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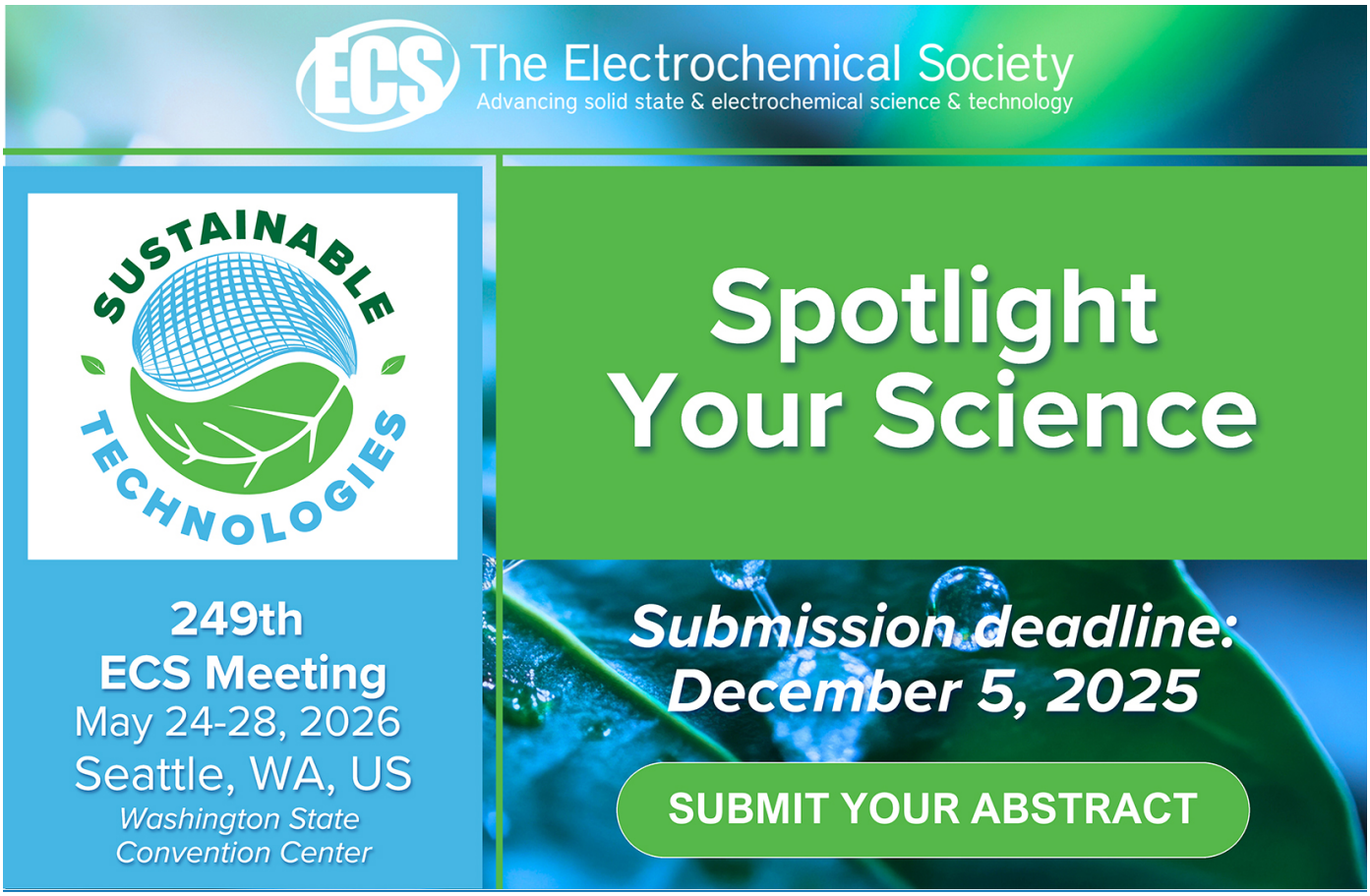
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# Cold production from a metallic salt and low temperature sources

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**Abstract.** Chemisorption cooling is a type of technology that facilitates energy saving and produces less environment impact than that produced by vapor compression cooling systems. The advantages or disadvantages of these systems can be explored from mathematical models through which the impact of different working pairs as well as construction and operating parameters on these cooling systems can be described. In this sense, the impact of design variables on performance coefficient of a chemisorption refrigeration system that uses sodium bromide and ammonia as working pairs are evaluated from a mathematical model that describes the heat transfer into the system. The results indicate that the cycle time affects favorably the coefficient of performance as well as the apparent specific density of the sorbent and the reactor radius. Although the coefficient of performance values is low when compared to vapor compression cooling systems, the system can be operated by low temperature thermal sources, found in thermal solar collectors or flue gases, and it can increase the energy efficiency of industrial or residential applications.

## 1. Introduction

Currently, the growing increase of energy and the strong global dependence on non-renewable energy sources are encouraging the study of alternative applications that use renewable or underutilized energy sources [1]. Under this scenario, there has been an increase in studies on adsorption refrigeration systems in recent decades, specifically, chemical adsorption systems [2,3]. The chemical adsorption refrigeration systems can be powered by heat sources with a wide range of temperatures found in thermal waste or solar energy applications, and do not require a liquid rectifier pump for the refrigerant [3]. In addition, adsorption systems do not present corrosion problems due to the commonly working pairs used and are less sensitive to shock and installation position [3,4].

The coefficient of performance (COP) achieved by chemical adsorption refrigeration systems are low compared with the COP of vapor compression systems [3], therefore, the key to increasing this performance is based on studies of working pairs (Sorbent bed/Refrigerant) that improve the heat transfer inside these systems. In this sense, a consolidated composite sorbent made from $BaCl_2$ and expanded graphite (EG) was analyzed by [5]. The authors showed that the composite sorbent can utilize effectively heat sources with temperature ranging from 75 °C to 90 °C. The assessed COP obtained with the consolidated composite sorbent varied between 0.50 and 0.53 when the evaporation temperature ranged from 0 °C to 15 °C and at a generation temperature of 80 °C [5]. Other

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consolidated composite material made from expanded graphite impregnated with lithium chloride salt was manufactured and tested for utilization in low temperature powered sorption icemaking systems in [6]. Experiments done with blocks with different proportion of EG, showed that the proportion of EG influence the cooling capacity per unit mass of salt and had almost no influence on the cooling capacity per unit mass of the block, the generation temperatures ranged between 75 °C and 80 °C. Although these studies show an increase in the COP of adsorption systems, it is necessary to evaluate applications that use temperature sources lower than 75 °C which are easy to achieve in solar thermal systems and as geometric and physical parameters influences their operation. In this sense, the present work addresses the modeling and simulation of the reactor for a chemical adsorption refrigeration system that allows evaluating how design parameters impact the performance of this system – It is important to mention that the reactor performs a similar operation to that of the compressor in traditional steam cooling systems and is, therefore, the main element of the system. For this purpose, the adsorbent/adsorbate pair used was sodium bromide (NaBr) and ammonia ($NH_3$), respectively. NaBr adsorptive capacities can be available at temperature levels of ~70 °C. These temperature levels can be reached in solar thermal applications and, therefore, have a great potential to reduce the cooling load of industrial and/or domestic appliances by using exclusively renewable energy sources.

## 2. Mathematical model and considerations

This section details the mathematical model that simulates the heat transfer inside of the reactor of chemical adsorption cooling systems. The reactor is the main component of the system and their sorbent bed is composed by metallic salt (NaBr) mixed with GE and uses ammonia as refrigerant gas.

### *2.1. Heat transfer in the annular region of the reactor*

To model the reactor of a chemical refrigeration system, it is important to understand how the refrigeration cycle works when a solid adsorbent is used. The basic cycle of chemical adsorption refrigeration does not require mechanical energy and can occur using only thermal energy [3]. Modeling and numerical simulation of the reactor are aimed at finding the impact on the COP exerted by the operational parameters required for the project of the reactor and the refrigeration cycle. The solid-liquid reactor is modeled like a conventional heat exchanger since a fluid (hot or cold) exchanges heat with an adsorption bed (solid), and this exchange occurs during the periods of adsorption and desorption of the refrigerant. Figure 1 shows in the Figure 1(a) shows that the modeled reactor is a concentric tube heat exchanger, where the heat transporting fluid (cold or hot) flows through the annular region of the heat exchanger, this annular region is between the inner tube reactor and the external tube of the heat exchanger. In addition, the refrigerant gas (ammonia) that can be adsorbed or desorbed by the solid adsorbent flows through the internal cylindrical cavity of the reactor.

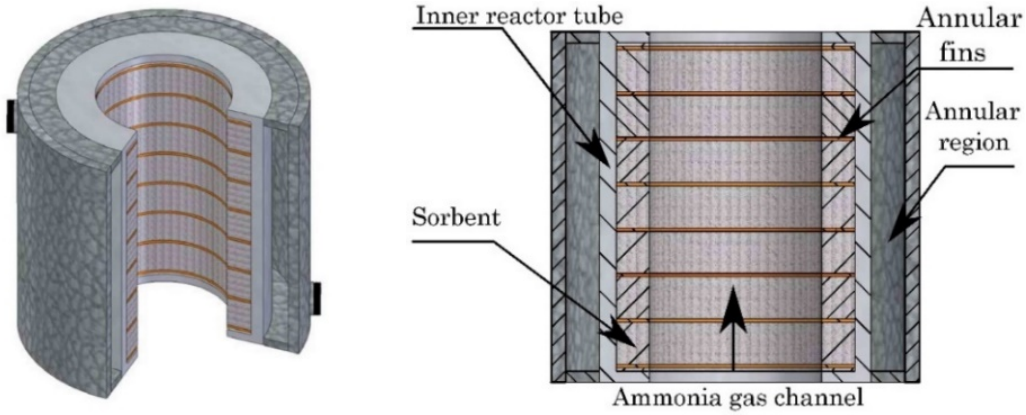



**Figure 1.** Reactor of the chemical adsorption refrigeration system (a) Isometric view of the reactor and (b) Reactor components.

Figure 1(b) shows the sorbent bed that is composed by metallic salt (NaBr) mixed with GE and the annular fins in contact with the adsorbent bed. These fins were used to promote greater internal temperature uniformity and to improve the thermal contact between the adsorbent and the fluid on the external surface. To calculate the rate of heat transfer over the total length of the tube, it is necessary to use average values of the Nusselt number defined in the Equation (1) according to [7].

$$\mathrm{Nu} = \frac{\mathrm{hx}}{\mathrm{k_f}} = \frac{1}{\mathrm{L}}\int_0^{\mathrm{L}} \mathrm{Nu_x dx}. \quad (1)$$

The Nusselt number in the concentric tube configuration of the reactor depends on several factors including the type of fluid, the type of flow, and the relationship between the internal and external diameters of the channel. Because the channel heat transfer model considers both laminar and turbulent flows, in both types of flow there is an inlet region, in which, depending on the hydrodynamic condition, the hydrodynamic boundary layer, the thermal boundary layer or the two boundary layers may or may not be fully developed [7]. To determine the numerical values of the Reynolds and Prandtl numbers, it was necessary to fit the polynomial functions according to [8] as a function of the average temperature of the water flowing through the angular region of the reactor (Tf). The experimental values of these properties were extracted from [7], and the correlation coefficients for each of the functions obtained by the Equation (2) to Equation (5) were R2 = 0.995, R2 = 0.998, R2 = 0.993 and R2 = 0.999, respectively.

$$\mathrm{k_f} = -7.35\mathrm{x}10^{-9}\mathrm{T_f^3} - 6.24\mathrm{x}10^{-6}\mathrm{T_f^2} + 0.002\mathrm{T_f} + 0.57, \quad (2)$$

$$\rho_\mathrm{f} = 1.49\mathrm{x}10^{-5}\mathrm{T_f^3} - 0.006\mathrm{T_f^2} + 0.006\mathrm{T_f} + 1000.24, \quad (3)$$

$$\mathrm{C_p} = -4.85\mathrm{x}10^{-8}\mathrm{T_f^5} + 1.54\mathrm{x}10^{-5}\mathrm{T_f^4} - 0.002\mathrm{T_f^3} + 0.12\mathrm{T_f^2} - 3.45\mathrm{T_f} + 4216.93, \quad (4)$$

$$\mu_\mathrm{f} = -2.92\mathrm{x}10^{-14}\mathrm{T_f^4} - 8.17\mathrm{x}10^{-12}\mathrm{T_f^3} + 9.01\mathrm{x}10^{-10}\mathrm{T_f^2} - 5.2\mathrm{x}10^{-8}\mathrm{T_f} + 1.74\mathrm{x}10^{-6}, \quad (5)$$

In which $k_f$, $\rho_f$, $C_p$ and $\mu_f$ represent the thermal conductivity, density, specific heat and kinematic viscosity of water flowing through the annular region, which are expressed in $Wm^{-1}K^{-1}$, $kgm^{-3}$, $Jkg^{-1}K^{-1}$ and $m^2s^{-1}$, respectively.

*2.2. Heat transfer in the adsorbent bed*

In the process of adsorption, there is an adhesion of a fluid molecule (adsorbate/refrigerant) to a solid surface (adsorbent). The amount adsorbed depends on the temperature or pressure of the chemical adsorbent. Keeping the pressure constant, the amount of adsorbed refrigerant decreases with an amount equal to the stoichiometric coefficient if the temperature of the adsorbent is higher than the equilibrium temperature of the reaction [5]. According to [9], it is possible to obtain an equation that describes the two-dimensional heat diffusion for the adsorption and desorption processes of the refrigerant into the cylindrical reactor. This equation is obtained from energy balances in the adsorbent bed and is presented in the Equation (6).

$$\mathrm{C(x)} = \frac{\partial \mathrm{T}}{\partial \mathrm{t}} = \lambda_{\mathrm{e,r}}\frac{\partial^2 \mathrm{T}}{\partial \mathrm{r}^2} + \frac{\lambda_{\mathrm{e,r}}}{\mathrm{r}}\frac{\partial \mathrm{T}}{\partial \mathrm{r}} + \lambda_{\mathrm{e,z}}\frac{\partial^2 \mathrm{T}}{\partial \mathrm{z}^2} + \mathrm{nN_s}\Delta\mathrm{H_r}\frac{\partial \mathrm{x}}{\partial \mathrm{t}}, \quad (6)$$

where C(x) is the specific capacity of the reaction bed ($J*m^{-3}K^{-1}$), ΔHr is the reaction enthalpy ($Jmol^{-1}$ of gas), $\lambda_e$ is the effective thermal conductivity of the medium ($Wm^{-1}K^{-1}$), $N_s$ is the number of moles of salt (adsorbent) per unit of volume of the medium ($mol*m^{-3}$), n is the number of moles of refrigerant adsorbed or desorbed. The mathematical expressions used to local advancement $\frac{\partial x}{\partial t}$ in

Equation (6) can be found in reference [9]. As initial conditions of temperature and local conversion to Equation (6) it was considered 25 °C and 0 °C, respectively. The boundary conditions in the r and z direction for Equation (6) were considered contact resistance between the reactor wall and the adsorbent bed and contact resistance between the fin and the adsorbent bed, respectively. Finally, the Equation (7) that shows the heat transfer in the thermal fluid flowing through the annular region is modeled according to [8].

$$(\mathrm{pC})_\mathrm{f}\frac{\partial \mathrm{T}}{\partial \mathrm{t}} + (\mathrm{pC_p})\mathrm{V}\left(\frac{\partial \mathrm{T}}{\partial \mathrm{t}}\right) = \frac{\mathrm{h}(2\pi \mathrm{r_{ext}})}{\mathrm{A_{anul}}}\left(\mathrm{T_p} - \mathrm{T_f}\right), \quad (7)$$

subjected to $\mathrm{T_{z=0}} = \mathrm{T_{entrada}}$, V is the flow velocity in the annular region and $A_{anul}$ in Equation (7) is the area of the annular region.

*2.3. Numerical method of solving the partial differential equation of the adsorbent bed*

Considering that the reactor to be analyzed in this study has a well-described geometry in cylindrical coordinates, the finite-difference technique with an implicit formulation was used to discretize the equation of two-dimensional heat transfer with energy generation in the adsorbent bed, as well as the energy transfer between the thermal fluid and the reactor wall [8].

*2.4. Simplifying hypothesis*

The following hypotheses were considered to perform the numerical simulation tests of the modeled refrigeration system:

- The evaporator pressure is 0.62 MPa and the condenser pressure is 1.17 MPa. With these pressure values, the initial equilibrium temperatures are $T_{e,evaporator}$ = 27.1 °C and $T_{e,condenser}$ = 56.01 °C, that is, these are the minimum temperatures for the solid adsorbent (NaBr) to initiate the adsorption and desorption of $NH_3$.
- 30 °C was arbitrated as the temperature of the thermal fluid (water at atmospheric pressure) during the adsorption phase and 70 °C during desorption phase. These values promote an adequate temperature difference to guarantee the operation of the cycle.
- The mass transfer resistance was neglected because the pressure for both the adsorption and desorption phases is higher than 300 kPa [10].
- To improve the heat transfer in the adsorbent bed [11], expanded graphite was added to NaBr. As a result, the apparent thermal conductivity of the adsorbent powder was $\lambda_e = 0.469\ \mathrm{Wm^{-1}K^{-1}}$.

*2.5. Coefficient of performance and design of experiments*

The coefficient of performance (COP) of the adsorption cycle for the powdered adsorbent mixed with expanded graphite and using ammonia as a cooling fluid was determined according to [5]. The experiment design [12] was used in the present work to determine the influence of the apparent density of the compound adsorbent (NaBr/Expanded graphite) in powder ($\rho_b$), the radius of the reactor tube ($R_T$) and the cycle time ($\tau$) on the COP of the system. The values considered for the previous design variables are shown in Table 1.

**Table 1.** Values and levels of the three independent variables used in the design of experiments for the considered powdered adsorbent.

| Level | $\rho_b$ (kg m$^{-3}$) | $\tau$ (min) | $R_T$ (mm) |
|---|---|---|---|
| -1.68 | 11.68 | 20 | 18.9 |
| -1 | 21.4 | 30 | 23.6 |
| 0 | 35.4 | 45 | 30.6 |
| +1 | 49.4 | 60 | 37.5 |
| +1.68 | 59.0 | 70 | 42.2 |

The values of thermal contact coefficient, reactor tube length, volumetric flow and thickness of the aluminum fins were considered constant for the simulations with values of 550 $Wm^{-2}K^{-1}$, 0.75 m, 3.7 Lpm and 0.25 mm, respectively.

## 3. Results and discussions

From the mathematical model, the successive simulations at the different levels of each of the variables considered in the design of experiments (see Table 1), and the execution of a central composite design [12], it was possible to adjust a polynomial for the reactor COP. From this polynomial model, it is possible to identify how the apparent density of the compound adsorbent ($\rho_b$), cycle time ($\tau$), and the radius of the reactor tube ($R_T$) impact this performance parameter. The polynomial model is shown in Equation (8) and has a value of the correlation coefficient of $R^2 = 0.993$.

$$\begin{aligned} COP = 0.130 + 0.028\rho_b - 0.0068\rho_b^2 + 0.017\tau - 0.005\tau^2 + 0.024R_T - 0.006R_T^2 + \\ 0.003\rho_b\tau + 0.002\rho_b R_T + 0.003\tau R_T. \end{aligned} \quad (8)$$

In this polynomial function, the coded values of the independent variables should be used, not their true values (see levels in Table 1). Figure 2 shows the influence of cycle time and bulk density of the adsorbent on the COP of the system. It can be observed that the increase in the COP due to the increase in cycle time and the specific mass of the adsorbent is the result of the increase in the ratio of the heat of reaction to the heat supplied to the system and, to the increase between the adsorbent mass and the metal mass of the reactor. Figure 2 also shows that an increase in the density (or specific mass) of the adsorbent from 14.4 $kgm^{-3}$ to 70.9 $kgm^{-3}$ produces an average increase in COP of 0.16. Consequently, an increase in the specific mass of the adsorbent results in a more compact adsorbent bed and, therefore, better thermal properties.

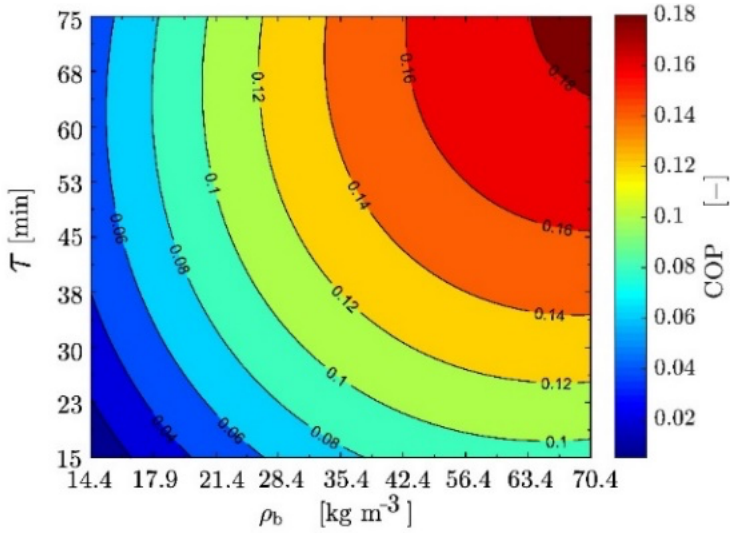



**Figure 2.** Variation of COP as a function of cycle time and specific bulk density of the adsorbent bed for a reactor tube radius of 30.6 mm.

Figure 3 shows the impact of the cycle time and the radius of the reactor tube on the COP, considering a specific bulk density of the adsorbent of 59 kg $m^{-3}$. The change from 15 minutes to. 75 minutes in cycle time (adsorption/desorption) produces an average increase in COP of 0.19 since the cooling capacity of the refrigerant shows a proportionally higher growth than the energy consumption. On the other hand, as the radius of the reactor increases, the adsorbent/metal mass ratio increases and, therefore, ends up reducing the negative inference of the sensible heat of the metal in

the COP.

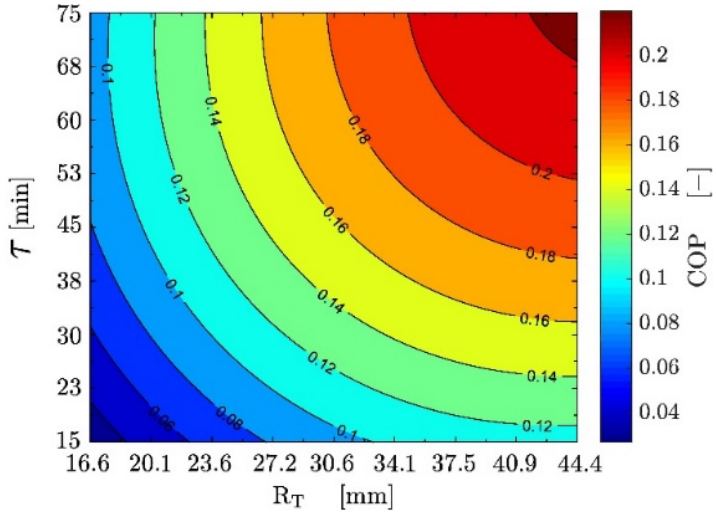



**Figure 3.** COP variation as a function of the cycle time and radius of the reactor tube for adsorbent apparent density of 59 $kgm^{-3}$.

Figure 4 shows the impact of the radius of the reactor tube and the specific apparent density on the COP, considering a cycle time of 30 min. A more compact adsorbent bed significantly increases the COP value of the cycle, that is, the constructive trend of these systems is to incorporate consolidated beds that are compacted before installation in the reactor to produce a better use of the heat that is supplied to the reactor, as well as a smaller system size to produce a given cooling power. However, this condition can cause an increase in the cost of the system. Therefore, economic aspects must be incorporated into the performance analysis of these systems.

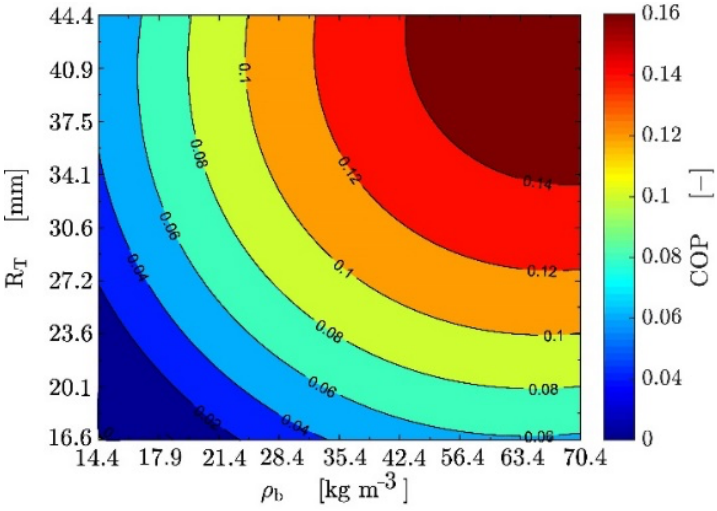



**Figure 4.** Variation of COP as a function of the radius of the reactor tube and the specific bulk density of the adsorbent bed for a cycle time of 30 minutes.

## 4. Conclusions

The polynomial equation adjusted in the present work allowed to determine how performance and operational parameters impact the COP of the system that uses $NH_3$ as the cooling fluid and consequently, the cold production of a metallic salt composed of NaBr/EG. Apparent density and time are the preponderant design variables at the moment of the design of the reaction system for the type of weighted adsorbent, that is, the increase in value of these variables allows a better use of the heat supplied to the system and, therefore, a better COP. The effect of increasing the cycle time on larger tube radio results in a greater average increase in COP than that observed when used on smaller radio. Finally, any system that uses powdered adsorbent must be designed with a high specific mass bed since when it operates with high values of this variable, the system reaches the maximum COP value.

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