

# Mathematical Modeling for Vacuum Distillation in the Kroll Process



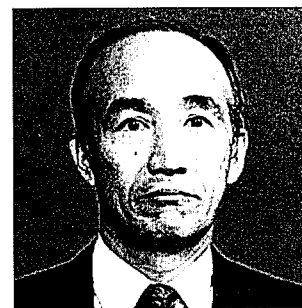
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## Abstract

*The distribution and morphology of residual chlorine in sponge titanium produced by the Kroll process was investigated.  $MgCl_2$  is the main species of the residual chlorine. The temperature distribution in the sponge titanium during the distillation process was measured. The temperature rise at the central part of the sponge is slower than that at peripheral region, and there are two temperature stagnant periods at 750 and 950 °C, which correspond to the vaporization of Mg and  $MgCl_2$ , respectively. Based on the above observation, a mathematical model has been developed to simulate heat transfer and vaporization phenomena. The temperature distribution and change was successfully expressed, thus the model can be a tool to quantitatively predict the effects of operation parameters.*

## 1. Introduction

In the manufacture of titanium sponge by the Kroll process, titanium tetrachloride is fed onto a molten magnesium bath in a closed vessel under an inert atmosphere to produce titanium sponge. This reduction step is followed by the vacuum distillation step wherein the reaction product magnesium chloride and reducing agent magnesium remaining in the vessel are vaporized and removed by heating under a vacuum. The titanium sponge thus obtained is melted in a vacuum arc furnace and cast into an ingot.

The residual chlorine content in conventional titanium sponge is about 500 to 1,500 ppm. A high chlorine concentration degrades the vacuum and destabilizes the arc during the vacuum arc melting of the titanium sponge. The titanium sponge also absorbs moisture and

results in oxygen and hydrogen contamination. These problems call for the amount of residual chlorine in the titanium sponge to be reduced as far as is possible.

The vacuum distillation operation of residual chlorine takes a few days or more to produce up to ten tons of titanium sponge. Improvement in the productivity in this process is desirable. The vacuum distillation step constitutes a complicated phenomenon in which the heat transfer in the titanium sponge cake is combined with the vaporization of magnesium chloride and magnesium. It is not easy to understand the effect of change in operating conditions. As such attempts, Arai and Kuramoto<sup>1, 2)</sup> conducted the two-dimensional unsteady-state heat transfer analysis of the titanium sponge cake in the vacuum distillation step, but did not treat the vaporization phenomenon itself. To investigate the form of residual chlorine and to

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semi-quantitatively evaluate the effect of the operation parameters, considered for shortening the vacuum distillation time, the present work measured the temperature change in the actual titanium sponge cake and developed a mathematical model for the heat transfer and vaporization phenomena taking place in the vessel.

**2. Forming Residual Chlorine in Titanium Sponge**

To study the mechanism of residual chlorine formation, the authors investigated the morphology of the chlorine in abnormally high residual chlorine portion at the center of titanium sponge after the reduction and vacuum distillation processes and the normal portion of titanium sponge for the form of residual chlorine.

**2.1 Forming residual chlorine after the reduction process (before the vacuum distillation process)**

Ten samples of about 10 grams each were taken from the top, middle, and bottom parts of titanium sponge cake in the vertical direction after the reduction and before the vacuum distillation. The chlorine and magnesium concentrations in the samples were investigated. The average chlorine and magnesium concentrations of the samples are given in **Table 1**. Table 1 also shows the magnesium chloride and metallic magnesium concentrations, calculated by assuming that chlorine exists entirely as magnesium chloride. The vertical distribution of magnesium chloride is more heterogeneous than metallic magnesium.

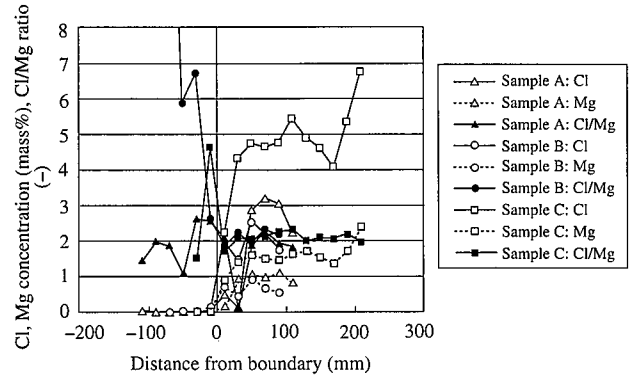
When the volumes of magnesium and magnesium chloride are calculated from their concentrations in Table 1 and the sum of these volumes is assumed to account for all of the pores in the titanium sponge, the porosity of sponge is about 30% in the top part and 55% or more in the bottom part. The porosity of the titanium sponge measured by the mercury porosity meter after the vacuum distillation process is 52% in the top part and 40% in the bottom part. It is presumed that the sponge cake before the vacuum distillation step has some pores in the top part and has almost all pores completely filled with the melt in the bottom part.

**2.2 High-chlorine portion remaining at center of titanium sponge cake after vacuum distillation process**

Titanium sponge cake formed in the reduction and vacuum distillation is cut along the horizontal section and crushed. At this time, the portion where chlorine remains to a high concentration can be confirmed with the naked eye at the center of the titanium sponge, though it is rare. **Fig. 1** shows the radial distributions of chlorine and magnesium concentrations across the boundary of the high-chlorine region in the titanium sponge cake. The chlorine concentration outside of the boundary is a few hundred parts per million, a level indicating the normal removal of chlorine. The chlorine and magnesium concentrations drastically rise at the boundary and remain constantly high inside of the boundary. The chlorine-to-magnesium molar concentration ratio is about 2. It can be thus inferred that chlorine exists mostly as magnesium chloride and little as metallic magnesium. If all of the chlorine analyzed is from magnesium chloride, the chlorine concentration is 3% to 8%. The highest chlorine concentration is similar to the magnesium chloride concentration of the top part of

**Table 1 Chlorine and magnesium concentrations in titanium sponge cake before vacuum distillation**

	Mg	Cl	Metallic Mg	MgCl <sub>2</sub>
Top	11.28	5.39	9.43	7.24
Middle	14.94	10.74	11.27	14.42
Bottom	18.49	16.75	12.76	22.48



**Fig. 1 Mg and Cl concentration distributions across the boundary of high-chlorine region observed at the center of titanium sponge cake**

the titanium sponge cake after the vacuum distillation.

In the vacuum distillation process, a temperature rise occurs from outside, so that the vaporization of magnesium, which has high vapor pressure, is possible. Chlorine presumably remained at a high concentration in the portions that were not hot enough for the vaporization of magnesium chloride. In the middle of the vacuum distillation, the boundary across which the chlorine concentration suddenly changes is thought to gradually move from the periphery to the center.

**2.3 Normal portions after the vacuum distillation process**

Two samples were taken from each of six portions, the center, mid-radius, and periphery of the top and bottom parts of titanium sponge cake after an ordinary vacuum distillation operation. Their chlorine and magnesium concentrations are given in **Table 2**.

The concentration of chlorine in a titanium sponge, with the vaporization normally completed in the vacuum distillation, is 1,200 to 1,600 mass ppm in the top part and 500 to 550 mass ppm in the bottom part. In the radial direction, the chlorine weight concentration has little or no difference in the bottom part, but is high at the center and declines toward the periphery in the upper portion. The vertical distribution of the magnesium concentration agrees with that of the chlorine concentration. The chlorine-to-magnesium molar ratio is also about 2 in general, and most of the chlorine and magnesium are considered to exist in the form of MgCl<sub>2</sub>.

The residual chlorine is found in the following three forms, by X-ray electron-probe microanalysis (EPMA) and other techniques. (1) magnesium chloride in pores in titanium particles observed on the polished cross section of the samples; (2) magnesium chloride trapped in the pores between the titanium particles observed on the crushed cross section of the samples; and (3) titanium dichloride adhering to the surfaces of the titanium particles. Of these compounds, the magnesium chloride entrapped in the pores between the titanium particles, as noted in (2), is considered to govern the residual chlorine concentration<sup>3)</sup>, because the particles are larger and observed more frequently than the other two.

**Table 2 Magnesium and chlorine concentrations (wt%) in titanium sponge after vacuum distillation**

	Center			Middle			Periphery		
	Cl	Mg	Cl/Mg	Cl	Mg	Cl/Mg	Cl	Mg	Cl/Mg
Top	0.16	0.06	1.8	0.133	0.05	1.8	0.124	0.05	1.4
Bottom	0.05	0.01	3.4	0.052	0.02	1.8	0.054	0.02	1.8

### 3. Temperature Measurement and Phenomena in Titanium Sponge Cake in Vacuum Distillation Process

#### 3.1 Temperature measurement

Chromel-alumel thermocouples were installed in an empty vessel used in the reduction process. The temperature change in the titanium sponge cake was measured, as the charge was processed by conventional reduction, vacuum distillation and cooling operations.

An example of temperature measurements is shown in Fig. 2. A general trend for the temperature change in the titanium sponge cake is as follows. At the start of the distillation, the inside of the titanium sponge cake is held at a practically uniform temperature of about 900°C. The internal temperature of the titanium sponge cake suddenly drops uniformly immediately after the start of the evacuation operation and remains constant at about 750°C for about 10 hours. The temperature then begins to rise from the periphery. The time required for the temperature at the center to rise thereafter is about 30 to 40 hours after the start of the distillation. This required time differs with the vertical position of the titanium sponge cake. In the middle to the center in the radial direction, there is a period during which the temperature rise from about 900°C becomes slow.

#### 3.2 Estimation of phenomena in vessel in vacuum distillation process

Magnesium and magnesium chloride remain in titanium sponge cake after the reduction and before the vacuum distillation. Some of the magnesium and magnesium chloride are also collected in the bottom of the vessel. Judging from their melting point, these substances are considered to exist in the molten state due to the heating up after the start of the vacuum distillation operation.

When the distillation is started with the entire titanium sponge cake held at about 900°C, the magnesium and magnesium chloride start to vaporize. The heat of the sponge cake is removed by the latent heat of vaporization of the magnesium and magnesium chlo-

ride. The amount of heat supplied from the outside is not enough to vaporize large amount of magnesium and magnesium chloride. As the temperature inside the sponge cake uniformly drops and the vapor pressure lowers, little or no vaporization takes place any more at the very beginning of the distillation process.

The magnesium chloride and magnesium in the bottom of the vessel are relatively low in heat transfer resistance. Heat is smoothly supplied to the magnesium chloride and magnesium to accelerate the progress of their vaporization. The vaporized gases rise through the gap between the sponge cake and the vessel inner wall and exit into the condenser. Since some of the vaporized gases are condensed in contact with the relatively low-temperature sponge, the heat supplied from the vessel outer wall is expended in the re-vaporization of the condensed gases in the peripheral region of the sponge cake. As a result, there occurs little or no apparent heat transfer to the sponge cake, the heat supplied from the vessel outer wall is consumed only in the vaporization in the bottom of the vessel, and the internal temperature of the sponge cake remains low.

When the vaporization from the bottom of the vessel, under the roster, is completed, heat starts to be supplied to the sponge cake itself. The sponge cake rises in temperature gradually from the periphery, and the vaporization of magnesium and magnesium chloride of high vapor pressure proceeds in that order. Since magnesium has a high latent heat of vaporization, the temperature rise is arrested during the vaporization of magnesium. The temperature suddenly rises when the vaporization of magnesium is completed. The temperature rise is slowed when the vaporization of magnesium chloride becomes active. When the magnesium chloride vaporizes at the center, the temperature at the periphery is considerably high, and the heat transfer from the vessel inner wall is retarded. The stagnation of the temperature rise is likely to appear at the center. The vacuum distillation operation ends with the completion of vaporization of the magnesium chloride and the temperature rise at the center. If the temperature rise is not large enough, there form portions where a large amount of magnesium chloride remains.

### 4. Mathematical Model for Vacuum Distillation Process

#### 4.1 Object of mathematical model

To shorten the vacuum distillation processing, it is necessary to identify the factors that govern phenomena leading to temperature rise at the center of the titanium sponge and to clarify their effects. A mathematical model has been developed to simulate the heat transfer in the titanium sponge and the vaporization behavior of magnesium and magnesium chloride in the vacuum distillation process. The purposes of the model was to clarify the factors governing the phenomena taking place in the titanium sponge and to understanding the effects of operating conditions semi-quantitatively. The model was designed as a one-dimensional cylindrical coordinate system, for simplicity. Thinking that modeling the period of vaporization from the inside of the sponge cake would be significant in studying the possibility of shortening the required vacuum distillation time, the mathematical model addressed the phenomena after the completion of vaporization from the bottom of the vessel.

Fig. 3 illustrates the relationships between the phenomena considered in the model. The temperature and the amount of vaporizing species are determined in the balance between the heat conduction in the titanium sponge, the vaporization rates, the latent heat of vaporization, while the macroscopic sponge properties change with the residual amounts of magnesium and magnesium chloride.

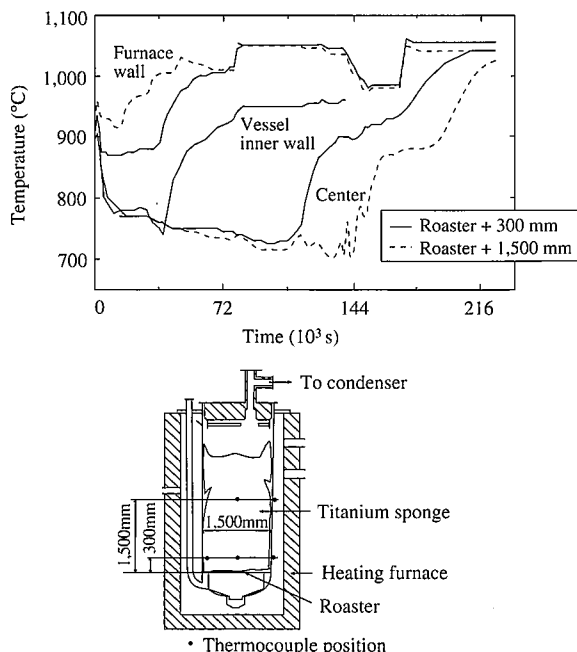


Fig. 2 Temperature measurement results of titanium sponge cake in vacuum distillation step

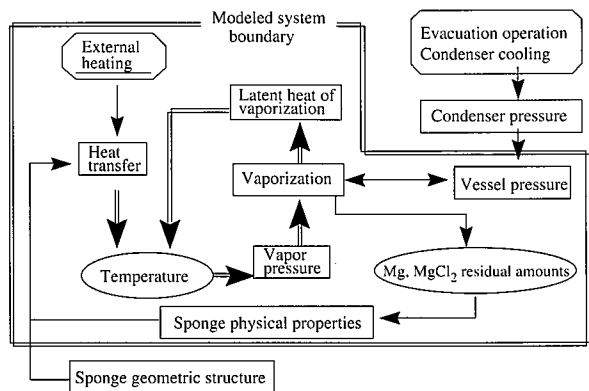


Fig. 3 Relationships between phenomena considered in model

4.2 Heat transfer mechanisms

In the commercial plant, the heat transfer routes are from the heater surface to the vessel outer wall and in the vessel wall. However, in the model the heat transfer between the sponge cake and the vessel inner wall, the heat transfer in the sponge cake, and the latent heat of vaporization of magnesium and magnesium chloride were calculated for the given vessel inner wall temperature. Because, in the actual operation, the vessel outer wall temperature is controlled, and the heat transfer rate of the metallic vessel wall is considered to be high.

The heat transfer phenomena in the sponge cake may be included conduction through the sintered particles, radiation through the pores, convection and conduction through the melt in the sponge, convection through the vaporized gases, and heat pipe-like heat transfer by repetition of vaporization and condensation. In this work, these heat transfer processes were represented by the effective thermal conductivity  $\lambda_{eff}$  and described by the following one-dimensional unsteady-state heat conduction equation, including the latent heat of vaporization:

$$\partial T/\partial t = (\lambda_{eff}/C\rho A) 2 \{ \partial A (\partial T/\partial r) \partial r \} - (H_{vap}/Cp) \quad \dots(1)$$

The heat transfer in the gap between the sponge cake and the vessel inner wall was assumed to be represented by the sum of radiation and conduction. The conduction term was expressed by the overall heat transfer coefficient that includes the effects of convection and conductive heat transfer.

$$q = \epsilon_g A \{ (T_w/100)^4 - (T_s/100)^4 \} + U_g A (T_w - T_s) \quad \dots(2)$$

4.3 Vaporization mechanisms

The vaporization rate was assumed to be controlled by mass transfer on the gaseous phase side and proportional to the difference between the saturation vapor pressure of the liquid and the partial pressure in the gaseous phase. The proportional coefficient was assumed to be constant over the radial position in the sponge cake.

$$W_i = k_a 2 r dr (P_{vap,i} - P_i) \quad \dots(3)$$

i: Mg or MgCl<sub>2</sub>

The vaporization area was assumed to be proportional to the differentiated cell volume for simplicity. The proportional constant, capacity coefficient  $k_a$ , is common for magnesium and magnesium chloride. The partial pressures<sup>4)</sup> of magnesium and magnesium chloride were assumed to be independent of each other and to depend only on the temperature. Although the pressure in the vessel depends on the balance between the vaporization rate and the velocity of the gases to be drawn out to the condenser, in the model it was treated as a given boundary condition.

5. Calculation Results

5.1 Estimation of heat transfer parameters

It is necessary to estimate the values of the effective thermal conductivity of the inside of the sponge cake  $\lambda_{eff}$  and the overall heat transfer coefficient  $U_g$  and effective radiation coefficient between the sponge cake and the vessel inner wall  $\epsilon_p$ . These values were determined by parameter fitting so that the temperature change in the cooling process after the vacuum distillation can be expressed. In the cooling, magnesium and magnesium chloride are absent, and the values of the titanium sponge cake alone are obtained.

The estimated effective thermal conductivity of the titanium sponge cake is  $8 \times 10^{-4} \text{ kcal m}^{-1}\text{s}^{-1}\text{C}^{-1}$ . The validity of this value is studied as follows. First, thermal diffusivity was measured by the laser flash method for a small piece with a diameter of 10 mm and thickness of 2 mm machined from the titanium sponge. The thermal conductivity determined was  $3.4 \times 10^{-3} \text{ kcal m}^{-1}\text{s}^{-1}\text{C}^{-1}$  and was about 4 times greater than the estimated value. Since the specimen size was small and there are large pores in the actual titanium sponge cake, it is considered natural that the actual thermal conductivity should be smaller than that measured using small specimens. Secondary, Hara et al.<sup>5)</sup> measured the effective thermal conductivity of iron ore pellets in the cohesive zone of an iron blast furnace. The effective thermal conductivity of the pellets they measured at a reduction degree of 100% and shrinkage of 0.38, conditions similar to those of the titanium sponge, was about  $1 \times 10^{-3} \text{ kcal m}^{-1}\text{s}^{-1}\text{C}^{-1}$  from 900 to 1,000°C. The thermal conductivity of iron at 1,000°C is approximately the same as that of titanium at 1,000°C. This means that the value of the effective thermal conductivity of the titanium sponge cake determined by this study is practically valid.

5.2 Calculation of temperature and melt distributions in vacuum distillation process

Numerical solutions were obtained by differentiating Eq. (1). The boundary conditions are the initial sponge temperature and the change in vessel inner wall temperature, and the absence of a temperature gradient across the central axis of the sponge cake. The standard operating conditions were established as listed in Table 3. The density, specific heat, and thermal conductivity of the titanium sponge where magnesium and magnesium chloride remained were expressed as the weighted values of physical properties of the titanium sponge, magnesium, and magnesium chloride at each position.

5.3 Estimation of vaporization rate coefficient

An unknown parameter for the numerical calculation is the capacity coefficient of vaporization in Eq. (3). The vaporization capacity coefficient depends on the diffusivity of the gases and the surface area of the melt, and changes with the pore structure of the sponge. It

Table 3 Standard operating conditions for model calculation

Diameter of titanium sponge cake	1.5 m
Initial temperature of titanium sponge cake	740°C
Vessel inner wall temperature	Initially 900°C Rise to 1,000°C over 10 hours thereafter Rise to 1,040°C over 10 hours thereafter Constant at 1,040°C thereafter
Vessel pressure	Initially 15 Torr Drop to 1 Torr over 40 hours thereafter Constant at 1 Torr thereafter
Initial residual amount of Mg	200 kg m <sup>-3</sup> -Ti sponge
Initial residual amount of MgCl <sub>2</sub>	80 kg m <sup>-3</sup> -Ti sponge

was set here so that the calculation results could represent well the temperature measurement results of the titanium sponge cake.

**5.4 Case study**

The mathematical model built in this work can be used to investigate the effects of vacuum distillation operating conditions, such as temperature pattern, pressure pattern, initial residual amount and temperature of magnesium or magnesium chloride, and diameter of the sponge cake, on the required vacuum distillation time<sup>6)</sup>. As an example, the results of the effect of pressure pattern change are shown in Fig. 4.  $R(\text{Mg})$  and  $R(\text{MgCl}_2)$  along the vertical axes are the residual amounts of magnesium and magnesium chloride normalized by the values at the start of the vacuum distillation operation, respectively.

According to the calculated results, the initial vacuum difference of 5 Torr results in a few hours with respect to the completion time of magnesium chloride vaporization. As internal phenomena, the temperature near the center of the sponge cake remains virtually constant during the period when magnesium or magnesium chloride vaporizes, and varies with the vessel pressure. This is because decreasing the vessel pressure increases the driving force for vaporization, accelerates the vaporization, and increases the latent of vapor-

ization. The temperature inside the sponge cake drops to the point where the latent heat of vaporization balances with the heat supplied from outside, and remains constant there.

**6. Conclusions**

The temperature rise at the center is markedly delayed as compared with the periphery and that temperature arresting periods appear in the vicinity of about 750 and 900°C. These temperature arrests correspond to the vaporization periods of magnesium and magnesium chloride, respectively. Most of the residual chlorine in the titanium sponge exists as magnesium chloride.

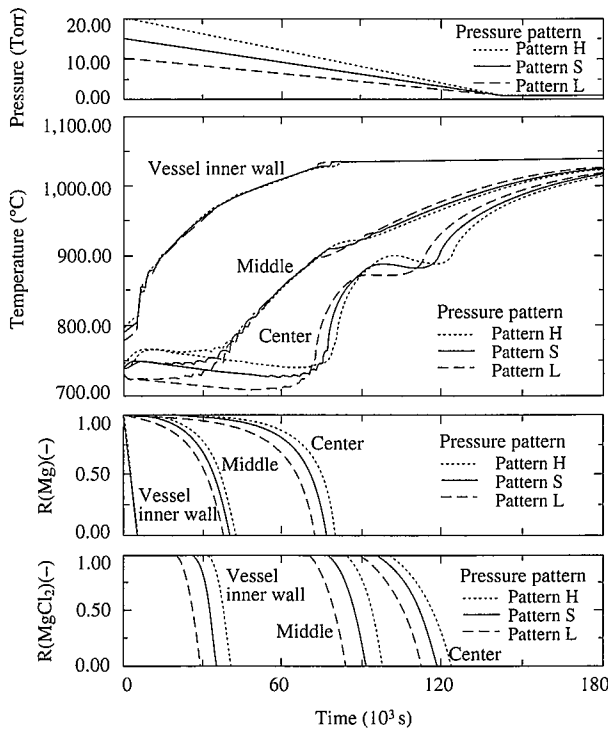
A mathematical model has been developed, combining one-dimensional unsteady-state heat transfer with mass transfer-controlled vaporization. The model describes well the change in the temperature of the sponge cake in the actual operation and quantitatively predict the effects of operating factors in the vacuum distillation process.

**Nomenclature**

- A : Area (m<sup>2</sup>)
- C : Heat capacity (kcal kg<sup>-1</sup>deg<sup>-1</sup>)
- H<sub>vap</sub> : Latent heat of vaporization (kcal kg<sup>-1</sup>)
- k<sub>a</sub> : Vaporization capacity coefficient (kg m<sup>-3</sup>s<sup>-1</sup>mmHg<sup>-1</sup>)
- P<sub>i</sub> : Partial pressure (mmHg)
- P<sub>vap, i</sub> : Saturation vapor pressure (mmHg)
- q : Heat transfer rate (kcal s<sup>-1</sup>)
- r : Distance in radial direction (m)
- T<sub>s</sub> : Sponge temperature (°C)
- T<sub>w</sub> : Vessel inner wall temperature (°C)
- t : Time (s)
- U<sub>g</sub> : Overall heat transfer coefficient between titanium sponge and vessel inner wall (kcal m<sup>-2</sup>s<sup>-1</sup>deg<sup>-1</sup>)
- W<sub>i</sub> : Vaporization rate (kg s<sup>-1</sup>)
- ε<sub>F</sub> : Radiation coefficient (kcal m<sup>-2</sup>s<sup>-1</sup>deg<sup>-4</sup>)
- λ<sub>eff</sub> : Effective thermal conductivity of titanium sponge (kcal m<sup>-1</sup>s<sup>-1</sup>deg<sup>-1</sup>)
- ρ : Density (kg m<sup>-3</sup>)

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**Fig. 4** Effects of pressure pattern change in the mathematical model