am. Ceram. Soc.} \text{2004, 87, 1550–1555.}\]
\[\text{[S4-5] Norman, J. H. Henry’s law constants for dissolution of fission products in a silicate fallout particle matrix.} \text{General Atomics Report GA-7058 (1966).}\]
\[\text{[S4-6] Spear, K. E.; Allendorf, M.D. Thermodynamic analysis of alumina refractory corrosion by sodium or potassium hydroxide in glass melting furnaces.} \text{J. Electrochem. Soc.} \text{2002, 149, B551–B559.}\]
\[\text{[S4-7] Kohli, R. The heat capacities of selected inorganic alkali metal compounds.} \text{J. Therm. Anal. Cal.} \text{1997, 49, 1321–1326.}\]
Table S2. Calculated gas phase speciation and equilibrium pressures of Cs species above various materials with literature information.

| System (phase) | Calculated speciation and equilibrium pressures | Experimental speciation (ion species in mass spectrometry) | Experimental equilibrium pressures |
|----------------|-----------------------------------------------|----------------------------------------------------------|-----------------------------------|
| CsOH (s)       | CsOH, (CsOH)_2, Pc(CsOH)=4·10^{-2} bar, Pc(CsOH)_2=8·10^{-5} bar at 700 K | CsOH, (CsOH)_2, (Cs^+, Cs_2OH^+, CsOH^-), mass spectrometry [ST2-1] | P_CsOH = 5·10^{-5} bar at 700 K [ST2-2] |
| CsCl (s)       | CsCl, CsCl_2, Pc(CsCl)=5·10^{-8} bar, Pc(CsCl)_2=2·10^{-8} bar at 700 K | CsCl (DTA unchanged by kind of buffer gas) [ST2-3] | P_CsCl = 1·10^{-8} bar at 700 K [ST2-6] |
| CsCO_3 (s)     | Cs, Pc(CsCO_3)=2·10^{-6} bar at 1080 K in Ar, 2·10^{-7} bar at 1224 K in CO_2. | Cs, Cs_2CO_3 (Cs^+, Cs_3CO_3^+, at 1150 K, mass spectrometry [ST2-1] | P_Cs_total = 8·10^{-6} bar at 1080 K, Knudsen [ST2-7] |
| CsSO_4 (s)     | Cs_2SO_4, Pc(CsSO_4)=5·10^{-6} bar at 1180 K | Cs_2SO_4 (Cs^+, Cs_2SO_4^+, at 1263 K) [ST2-1], CsSO_4 (95% Cs_2SO_4 at 1170 K, Knudsen (Pt cell) [ST2-9] | P_CsSO_4 = 5.28·10^{-6} bar at 1180 K [ST2-9] |
| Cs_2Si_2O_5 (s,l)| Cs, Pc(Cs_2Si_2O_5)=1·10^{-6} bar at 1033 K (above ideal solution) | Cs, 3 %, Cs_2O_2 at 50-600 °C, Knudsen (Mo cell) [ST2-10] | P_Cs = 1.84·10^{-4} atm at 1033 K [ST2-10] |
| Cs_2SiO_3 (s,l)| Cs, Pc(Cs_2SiO_3)=2·10^{-10} bar at 1033 K (above solid) | Cs, 3 % Cs_2O_2 at 50-600 °C, Knudsen (Mo cell) [ST2-10] | P_Cs = 6.8·10^{-6} atm at 1033 K [ST2-10] |
| CsAlO_2O_5 (s) | Cs, Pc(CsAlO_2O_5)=4·10^{-9} bar at 1373 K | Cs (Cs^+, Knudsen (Mo cell)) [ST2-12] | log(P_Cs/Pa) = -18497/T + 11.85 P_Cs = 2·10^{-7} bar at 1373 K [ST2-12] |
| CsAlO_2O_6 (s) | Cs, Pc(CsAlO_2O_6)=2·10^{-8} bar at 1550 K | Cs (Cs^+, Knudsen (Mo cell)) [ST2-11] | log(P_Cs/Pa) = -21828/T + 12.4 P_Cs = 2·10^{-7} bar at 1550 K [ST2-11] |
| CsAlO_2O_12 (s) | Cs, Pc(CsAlO_2O_12)=4·10^{-9} bar at 1673 K | Cs (Cs^+, Knudsen (Mo cell)) [ST2-12] | log(P_Cs/Pa) = -26974/T + 14.6 P_Cs = 3·10^{-7} bar at 1673 K [ST2-12] |
| Cs in CaO-Al_2O_3-SiO_2 eutectic (l) | CsO_2, CsO, Cs, Pc(Cs_2O_2)=7·10^{-11} atm at 1473 K, 0.00001 g-Cs/g-silicate in pO_2=1 atm, γCsO_2/Cs_2O_2=10^{14.9} | not assigned (assigned as Cs by Knudsen mass spectrometry but not commented on transpiration study with 1 atm O_2) [S4-5] | log ((P_Cs/atm)/(CsO_2,g-Cs/g-silicate)) = -17300/T + 6.6 in 1 atm pure O_2, P_Cs=7·10^{-11} atm at 1473 K, 0.00001 g-Cs/g-silicate [S4-5] |

[ST2-1] Büchler, A.; Berkowitz-Mattuck, J. B. Gaseous Ternary Compounds of the Alkali Metals. in Advances in High Temperature Chemistry, vol.1, Academic Press. (1967) pp.95–128.
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Condition: CsOH 1 mol in 1 mol air or Ar at 1 bar.
Calculated gas speciation was almost CsOH and (CsOH)\textsubscript{2}. \(P_{\text{CsOH}} = 4 \cdot 10^{-5}\) bar, \(P_{(\text{CsOH})_2} = 8 \cdot 10^{-5}\) bar at 700 K both in Ar and in air. According to the literature, most abundant gas species was CsOH and (CsOH)\textsubscript{2}. [ST2-1] Vapor pressure above CsOH (\(P_{\text{CsOH}}\)) was \(5 \cdot 10^{-5}\) bar, at 700 K. [ST2-2]
Figure S5-2. Calculated gas phase speciation and partial pressures above CsCl(s) to compare with Knudsen effusion-gas spectrometric experiment.

Condition: CsCl 1 mol in 1 mol Ar or air at 1 bar.
Calculated gas speciation was almost CsCl and Cs₂Cl₂. \( P_{\text{CsCl}} = 5 \times 10^{-8} \text{ bar}, \) \( P_{\text{Cs}_2\text{Cl}_2} = 2 \times 10^{-8} \text{ bar} \) at 700 K both in Ar and in air. According to the literature, most abundant gas species was CsCl. [ST2-3 to ST2-5] Vapor pressure above CsCl (\( P_{\text{CsCl total}} \)) was 1 \( \times 10^{-8} \) bar at 700 K. [ST2-6]
Figure S5-3. Calculated gas phase speciation and partial pressures above Cs₂CO₃(s) to compare with transpiration vapor pressure.

Condition: Cs₂CO₃ 1 mol in 1 mol Ar or CO₂, total pressure of 1 bar. Gaseous Cs₂CO₃ was not included in this equilibrium calculation, because the molecular constants could not be obtained.

Calculated gas speciation was almost 100% Cs(g). $P_{Cs} = 2 \times 10^{-6}$ bar at 1080 K in Ar, and $2 \times 10^{-7}$ bar at 1224 K in CO₂.

According to the literature, $P_{Cs, total} = 0.8$ Pa at 1080 K, 0.01 Pa at 916 K [ST-7] and $P_{Cs, total} = 10$ Pa in 1 atm CO₂ at 1224 K by transpiration method (No.40 in Table .9 of the reference) [ST-8].
Figure S5-4. Calculated gas phase speciation and partial pressures above Cs$_2$SO$_4$(s) to compare with Knudsen effusion – mass spectrometric study.

Condition: Cs$_2$SO$_4$ 1 mol in 1 mol Ar, total pressure of 1 bar. Calculated gas speciation was almost 99% Cs$_2$SO$_4$(g) and 1 % Cs. $P_{\text{Cs}_2\text{SO}_4}$ = 5.4·10$^{-6}$ bar at 1180 K. According to the literature [ST2-9], 95% of gas species was Cs$_2$SO$_4$ and 5% of cesium sulfate decompose into Cs(g) + SO$_2$+1/2O$_2$ at 1180-1280 K. $P_{\text{Cs}_2\text{SO}_4,\text{total}}$ = 5.28·10$^{-6}$ bar at 1180 K. [ST2-9]
Figure S5-5. Calculated gas phase speciation and partial pressures above Cs$_2$Si$_2$O$_5$ (s, l) and Cs$_2$Si$_4$O$_9$ (s, l) to compare with Knudsen effusion experiment.

Condition: Cs$_2$Si$_2$O$_5$ or Cs$_2$Si$_4$O$_9$ 1 mol in 1 mol Ar, total pressure of 1 bar, 673-1073 K.
Calculated gas speciation was almost 100 % Cs(g) and CsO occupies 0.006 % (Cs$_2$Si$_2$O$_5$) or 0.02% (Cs$_2$Si$_4$O$_9$). $P_{Cs, total} = 1 \times 10^{-9}$ bar at 1033 K (above liquid Cs$_2$Si$_2$O$_5$) and $2 \times 10^{-10}$ bar at 1033 K (above solid Cs$_2$Si$_4$O$_9$).

According to the literature [ST2-10], most abundant phase was Cs(g) and 3 % of gas species was Cs$_2$O$_2$ at 873 K, and at 1033 K, $P_{Cs} = 1.84 \times 10^4$ atm (above liquid Cs$_2$Si$_2$O$_5$) and $6.8 \times 10^4$ atm at 1033 K (above solid Cs$_2$Si$_4$O$_9$).
Figure S5-6. Calculated gas phase speciation and partial pressures above CsAlSiO₄, CsAlSi₂O₆, and CsAlSi₅O₁₂ to compare with Knudsen effusion-mass spectrometric data.

CsAlSiO₄ Condition: CsAlSiO₄ 1 mol in 1 mol Ar, total pressure of 1 bar, 1223-1573 K. Ar was a dummy to calculate the vapor pressure. Calculated total equilibrium pressure, $P_{Cs,\text{total}}$, was $4 \times 10^{-9}$ bar at 1373 K. According to the literature, $\log(P_{Cs}/\text{Pa}) = -18497/T + 11.85$, $P_{Cs} = 2 \times 10^{-7}$ bar at 1373 K. [ST2-12]

CsAlSi₂O₆ Condition: CsAlSi₂O₆ 1 mol in 1 mol Ar, total pressure of 1 bar, 1324-1748 K. Calculated equilibrium pressure of Cs was $2 \times 10^{-8}$ bar at 1550 K. According to the literature, $\log(P_{Cs}/\text{Pa}) = -21828/T + 12.4$, $P_{Cs} = 2 \times 10^{-7}$ bar at 1550 K. [ST2-11]

CsAlSi₅O₁₂ Condition: CsAlSi₅O₁₂ 1 mol in 1 mol Ar, total pressure of 1 bar, 1523-1825 K. Calculated equilibrium pressure of Cs was $4 \times 10^{-9}$ bar at 1673 K. According to the literature, $\log(P_{Cs}/\text{bar}) = -26974/T + 14.6$, $P_{Cs} = 3 \times 10^{-7}$ bar at 1673 K. [ST2-12]
Figure S5-7. Calculated equilibrium pressure above CaO-Al₂O₃-SiO₂ melt in pure O₂ vs. cesium concentration in the liquid phase.

Condition: 1 g of CaO-Al₂O₃-SiO₂ at eutectic composition (0.651 SiO₂ – 0.91Al₂O₃ – 0.258CaO) with 1–11 mg/kg Cs₂O + 100 g O₂, total pressure of 1 atm, 1473 K. The activity coefficient of Cs₂O in the melt phase ($\gamma_{Cs_2O}$) was set to be $10^{-14.9}$ (adjusted).

Calculated $P_{Cs,total} = 7.2 \cdot 10^{-11}$ atm at 1473 K, $C_{Cs_2O} = 0.00001$ g-Cs/g-silicate.

According to the literature [S4-5], $\log(P_{Cs}/atm) / C_{(g-Cs/g-silicate)} = -17300/T + 6.6$. $P_{Cs}=7.2 \cdot 10^{-11}$ atm at 1473 K, $C_{Cs_2O} = 0.00001$ g-Cs/g-silicate.
Figure S6. Estimated leachability of cesium aluminosilicates in water.

All minerals and aqueous solutions were included in the equilibrium calculations. Here, we used the solution data for dilute aqueous solution (FThelg-AQID) of FactSage7.0 (GTT-technologies).

CsAlSiO₄ Condition: 100 mg CsAlSiO₄ with 1 L water. Calculated leachability (nCs⁺ / nCsAlSiO₄) was 0.95 % at 298 K. According to literature, leachability of CsAlSiO₄ in water without pH adjustment was 1.03 %. [ref. 68]

CsAlSi₂O₆ Condition: CsAlSi₂O₆ 100 mg / 1 L water. Calculated leachability (nCs⁺ / nCsAlSi₂O₆) was 0.24 % at 298 K. According to literature, leachability of CsAlSi₂O₆ was approximately 3 to 10 % at pH=1.02. [ref. 69]

CsAlSi₅O₁₂ Condition: CsAlSi₅O₁₂ 100 mg / 1 L water. Calculated leachability (nCs⁺ / nCsAlSi₅O₁₂) was 0.0001 % at 298 K. According to literature, leachability of CsAlSi₅O₁₂ was about 0.4 % at pH = 1.02. [ref. 69]
Figure S7. Main components of calculated equilibrium products from the incineration of RDF1 and MSW2-4.
The letters (g), (s), (SLAG) in the legends indicate that the species are pure gas-phase species, pure solids, or a species in a molten slag, respectively. The letters (SPINA), (Mel_A), and (WOLLA) indicate that the species are part of a solid solutions of spinel, melilite, or wollastonite, respectively. The vertical axis in each bar graph represents the amount of species in mol per 100 g of waste (wet base).
Figure S8. Calculated equilibrium products of alkali species generated from the incineration of RDF1 and MSW2-4.

The letters of (g), (s), (ss), (KNSO), (SLAG) in the legends indicate that the species are pure gas-phase species, pure solids, part of a solid-solution of pollucite-leucite system, part of a solid-solution of sulfate, or a species in the molten slag, respectively.
Figure S9. Predominance diagram of Cs-Cl-O-H system at 1000 °C showing the most stable gas species at equilibrium as a function of the H$_2$O and HCl partial pressures.

$P_{O_2}$ was 0.1 atm and the pressures of Cs species were set to be $P_{Cs} = 1 \times 10^{-8}$ atm. (1×10$^{-8}$ atm for Cs, CsO, CsO$_2$, CsOH, and CsCl, and 5×10$^{-9}$ atm for Cs$_2$, Cs$_2$O, Cs$_2$O$_2$, (CsOH)$_2$, and (CsCl)$_2$)

The calculation was performed using Predom module of FactSage7.0 (GTT-technologies). The gas species included were all Cs oxide species listed in Table 3 and all other constituents of Cs-Cl-O-H systems, such as Cs, CsOH, CsCl, O, O$_2$, Cl, Cl$_2$, H, H$_2$, OH, HO$_2$, HCl, H$_2$O, and H$_2$O$_2$ from FactPS database.