



## ADIABATIC FLAME TEMPERATURE OF SODIUM COMBUSTION AND SODIUM-WATER REACTION

**Y. OKANO, Japan Nuclear Cycle Development Institute**

4002 Narita, O-arai, Ibaraki, 311-1393 Japan  
okano@oec.jnc.go.jp

**A. YAMAGUCHI, Japan Nuclear Cycle Development Institute**

4002 Narita, O-arai, Ibaraki, 311-1393 Japan  
yamaguti@oec.jnc.go.jp

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### Introduction

Sodium is used as a coolant of liquid metal fast breeder reactor (LMFBR) because it has excellent thermal conductivity, hardly moderates or absorbs fast neutron, and shows good compatibility with steel structural materials. However, pure sodium is very reactive from the chemical point of view. Sodium easily reacts with oxygen and water accompanying heat release in most cases. Sodium combustion can occur in the atmospheric air in at temperature high enough to ignite. More active reaction can occur when it contacts with water.

In the safety analysis, sodium combustion and sodium-water reaction have been dealt as not flame/reaction zones but sheets, where whole fuel and oxidizer react into product. The 'sheet' temperature can be numerically calculated from mass and energy conservation equations, but it is overestimated and conservative one. According to combustion engineering, reaction 'zone' temperature can be analyzed as adiabatic flame/reaction zone temperature.

Numerical calculation program for adiabatic temperature of sodium reactions (GENESYS) is developed. In this paper, background information of sodium fire and sodium-water reaction accidents of LMFBR is mentioned at first. Next, numerical analysis method of GENESYS is described in detail. Next, adiabatic flame temperature and composition of sodium combustion are analyzed, and affect of reactant composition, such oxygen and moisture, is discussed. Finally, adiabatic reaction zone temperature and composition of sodium-water reaction are calculated, and affects of reactant composition, sodium vaporization, and pressure are stated.

### Sodium Combustion and sodium-water reaction in LMFBR

Liquid sodium as a coolant flows in piping during reactor operating period above melting point of 98 degree centigrade. For example, in the prototype fast reactor MONJU in Japan, sodium temperature is approximately 500 degree centigrade in the hot-leg of the secondary cooling system. The piping room of the secondary loop is

filled with air, while that of the primary loop is filled with inert gas, or nitrogen. In the fire, combustion heat and products are generated. Combustion heat is transferred to the steel-plate floor and the atmosphere by thermal conductivity and radiation. As combustion products, corrosive material of sodium compounds such as sodium oxide ( $\text{Na}_2\text{O}$ ), sodium peroxide ( $\text{Na}_2\text{O}_2$ ) and sodium hydroxide ( $\text{NaOH}$ ) are observed, and they are transferred in aerosol form to the molten pool on the floor and the atmosphere. Combustible gas such as hydrogen ( $\text{H}_2$ ) can be produced in peculiar atmosphere conditions. The combustion behaviors, such as how much heat is generated and what kind of reaction product is produced, are focussed on and dealt with in detail in the fire analyses [2],[3].

In the steam generator (SG) between the secondary loops and the main-steam loops, water is heated and changed from liquid into vapor for the steam turbine and the electric power generation. In the SG, water flows in the helical-shaped tubes, and liquid sodium flows outside the tubes [4]. In the majority of the SG design, water/steam inside tubes is under high-pressure condition, and sodium outside is under low-pressure one. When water leaks from the tubes incidentally, sodium and water contact with directly. This is so-called sodium-water reaction accident of the LMFBR. A sodium leak accident happened in the superheater on the fast reactor, PFR [4]. Reaction products such as  $\text{NaOH}$ ,  $\text{Na}_2\text{O}$  and  $\text{H}_2$ , and reaction heat are liberated. The  $\text{NaOH}$  and  $\text{Na}_2\text{O}$  are corrosive. The  $\text{H}_2$  causes the increase in the pressure on the sodium-side of the SG, and the reaction heat causes the increase in the temperature of the tubes. The heat liberated and the corrosive reaction products can damage surrounding tubes, and caused the event to escalate.

#### Reaction Models in the Safety Analysis Code

Fire analyses had been done with CONTAIN [5], SPARY [6] and NACOM [7] in the past. In these codes, sodium combustion was dealt based on many experiments to investigate amounts of reaction heat and product. Combustion flame is dealt by analytical model so-called flame sheet one as schematically depicted in Figure 1. In this model, combustion flame is dealt as infinitesimally thin reaction plane, where fuel and oxidizer contact and react into product. Reaction is dealt as overall one. The temperature at the reaction plane is calculated by solving mass and energy conservation equations. Hence, reaction rate is determined from the mixing of the fuel and oxidizer by convection and diffusion.

Analyses of sodium-water reaction accident had been done with numerical code such as PLEXUS [8] and CHAMPAGNE [9]. In these numerical codes, reaction of sodium with water is dealt as overall reaction, and reaction rate is determined from mixing of two compounds or given as input valuable.

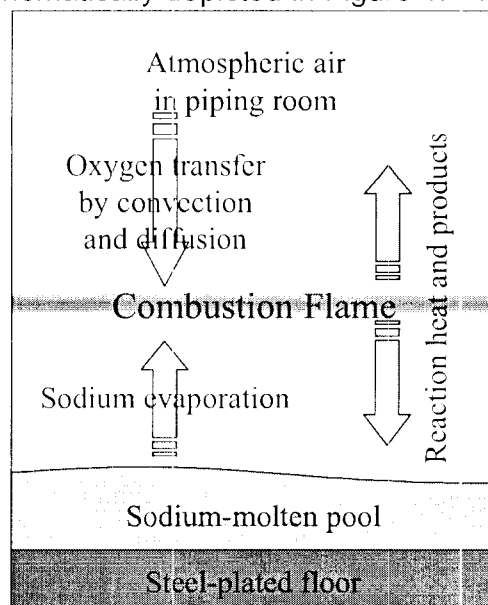


Figure 1 Schematic of flame sheet model of sodium combustion

### Adiabatic temperature of flame and reaction zone

Using the analytical models mentioned above, the temperature of flame and reaction zone is determined by mass and energy conservation equations, and is calculated to be high unlimitedly as supply of fuel and oxidizer increases. The maximum temperature, which should subsist physically, is not theoretically defined. This is because, reverse reactions and intermediate reaction products are not considered in overall reaction. When reaction proceeds, the temperature of reaction zone increases by the heat of reaction. Simultaneously, chemical equivalence in the reaction equation gradually declines from production side to fuel-oxidizer one, and progress of reaction becomes slower. Moreover, reaction products are not only species described explicitly in the chemical equation, but some radical and ionized ones. These branching processes take the heat of reaction away from the flame and reaction zone. Consequently, solving only mass and energy conservation equations is not enough to determine the flame and reaction zone temperature. The change of chemical reaction with temperature must be considered.

From the combustion-engineering point of view, adiabatic flame temperature in the combustion is well known as the maximum theoretical temperature of flame and reaction zone. The temperature of actual combustion flame is lower than adiabatic flame temperature because of the heat loss by radiation and thermal conduction from hot flame / reaction zone to surrounding environment.

In a closed, adiabatic system at constant pressure, the first law of thermodynamics gives energy conservation of the chemical reaction system. Furthermore, the overall mass is constant. Moreover, g-atom number of element is also constant during the reaction, although the amount of molecules usually changes in a chemical reaction. By using energy, mass and element conservation equations, kind and amount of reaction product and temperature can be calculated for chemical equilibrium system. Detail is described in the next chapter.

### **Chemical Equilibrium Calculation Program, GENESYS**

The chemical equilibrium composition describes theoretical thermochemical properties, which can be applied to a variety of problems in chemistry and chemical engineering. Some numerical codes are used to design equipment such as compressors, turbines, engines, heat exchangers, and chemical processing equipment [10]. But most of them are design for applying conventional fuel and chemical compounds, and are not for dealing with sodium compound, such as  $\text{Na}_2\text{O}$ ,  $\text{Na}_2\text{O}_2$ ,  $\text{NaH}$  and so on. Hence, chemical equilibrium calculation program for generic chemical system (GENESYS) is developed in this study for analyzing sodium combustion and sodium-water reaction, and for using as sub-routines in sodium-fire analysis code [11].

A numerical calculation of equilibrium of complex chemical systems requires a number of numerical calculations for non-linear equation system. Chemical equilibrium is usually described by either of two equivalent formulations. One is equilibrium constant; the other is minimization of free energy. It has been shown that the two formulations reduce to the same number of iteration equation, namely equivalent. The calculation method using equilibrium constant has advantages that

relationship between reactants and products can be directly described in chemical equations, and easy to formulate this relationship into equation system for numerical calculation. However, there are disadvantages of numerical difficulties when dealing with more kind of species, and dealing with condensed species. For these reasons, the free-energy minimization formulation is selected to use in this study.

### Governing equation

Governing equations are given by conservation of element mass and energy, equation of state, and equation of Gibbs free energy.

The atom numbers of element are defined as follows.

$$e_i \equiv \sum_j \sum_k (a_{ij} \cdot n_{j,k}) = \text{const.} (\equiv e_i^0) \quad (1)$$

The energy conservation equation can be written using species enthalpy as follows.

$$H \equiv \sum_j \sum_k (n_{j,k} \cdot h_{j,k}) = \text{const.} (\equiv H^0) \quad (2)$$

The equation of state for the mixture of gas is as follows.

$$PV = n_{\text{all, gas}} RT \quad (3)$$

Relationship mole of species (j) in phase (k) and total mole number of phase (k) is described as follows.

$$n_{\text{all, k}} = \sum_j n_{j,k} \quad (4)$$

Gibbs free energy for a mixture of species is given by

$$G = \sum_j \sum_k (\mu_{j,k} \cdot n_{j,k}). \quad (5)$$

Assigning any two of state functions can specify thermodynamic state. Chemical composition of 'T-P system', where temperature and pressure are given, can be specified from the equations of (1), (4) and (5). This system is used to know the equilibrium composition at the reaction zone where temperature and pressure are measured. It can be known from equation (2) that reaction is exothermic or endothermic ones, and from (3) volume change by the reaction can be known. In the 'H-P system', where pressure and initial temperature are given, not only chemical composition but also reaction temperature can be specified from the equations of (1), (2), (4) and (5). This system is used to know adiabatic flame and reaction zone temperature and composition.

### Chemical Potential

In this paper, it is assumed that whole gaseous species to be ideal, all liquid ones regular solution, and solid ones pure. Equation (3) is assumed correct even when amounts of condensed species are present. Namely, the condensed species are assumed to occupy a negligible volume. In the variables V, n, and P, the volume and moles refer to gases only while the mass is for the entire mixture including condensed species. Based on the assumptions in the selection of equation of state as (3), the chemical potential can be obtain for gaseous species as follows.

Gaseous: 
$$\mu_{j,gas} = \mu_{j,gas}^0 + RT \ln \left[ P \cdot \frac{n_{j,gas}}{n_{all,gas}} \right] \quad (6)$$

Liquid and solid species are as follows.

Liquid: 
$$\mu_{j,liquid} = \mu_{j,liquid}^0 + RT \ln \left[ \frac{n_{j,liquid}}{n_{all,liquid}} \right] \quad (7)$$

Solid: 
$$\mu_{j,solid} = \mu_{j,solid}^0 + RT \ln \left[ \alpha_{j,solid} \right] \quad (8)$$

In this study, chemical reactivity of solid species is dealt as ideal one under assuming solid compounds can be dealt as to be pure and within one phase. The condition for chemical equilibrium between phases can be written as the relationship between chemical potentials in ether phases as follows.

$$\mu_{j,gas} = \begin{cases} \mu_{j,liquid} & (T \geq T_{melt}) \\ \mu_{j,solid} & (T < T_{melt}) \end{cases} \quad (9)$$

The Gibbs free energy of mixture should be minimized under the binding conditions of element constraints. Lagrangian's method of undetermined multipliers is used to solve the system, and it is given by

$$L = G + \sum_i \left[ \lambda_i (e_i - e_i^0) \right] \quad (10)$$

Variational principle is applied to equation (10), and following equation is deduced.

$$\delta L = \sum_j \sum_k \left\{ \left[ \mu_{j,k} + \sum_i (\lambda_i \cdot a_{ij}) \right] \delta n_{j,k} \right\} + \sum_i \left[ (e_i - e_i^0) \delta \lambda_i \right] = 0 \quad (11)$$

Treating the variations  $\delta n$  and  $\delta \lambda$  as independent gives

$$\mu_{j,k} + \sum_i (\lambda_i \cdot a_{ij}) = 0 \quad (12)$$

and also the mass balance equations for element (1). As the equation, which gives the minimization condition of the Gibbs free energy, equation (11) is used in the calculation instead of equation (5). The numerical values of chemical potential at standard state are generally stated in reference data such as JANAF table [12],[13].

### Calculation algorithm and procedure

The equation system is non-linear, simultaneous one. A descent Newton-Raphson method is used to solve it numerically. A Taylor series expansion is applied to equations (1), (4) and (11), and the following equation can be take.

$$\sum_j \sum_k (a_{ij} \cdot n_{j,k} \Delta \ln n_{j,k}) = \sum_j \sum_k (a_{ij} \cdot n_{j,k}) - e_i^0 \quad (13)$$

$$\sum_j n_{j,k} \Delta \ln n_{j,k} - n_{all,k} \Delta \ln n_{all,k} = n_{all,k} - \sum_j n_{j,k} \quad (14)$$

$$\Delta\mu_{j,k} + \sum_i (\Delta\lambda_i \cdot a_{ij}) = -\mu_{j,k} - \sum_i (\lambda_i \cdot a_{ij}) \quad (15)$$

Here,  $\Delta n_{j,k}$  can be written using mole numbers of species ( $n_{j,k}$ ) and in ether phase ( $n_{all,k}$ ) by making variations of equations (6), (7) and (8) as follows.

$$\Delta\mu_{j,gas} = RT (\Delta \ln n_{j,gas} - \Delta \ln n_{all,gas}) \quad (16)$$

$$\Delta\mu_{j,liquid} = RT (\Delta \ln n_{j,liquid} - \Delta \ln n_{all,liquid}) \quad (17)$$

$$\Delta\mu_{j,solid} = 0 \quad (18)$$

Correcting variables are changed gradually in the iteration as follows.

$$n_{j,k}^{l+1} = n_{j,k}^l + n_{j,k} \Delta \ln n_{j,k} \quad (19)$$

$$n_{all,k}^{l+1} = n_{all,k}^l + n_{all,k} \Delta \ln n_{all,k} \quad (20)$$

$$\lambda_{j,k}^{l+1} = \lambda_{j,k}^l + \Delta \lambda_{j,k} \quad (21)$$

The calculation procedure is;

- 1) Estimate initial values of mole number of species ( $n_{j,k}$ ), Lagrangian multipliers ( $\lambda_i$ ),
- 2) Solve the matrix which is made from equations of (13) to (18),
- 3) Change correction variables with a small amount using equations (19) to (21),
- 4) Chemical potentials are recalculated using equations (6) to (8),
- 5) If the correction values are sufficiently small, equation solving by iteration is converged, and in case of T-P system calculation is finished,
- 6) In case of H-P system, temperature is sought for satisfying energy conservation (2) by using bi-section method.

### Chemical species dealt in GENESYS

Characteristics of GENESYS from the viewpoint of thermodynamics and applicable subject are listed in Table.1. Not only sodium combustion and sodium-water reaction, but also steel corrosion by sodium and combustion of conventional fuels can be dealt. Recently steel corrosion by sodium is observed in sodium fire experiment [1], and that should be considered in safety analysis of FBRs. Conventional fuels combustion, especially hydrogen combustion, is currently discussed in the safety analysis of CDA condition of LWRs. Chemical elements and species dealt in GENESYS are listed in Table.2. As reaction product of sodium combustion and sodium water reaction, not only species observed in experiments, but also ones listed in books of thermochemical reference data are considered in this study. This

<b>Analysis Objects</b>	Sodium Combustion, Sodium-Water reaction, Steel Corrosion by Sodium, Fuel combustion
<b>Chemical Species</b>	Sodium combustion products, Sodium-Water reaction products, Iron-Based compounds, Iron-Sodium Oxides, Combustion product of conventional fuel
<b>Phase</b>	Multi-phase (Solid + Liquid + Gas)
<b>Thermochemical System</b>	TP system for equilibrium state, HP system for adiabatic reaction change and state, SP system for isentropic change and state,

**Table.1 Characteristics of GENESYS**

is because more number of considered species, more accurate chemical composition at equilibrium and adiabatic mixture and temperature. And also because species detected at experiments should be only reaction product enough to be detected by measure devices, and small amount species may be neglected in those experiments. Iron based compounds and iron-sodium-oxide are included for extend GENESYS to corrosion problem. Carbon-based and nitrogen-based compound is also included for extend to conventional fuel and hydrogen combustion.

Element	Classification	C, H, N, O, Na, Fe, Cl, Ar,
Gas	C / H / N / O	C, C <sub>2</sub> , C <sub>3</sub> , H, H <sub>2</sub> , N, N <sub>2</sub> , O, O <sub>2</sub> ,
	CH / CN	CH, CH <sub>2</sub> , CH <sub>3</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>4</sub> , CN, C <sub>2</sub> N <sub>2</sub> , HCN,
	CO <sub>2</sub> / OH	CO, CO <sub>2</sub> , HCO, H <sub>2</sub> O, OH,
	NO <sub>x</sub> / NH	NO, NO <sub>2</sub> , N <sub>2</sub> O, NH, NH <sub>3</sub> ,
	Na	Na, Na <sub>2</sub> , NaH, NaOH, Na <sub>2</sub> (OH) <sub>2</sub> , NaO, Na <sub>2</sub> O, Na <sub>2</sub> O <sub>2</sub> , NaO <sub>2</sub> ,
	Fe	Fe, FeO, Fe(OH) <sub>2</sub> ,
Liquid	Cl / Ar	Cl, Cl <sub>2</sub> , CCl, CCl <sub>4</sub> , ClCN, HCl, ClO, ClO <sub>2</sub> , Cl <sub>2</sub> O, COCl <sub>2</sub> , Ar
	OH	H <sub>2</sub> O,
	Na	Na, NaOH, Na <sub>2</sub> O, Na <sub>2</sub> O <sub>2</sub> , NaO, Na <sub>2</sub> CO <sub>3</sub> ,
Solid	Fe	Fe, FeO, Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub> ,
	NaFe	NaFeO <sub>2</sub> , Na <sub>2</sub> FeO <sub>4</sub> , Na <sub>3</sub> FeO <sub>5</sub> , Na <sub>4</sub> FeO <sub>6</sub> ,
	Na	Na, NaH, NaOH, Na <sub>2</sub> O, Na <sub>2</sub> O <sub>2</sub> , NaO, Na <sub>2</sub> CO <sub>3</sub> , NaHCO <sub>3</sub> ,
	Fe	Na <sub>4</sub> FeO <sub>6</sub> , Na <sub>3</sub> FeO <sub>5</sub> , Na <sub>2</sub> FeO <sub>4</sub> , Na <sub>4</sub> Fe <sub>2</sub> O <sub>7</sub> , Na <sub>2</sub> Fe <sub>2</sub> O <sub>7</sub> , Na <sub>4</sub> Fe <sub>3</sub> O <sub>11</sub> , Na <sub>8</sub> Fe <sub>5</sub> O <sub>23</sub> .

Table.2 Elements and species dealt in GENESYS

### Adiabatic Flame Temperature at the sodium combustion

Chemical composition and temperature of combustion flame is calculated for conditions of sodium-fire accident in piping room. Sodium combustion in gas mixture of oxygen, nitrogen, and water vapor is analyzed with sodium temperature of leaked from piping. The pressure is one atm, and initial temperature of sodium and gas mixture is 500C. Initial chemical compositions for combustion in dry air can be described in ternary system of sodium-oxygen-nitrogen. Those for in moist air can be in pseudo-quaternary system of sodium-oxygen-nitrogen-water. Radiation heat remove from flame is neglected in this study for conservative estimation. Initial composition of sodium is assumed pure monatomic molecule of sodium gas (Na<sub>(g)</sub>), instead of practical mixed composition of Na<sub>(g)</sub>, diatomic gaseous molecules (Na<sub>2(g)</sub>) and liquid sodium (Na<sub>(l)</sub>). This is also for conservative analysis. Namely, decomposition energy from Na<sub>2(g)</sub> to 2Na<sub>(g)</sub>, and evaporation energy from Na<sub>(l)</sub> to Na<sub>(g)</sub> are assumed injected initially.

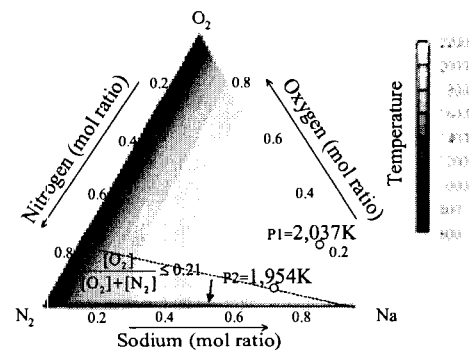


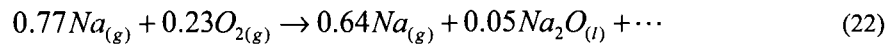
Figure 2 Adiabatic flame temperature of sodium combustion in dry air

Calculations are carried out for initial compositions to fill ternary diagram sufficiently for drawing continuous contour lines. Calculation result of adiabatic flame temperature of sodium combustion in dry air is shown in Figure.2. The initial composition at point #1 represents the maximum temperature condition, and its value is 2,037K. This condition can be expressed as the 'combustion in oxygen'. Ratio of Na : O<sub>2</sub> : N<sub>2</sub> equals to .77 : .23 : 0.0. The reaction product composition is shown in

	Point #1 Combustion in Oxygen	Point #2 Combustion in Dry Air	Point #3 Combustion in Moist Air	
Initial Composition [mol]	Na:O <sub>2</sub> = .77:.23	Na:Air = .7:3	Na:Air:H <sub>2</sub> O = .69:.29:.02	
Adiabatic Flame Temperature [K]	2,037	1,954	1,946	
Composition of Flame	Na <sub>2</sub> O(l)	0.0488	0.0523	0.0372
	Na <sub>2</sub> O(g)	0.0094	0.0052	0.0046
	Na <sub>2</sub> O <sub>2</sub> (l)	0.0022	0.0011	0.0007
	Na <sub>2</sub> O <sub>2</sub> (g)	~ 0	~ 0	~ 0
	NaO <sub>2</sub> (l)	0.0043	0.0011	0.0006
	NaO <sub>2</sub> (g)	0.0005	0.0001	0.0001
	NaO(g)	0.0130	0.0045	0.0038
	NaOH(l)	0	0	0.0011
	NaOH(g)	0	0	0.0464
	Na(g)	0.6363	0.5721	0.5387

Table 3 Composition of Adiabatic Combustion Flame

Table.3. Liquid sodium oxide ( $\text{Na}_2\text{O}_{(l)}$ ) is the main product, and produced approximately 5 percent. The second one is gaseous sodium monoxide ( $\text{NaO}_{(g)}$ ) of around 1.5 percent. Subsequently, gaseous sodium oxide ( $\text{Na}_2\text{O}_{(g)}$ ), liquid sodium superoxide ( $\text{NaO}_2_{(l)}$ ), and liquid sodium peroxide ( $\text{Na}_2\text{O}_2_{(l)}$ ) are produced below unity percent. Unreacted  $\text{Na}_{(g)}$  stay as residue, whose mole fraction in adiabatic flame is over 60 percent. The chemical reaction at the point #1 can be outlined as follows.



The small amount of  $\text{Na}_{(g)}$  ( $0.77-0.64=0.13$ ) reacted in this reaction. This is due to chemical unstably of the main product ( $\text{Na}_2\text{O}$ ) in high temperature condition. Figure 3 shows calculation result in T-P system of sodium and oxygen reaction with inert nitrogen gas ( $\text{N}_2$ ). This calculation is carried out with initial composition of ( $\text{Na}, \text{O}_2, \text{N}_2$ )=(10, 8, 20 mol), pressure of  $1 \times 10^5$  Pa, and variable value of temperature from 500K to 3000K. As shown in this figure,  $\text{Na}_2\text{O}_{2(s)}$  and  $\text{Na}_2\text{O}_{2(l)}$  are chiefly produced at relatively low temperature, and  $\text{Na}_2\text{O}_{(s)}$  and  $\text{Na}_2\text{O}_{(l)}$  is at the temperature relatively high but below ca.1,900K. Small amount of  $\text{NaO}_2_{(l)}$  is also produced below ca. 1,900K. Above ca. 1,900K, all sodium compounds in condensed phase is decomposed into sodium and oxygen, and only sodium monoxide gas ( $\text{NaO}_{(g)}$ ) is stable as a sodium compound. Hence, residue  $\text{Na}_{(g)}$  affect on chemical equilibrium to incline from reactant side to production side to oppose thermal decomposition of sodium compounds.

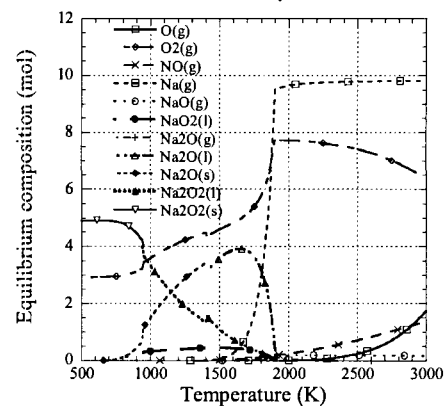


Figure 3 Equilibrium composition of sodium reaction with oxygen

Broken line in Figure 2 represents dry air condition as mixture of oxygen and nitrogen with 21 : 79 mole ratio. Oxygen concentration decreases with proceeding sodium fire accident, which is represented by area below this line. The initial composition in this area that gives the maximum temperature is shown as point #2. The point #2 is on the line of oxygen concentration of 21 percent. The temperature of the point #2 is 1,954K, which is lower than that of point #1. This is because nitrogen is inert gas and works as heat sink to suppress the increase in temperature. Chemical composition at point #2 is shown in Table.3. The mole ratio of sodium and air of the initial mixture is .70 : .30. Main product is, same as in case of point #1,  $\text{Na}_2\text{O}_{(l)}$ . However, the second and third most ones are  $\text{Na}_2\text{O}_{(g)}$  and  $\text{NaO}_{(g)}$  respectively, and the order is opposite to that at point #1. This is because the change of chemical potential by inert  $\text{N}_2$  much affects on activity on  $\text{NaO}_{(g)}$  than that on  $\text{Na}_2\text{O}_{(g)}$ .

The adiabatic flame temperature is calculated for the initial conditions described as a gray-colored plane in quaternary system in Figure 4. The point A corresponds to the atmospheric air condition with saturated water vapor at the temperature of 40C. Line between points A to B is the condition where sodium combustion occurs and oxygen concentration decreases. Line between points A to

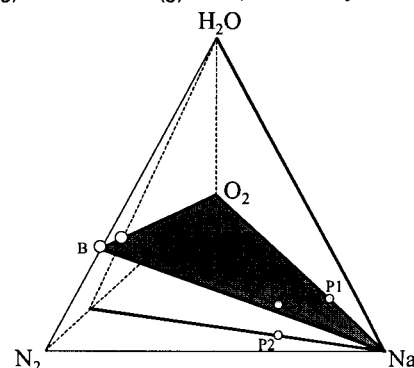


Figure 4 Pseudo-quaternary system for sodium-water reaction



Na describes the change of mole ratio of sodium to air. Calculation result is shown in Figure 5. The point #1 gives the maximum flame temperature, which is the same as in the dry air. Oxygen concentration of 21 mole-percent is drawn as broken line in the figure. The initial condition which gives the maximum temperature below the line is point #3, where mole ratio of initial sodium and moist air is .69 : .31., adiabatic temperature is 1,946K, and chemical composition is shown in Table 3.  $\text{NaOH}_{(g)}$  is produced mainly as much as approximately 5 percent. The second most one is  $\text{Na}_2\text{O}_{(l)}$  of around 4 percent. By comparing point #3 with point #2, it can be known that, roughly speaking, added water vapor reacts with residue  $\text{Na}_{(g)}$  and produced  $\text{Na}_2\text{O}_{(l)}$  in the case of point #2, and reacts into  $\text{NaOH}_{(g)}$ . The reason for formation of  $\text{NaOH}_{(g)}$  is due to its low chemical potential. Moreover, it is a stable compound at high temperature in comparison with  $\text{Na}_2\text{O}$ . Figure 6 shows the calculation result of sodium reaction with oxygen and water in T-P system. Na reacts with water easier than oxygen due to lower chemical potential, and gaseous NaOH can be produced over 1,700K where sodium oxide is decomposed. Adiabatic flame temperature of point #3 is lower than that of point #2, despite that whole amount of sodium compound (mainly  $[\text{NaOH}] + [\text{Na}_2\text{O}]$ ) is large. This is because reaction heat of  $\text{Na}_2\text{O}_{(l)}$  is higher than that of  $\text{NaOH}_{(g)}$  due to condensation heat release by the reaction from  $\text{Na}_2\text{O}_{(g)}$  to  $\text{Na}_2\text{O}_{(l)}$ .

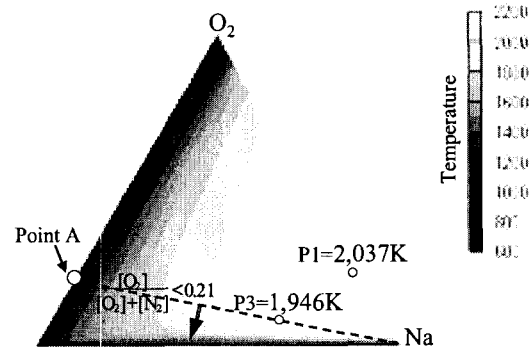


Figure 5 Adiabatic reaction zone temperature of sodium-water reaction

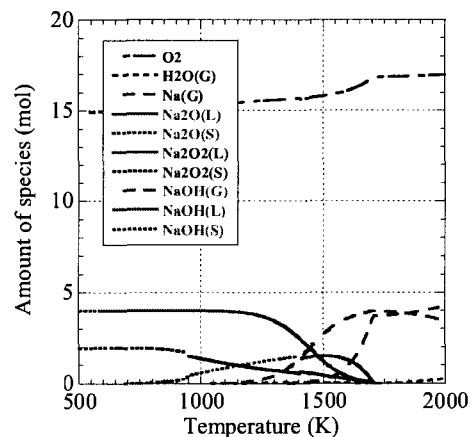


Figure 6 Equilibrium composition of sodium reaction with oxygen and water

### Adiabatic reaction zone temperature of sodium-water reaction

Chemical composition and temperature at the sodium-water reaction zone is calculated using GENSYS for accidental conditions in the SG. After water leaked from tube into sodium, it is estimated that water evaporates into critical flow, and contacts with liquid sodium or vaporized sodium [4]. Initial temperature of sodium and water is 480C. Initial compositions can be given in binary system of sodium and water. System pressure is dealt as variable parameter because the pressure during the leakage can be estimated from a few bars as low as that in sodium secondary loop up to approximately 150 bars as high as that of water-cooling system. Radiation heat remove from reaction zone is neglected due to the same reason as in sodium combustion case. Two initial compositions are assumed for Na; one is a pure monatomic molecule of sodium gas ( $\text{Na}_{(g)}$ ), and the other is liquid sodium ( $\text{Na}_{(l)}$ ). The former one is for the conservative analysis, because evaporation and decomposition energy is added before the reaction. The latter is to investigate the effect of sodium evaporation on reaction zone temperature.

Adiabatic temperature and composition changes is shown in Figure 7 for the case of reaction of  $\text{Na}_{(g)}$  with  $\text{H}_2\text{O}_{(g)}$  at the pressure of unity in bar. The maximum temperature of 1,616K is given at the initial composition of Na of 0.53 mole and  $\text{H}_2\text{O}$  of 0.47 mole. This point (named point #4) is a little bit inclined to sodium rich condition (left-hand side) in the figure. This is due to the change in product composition. Main reaction product is  $\text{NaOH}_{(l)}$  and  $\text{NaOH}_{(g)}$ , and summation of two species is symmetric with respect to the equivalent mole condition ( $[\text{Na}] = [\text{H}_2\text{O}] = 0.5 \text{ mol}$ ). On the other hand, residual gaseous species is different in both sides. Namely, the amount of  $\text{Na}_{(g)}$  is larger than that of  $\text{H}_2\text{O}_{(g)}$  in the left-hand side of the figure, and the amounts are reversed on the right-hand side. The specific heat of these two gaseous species is different, and that makes adiabatic temperature different. Specific heat of monatomic gas  $\text{Na}_{(g)}$  is smaller than that of triatomic gas  $\text{H}_2\text{O}_{(g)}$ . Hence, in the left-hand side, heat reaction to be spent for increasing residual gas becomes smaller and system temperature becomes higher than those do in the right-hand side.

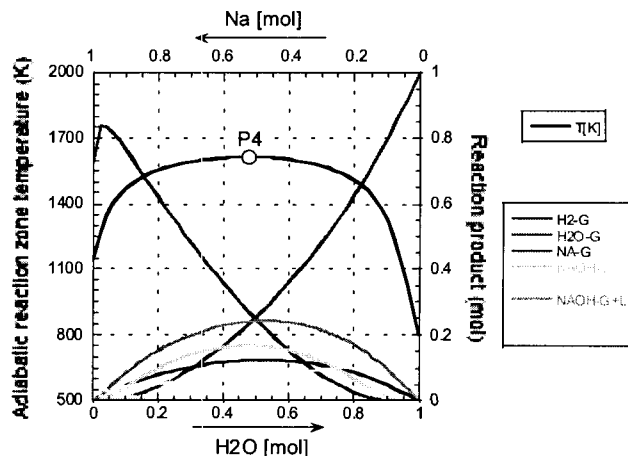


Figure 7 Changes of adiabatic temperature and composition with initial sodium-water ratio at 1 bar

Adiabatic temperature change with the system pressure is shown in Figure 8. The temperature increases with the system pressure, which agrees with the previous studies on sodium-water reaction [4]. Reaction products at the points #5 and #6 in Figure 8 are shown in Table 4. The main products are  $\text{NaOH}$  and  $\text{H}_2$ , and their amounts increase with the system pressure. Moreover, small amount of  $\text{Na}_{2(g)}$ ,  $(\text{NaOH})_{2(g)}$ ,  $\text{Na}_2\text{O}_{(l)}$ ,  $\text{NaH}_{(g)}$ ,  $\text{NaH}_{(l)}$  is produced in the sodium-water reaction. The reason for the increase in temperature with the pressure can be understood from mole change between those before and after the reaction. Mole number before the reaction is unity in binary system. That after the reaction can be known from the calculation by GENESYS as shown in Table 4. These ratio is below unity, which means more pressurized the system is, more inclined to the production side the chemical equation is.

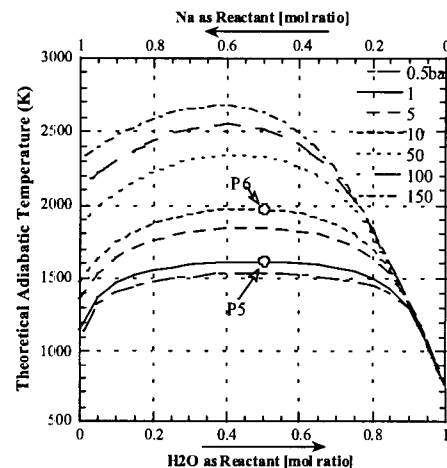


Figure 8 Adiabatic reaction zone temperature of  $\text{Na}_{(g)}\text{-H}_2\text{O}$  reaction

In the case of initial sodium as  $\text{Na}_{(l)}$ , adiabatic temperature change with the pressure is shown in Figure 9. Reaction productions at the points #7 and #8 are shown in Table 4. Comparing Figures 8 and 9, Na rich sides in two figures are different significantly. This is because that, in the  $\text{Na}_{(g)}$  case, monatomic sodium gas  $\text{Na}_{(g)}$  reacts into  $\text{Na}_{2(g)}$  and condenses to  $\text{Na}_{(l)}$ , and heat of reaction and condensation is released, and the adiabatic temperature increases. It can be concluded that to

assume initial sodium as to be  $\text{Na}_{(g)}$  is too much conservative, especially in the sodium rich condition. When comparing the maximum temperature around equivalent mole condition in the same pressure cases in Figures 8 and 9, the difference is small (approximately 50K) under 5 bar conditions. However, in cases of above 10 bar, the difference become large, and the effect of sodium evaporation should be considered in the sodium-water reaction analysis.

The adiabatic reaction zone temperature and composition of sodium-water reaction can be summarized as follows.

- 1) The maximum adiabatic temperature is achieved when equivalent moles of sodium and water react.
- 2) Main reaction products are  $\text{NaOH}_{(g)}$ ,  $\text{NaOH}_{(l)}$  and  $\text{H}_{2(g)}$ . Small amounts of  $\text{Na}_{2(g)}$ ,  $(\text{NaOH})_{2(g)}$ ,  $\text{Na}_2\text{O}_{(g)}$ ,  $\text{NaH}_{(g)}$  and  $\text{NaH}_{(l)}$  can be observed.
- 3) The temperature increases with the pressure due to the decrease in mole number by the reaction.
- 4) In the sodium-rich condition, initial sodium composition (the ratio of  $\text{Na}_{(g)}$ ,  $\text{Na}_{2(g)}$  and  $\text{Na}_{(l)}$ ) affects the temperature significantly.
- 5) At the sodium-water equivalent condition and the system pressure above 10 bar, initial sodium composition affects the adiabatic temperature. However, below 5 bar, it does not.

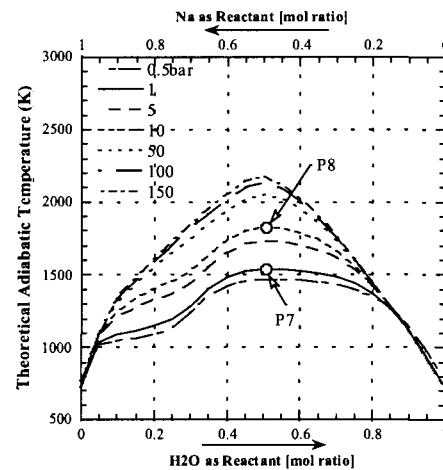


Figure 9 Adiabatic reaction zone temperature of  $\text{Na}_n\text{-H}_2\text{O}$  reaction

Table 4 Product compositions and Products/Reactants mole ratio of sodium-water reaction

Point #	$\text{H}_2\text{O}_{(g)}$	$\text{Na}_{(l)}$	$\text{Na}_{(g)}$	$\text{Na}_{2(g)}$	$\text{NaOH}_{(l)}$	$\text{NaOH}_{(g)}$	$(\text{NaOH})_{2(g)}$	$\text{Na}_2\text{O}_{(l)}$	$\text{NaH}_{(g)}$	$\text{NaH}_{(l)}$	$\text{H}_{2(g)}$	Products / Reactants mol ratio
5	251.1	1.662	245.4	1.082	79.41	165.0	1.572	1.325	0.003673	0.5637	124.8	0.872
6	202.5	7.536	185.1	2.481	139.6	153.3	0.8513	2.915	0.03459	1.959	149.2	0.846
7	135.8	6.965	124.1	0.5657	303.7	56.13	0.6037	3.153	0.0274	0.4091	183.5	0.815
8	97.87	18.94	71.97	0.9018	356.9	40.71	0.2747	3.942	0.1584	1.059	202.4	0.795

## Conclusion

Chemical equilibrium calculation program for generic chemical system (GENESYS) is developed in this study for the research on adiabatic flame temperature of sodium combustion and adiabatic reaction zone temperature of sodium-water reaction. The maximum flame temperature of the sodium combustion is 1,950K at the standard atmospheric condition, and is not affected by the existence of moisture. The main reaction product is  $\text{Na}_2\text{O}_{(l)}$ , and in combustion in moist air, with  $\text{NaOH}_{(g)}$ . The maximum reaction zone temperature of the sodium-water reaction is 1,600K, and increases with the system pressure. The main products are  $\text{NaOH}_{(g)}$ ,  $\text{NaOH}_{(l)}$  and  $\text{H}_{2(g)}$ . Sodium evaporation should be considered in the cases of sodium-rich and high pressure above 10 bar.

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