EXPERIMENTAL AND NUMERICAL INVESTIGATIONS OF ICE CRYSTALLIZATION IN AQUEOUS SOLUTIONS

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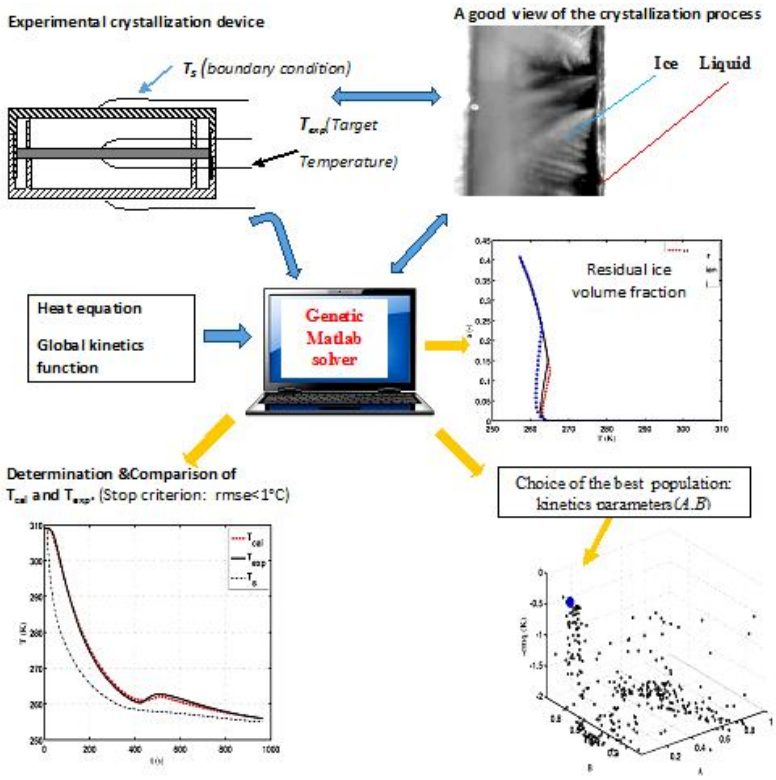
The formation of ice slurry from pure water or different aqueous solutions of Mono Propylene Glycol (MPG) immersed in an isothermal cooling bath is studied. The mathematical model is based on the unsteady heat equation coupled with a kinetic description of crystal growth obtained from classical nucleation theory. The kinetics approach takes into account the stochastic behaviour of nucleation and includes molecules diffusion involved in crystal growth. A focus is made on the implementation of the method and its validity. The approach is suitable to describe ice growth in MPG-water binary solutions (weight concentration range *wc* % from 0 to 25). A correlation is proposed to address ice kinetics of crystallisation for slurries obtained from MPG solutions.

Keywords: ice slurry, crystallization, secondary refrigerant, sustainable development, energy saving, secondary refrigerant, inverse method, energy storage, ice formation, nucleation, refrigeration, genetic algorithm

Графическая аннотация (Graphical annotation)



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ЭКСПЕРИМЕНТАЛЬНЫЕ И ЧИСЛЕННЫЕ ИССЛЕДОВАНИЯ КРИСТАЛЛИЗАЦИИ ЛЬДА В ВОДНЫХ РАСТВОРАХ

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В статье изучены процессы кристаллизации льда из чистой воды и различных водных растворов монопропиленгликоля (MPG), погруженных в баню с изотермическим охлаждением. Принятая математическая модель процесса основана на использовании нестационарного уравнения теплопроводности в сочетании с кинетическим описанием роста кристаллов, полученных из классической теории нуклеации. Кинетическое приближение учитывает стохастическое поведение для процессов зарождения кристаллов; включает в себя молекулярную диффузию, вовлеченную в процесс роста кристаллов. Акцент сделан на численной реализации метода. Описанный в статье подход пригоден для описания образования кристаллов льда в бинарных растворах MPG воде (весовой диапазон концентраций масс от 0 до 25 %). Исследована корреляция между кинетикой процессов кристаллизации для шламов, полученных из растворов MPG.

Ключевые слова: лед, кристаллизация, шламовые, вторичный хладагент, устойчивое развитие, энергосбережение, вторичный хладагент, обратный метод, накопление энергии, образование льда, зарождение, холодильная техника, генетический алгоритм

Introduction. In scientific and engineering literature have been widely discussed and proven the advantages of using ice slurry as a secondary coolant for energy saving [14, 20]. In the literature can be found even some original applications in medicine [15]. Yet it's still worth outlining that the main interesting properties of ice slurries and other phase change materials are their high cooling energy storage potential. Moreover usage of ice slurries make it possible the distribution of cold working fluid at an almost constant temperature. When applying these matters in cooling systems, less quantity of fluid is needed, compared with classical secondary refrigerant (cooled water or one-phase aqueous solutions) and are available high thermal and environmental performances.

But the key drawbacks of this technology remain the costs of ice slurry generation and the building of the necessary secondary distribution loop. But these hindrances will be overcome by improving energy storage devices and systems by the means of fundamental research works and technical improvements on the subject. In this context some research works are interested in «phase change materials» (PCMs) slurries modelling in order to improve ice generators and their monitoring, or to produce better quality PCMs and to develop energy efficient distribution loops.

The main goals of this article have been experimental investigation of ice crystallization in aqueous solutions; comparing experimental data with results of numerical (computer) modeling for such processes.

Authors have grouped all symbols, used for parameters, in table 1.

Table 1 – **List of symbols, associated with parameters**

A, B	Kinetic parameters	*Greek symbols*	
C	Mass concentration (%)	α	Ice volume fraction
e	Thickness of fluid (m)	γ	Superficial tension (Nm^{-1})
G	Gibbs free energy (J)	ρ	Density (kgm^{-3})
I	Nucleation rate	σ	Standard deviation
J	Nucleation probability	ΔT	Supercooling degree (K)
k	Boltzmann number	*Subscript*	
K(T)	Kinetics function	*c*	Crystal
L_f	Melting heat (Jkg^{-1})	*eq*	Equilibrium
MPG	Mono propylene glycol	*exp*	Experimental
n	Avrami number	*heart*	At the center (e/2)
rmse	Root mean square error (K)	*l*	Liquid
T	Temperature (K)	*median*	At abscissa e/4
T_f	Melt temperature (K)	*s*	Surface
		wall	Inner wall (at x=0)

Some considerations of PCM modelling. Many reports are now available in the literature on the intrinsic behaviour of PCMs slurries or when PCMs are used into hydraulic distribution loops as secondary working fluids.

A thorough review is presented by Dutil et al. [6] on modelling PCM crystallization. Most of the models are based on the Stefan problem or the enthalpy formulation, with various boundary conditions depending on the geometry (rectangular, spherical or cylindrical). The studied materials are homogeneous. So the composition of liquid phase does not vary during crystallization. Focus is made rather on microencapsulated slurries and clathrate hydrate slurries. The latter are suitable for building air conditioning as their melting temperatures are relatively high. But ice slurries made from mono propylene (or with other antifreeze) solutions can be very competitive for lower temperature applications because their apparent heat capacity remains relatively large.

Numerical modelling is still needed for a better understanding of the phenomena of ice slurry formation for an accurate design of energy storage generators and materials. Yet several investigations can be found in the literature.

Charunyakor et al. [3] worked on a model for heat transfer of microencapsulated phase-change material slurry flow in circular ducts. The energy equation is solved by taking into account the heat absorption due to the phase change process and the conductivity improvement caused by PCM particles flow. The numerical results pointed out that heat fluxes with PCMs can be about 2–4 times higher than single phase flow. The most important parameters appeared to be particle concentration and the Stefan number.

Alisetti et al. [1] used an effective heat capacity to model heat transfer in PCMs. The method has been found accurate and simple to be adapted for standard fluid dynamic software [6].

Roy and Avanic [25] presented a model based on effective specific heat capacity for PCMs in a circular tube with constant heat flow. Three important parameters are exhibited from the results: the non-dimensional melt temperature; the super cooling degree; the Stefan number. Furthermore, the model predicts the location where phase change impacts are more important with the last two parameters.

Hu and Zhang [10] studied the forced convective heat transfer of microencapsulated phase change material slurries flow in a circular tube with constant heat flux. This model is also based on the effective specific heat capacity. It results from this work that the conventional Nusselt number correlations for internal flow of single phase fluids are not suitable for a correct analysis of the heat transfer enhancement with microencapsulated phase-change materials. A modification is then proposed for the evaluation of the convective heat transfer in internal flows. Two important parameters are used to describe the heat transfer of PCM slurries: the Stefan number and the heat capacity. The heat transfer enhancement may depend also on the dimensionless supercooling, the dimensionless phase change temperature range, and the considered microcapsule's diameter.

Inaba et al. [11] conducted a two-dimensional numerical study to characterize fluid flow and heat transfer characteristics for Rayleigh–Bénard natural convection of non-Newtonian phase change-material slurries in a rectangular enclosure with isothermal horizontal plates and adiabatic lateral walls. They showed that PCM slurries enhance the natural convection heat transfer in enclosures if it's insured that the fluids have a continuous variation in density and enthalpy with temperature. According to the study, the Rayleigh number, the Prandtl number and the aspect ratio are not enough to evaluate natural convection for PCM slurries. A modified Stefan number is therefore added to address this issue.

Some research works are rather interested in the development of energy efficient generators with good quality homogeneous slurries and also in the necessary investigations to build more efficient cooling loops. It's believed that an accurate understanding of the phenomena of ice nucleation and crystal growth may contribute to a better control of the parameters impacting ice slurry generation.

However few research works has examined ice slurry formation with kinetics fundamentals. Therefore, the focus of this paper is to contribute to the understanding of the mechanism of crystallization of slurries with usage kinetics tools. The goal pursued is to search for a general correlation fitting kinetics law of ice slurry crystallization from MPG solutions.

Fundamentals of the kinetic function. We are interested here only with crystallization occurring when a liquid sample is cooled down to a critical value below which nucleation appears.

Generally crystal nucleation, whether homogeneous or heterogeneous, is viewed as an activated process requiring the crossing of an energy barrier which is similar to energy of activation. The formation of nuclei involves a Gibbs free energy composed of two conflicting energies: the change in volumic energy (due to the transformation of a certain volume of liquid into ice crystal) added to the surface energy needed for the formation of the solid-liquid interface. Thus the Gibbs free energy presents a maximum value (the activation work) corresponding to a critical radius above which the crystallization takes place. More details can be found in the literature [2, 12, 17].

The activation work depends on the super cooling degree ΔT meaning implicitly that nucleation occurs only in non-equilibrium state. A widely adopted quantitative parameter to characterize crystallization process is the nucleation rate *(I (T))*, which is the number of critical nuclei formed by unit of time. It represents the probability for a tiny nucleus to grow up to the critical size by means of thermal fluctuations and molecule diffusion.

For spherical crystal embryos, it's proven that the activation work ΔG_{crit} is a function of ΔT^2, ΔT being the undercooling degree [4, 8]. Thus the nucleation rate can be evaluated as:

$$I(T) \propto \exp\left(-\frac{\Delta G_{diffusion}}{kT}\right).\exp\left(-\frac{16\pi\gamma^3 T_f^2}{3kL_f^2 T\Delta T^2}\right). \quad (1)$$

The expression of the nucleation rate shows two competing exponential terms. The first term containing the activation energy of diffusion of molecules – it is proportional to the expression «–1/*T*». The second exponential term having link with the activation work of nucleation – it is proportional to «$-1/(T\,\Delta T^2)$». Thus a low temperature inducing a larger undercooling degree (so a lower activation work) is favourable to the nucleation of many critical nuclei of small sizes. But in the same condition of low temperature, the term of diffusion decreases. Consequently, mobility of molecules towards those nuclei can be compromised. From the competition of the two terms results an optimum value of temperature, where occurs simultaneously nucleation and growth. The taking into account of the term of diffusion sets the optimum value of the nucleation rate towards greater temperatures.

Succinctly ice crystallization, according to nucleation theory, depends principally on undercooling degree, superficial tension, and mobility of molecules. Crystal nucleation does not occur theoretically at equilibrium temperature [2].

Nucleation and crystallization probability are sometimes presented in the following form:

$$J = Ae^{-\frac{B}{T(T-T_f)^2}},\ with \quad A = A_0\exp(-\frac{\Delta G_{diffusion}}{kT}), \quad B = \frac{16\pi\gamma^3 T_f^2}{3kL_f^2} \quad . \quad (2)$$

According to Kashchiev et al. [13], A_0 is a prefactor depending on some parameters as the number of attachment sites at the super critical nucleus surface, another factor related to the molecular vibration frequency and the so-called Zeldovich factor. That expression of nucleation probability is used in the following as a kinetic function depending on the two parameters *A* and *B*.

Mathematical modelling and simulations of phase change

Kinetics functions

Crystallization starts with germination of nuclei that grow forth. Therefore appears to be important and logical to take into account the introduction of kinetics function, describing the microscopic behaviour of materials in the mathematical description of the phenomenon.

Many research works are available on crystallization kinetics, especially in metallurgy and polymer science. The degree of crystallization is generally searched in the form $\alpha = \alpha\,(t, T)$, a function of time and temperature representing the ratio of the volume of crystallised particles to the total initial volume of liquid. The time derivative of that function is mostly defined as:

$$d\alpha / dt = f(t)g(\alpha)\,, \quad (3)$$

f(t) is a function depending merely on the temperature for pure and homogeneous materials, while *g(α)* correlates with the already transformed volume fraction. These functions can be deduced from the standard theory of nucleation linked with the motion and interaction of molecules on a microscopic scale.

The study of crystallization kinetics is usually approached from three aspects: *isothermal kinetics* (derived from the so-called Avrami's analysis), the *constant cooling rate* crystallization kinetics and finally crystallizations under *varying cooling rate*.

The general kinetics of isothermal cooling is [21]:

$$\alpha = 1 - \exp\left[-k(T)t^n\right]; \quad k(T) = \frac{k_o \rho_l}{V_0 \rho_c} N(T) G(T), \tag{4}$$

where: *k(T)* – crystallization rate constant; k_0 – geometrical constant; *N(T)* – nucleation rate; *G(T)* – average growth rate; *n* – Avrami constant depends on molecular weight, nucleation type and slightly on temperature; V_0 – initial liquid volume.

Note that *k(T)* contains the micro-kinetics of nucleation and crystal growth. Further assumptions considered to constant temperature phase change: crystallization is slow compared to thermal diffusion and the release of latent heat is less than the rate of heat transfer.

The crystallized fraction α under *constant cooling rate* has the same form as for the previous kinetics description of Avrami. But *k(T)* is not constant. This approach is frequently adopted to determine the time and the rate of crystallization of polymers. Harnisch and Muschik [9] used successfully the method to calculate the Avrami exponent *n* from non–isothermal constant cooling rate crystallization of polymers from DSC experiments. For the crystallization of polymers under cooling rate, Ozawa found that the transformed volume obeys the following law [23]:

$$\alpha = 1 - \exp\left[-\frac{K_0(T)}{C^n}\right]; \quad C = \frac{dT}{dt}, \tag{5}$$

K_0 is a kinetic parameter according to the author. This approach provides a simple way to analyse solidification under constant cooling rate and to obtain the concerned Avrami number. According to their analysis, accurate results are obtained when there exists a linear link between *log[-ln(1-a(t))]* and *log(C)*.

Non-isothermal crystallization under *arbitrary cooling* rates has been investigated with the integral methods by many authors. Chew et al. [5] determined the solidified fraction of high density polyethylene. Piorkowska and Galeski [24] computed the relative cristallinity of iPP/GH composite as a function of time. Yu et al. [26] used the method to characterize the kinetics of crystallization of isotactic polypropylene and its blends under variable cooling rates. They established a relationship between spherulite growth and the overall crystallization rate. But the approach requires the availability of the number of nuclei and the crystal growth rate. Another approach of kinetic description under arbitrary thermal condition is presented by Nakamura [22]. The method has been successfully applied by many authors [17, 18] for different polymers.

Chegnimonhan et al. [4] have adapted it to a completely different phase change material constituted of crystallizing water and 15 % MPG-water mixtures. The practical kinetic formulation of the overall transformed volume fraction was then:

$$\frac{\partial \alpha}{\partial t} = nK(T)(1-\alpha)\left[-\ln(1-\alpha)\right]^{1-\frac{1}{n}}. \tag{6}$$

A special attention was paid to the formulation of the kinetic function *K(T)* which is written as the function of two kinetic parameters *A* and *B* according to the well-known classical nucleation theory and growth of crystal nucleation [8]:

$$K_{AB}(T) = J = A\exp\left(-\frac{B}{(T-T_f)^2 T}\right). \tag{7}$$

The expression of K_{AB} formulated as a function of the undercooling degree takes into account the fact that crystallization starts in metastable state. The terms *A* and *B* expressed the micro and macroscopic phenomena taking place during the formation of ice crystal.

According to the formulation, *A* depends on the prefactor A_0 (which relies on many factors as mentioned in section above) and on the motion capability of molecules in the crystallizing solution. Factor *B* is a function of the superficial tension, the melt temperature and the specific heat of fusion. Table2 presents some values of *A* and *B* compiled from the literature. For water, we computed *B* analytically at 0 °C using the following data:

$$\gamma_{water} = 75\, Nm^{-1}; \quad L_f = 333500\, Jkg^{-1}; \quad T_f = 273.15\, K; \quad k = 1.38 * 10^{-23}.$$

Table 2 – **Values of Kinetics parameters**

	Water (°C)	**Iron [19]**	**Plastic [2]**	**22 % Ethanol [16]**	**Emulsion [8]**
A	Not available	10^{33} cm^{-3} s^{-1}	10^{25} cm^{-3} s^{-1}	17.14 s^{-1}	1.8×10^{10} s^{-1}
B	3.43×10^{23} K^3	Not available	Not available	974 K^3	1.6×10^{6} K^3

There are information lakes in the literature to calculate *A* analytically: the activation energy due to diffusion is not available for mixtures, nor the number of attachment sites, some parameters involved into the expression of *A*. Therefore a numerical determination appears more suitable. Moreover, the kinetics parameters *A* and *B* depend probably on the varying concentration during ice-slurry crystallization. Therefore, to a first approach we assume that *A* and *B* depend merely on samples initial mass concentrations.

Experimental apparatus and formulation of the problem

The main goal pursued is to study the influence of MPG concentration from range 0 to 25 *wc %* on the kinetic parameters *A* and *B*. We use an inverse method based on genetic algorithm to check the optimal couple (*A, B*) according to [4].

The samples are crystallized in a small platelet polymer container, appropriately instrumented with K-type thermocouples of 80µm diameter. Please, refer to [4] for more details. Each crystallization experience gives access to the time evolution of the surface temperature T_s (which serves as boundary conditions in the mathematical model) and to the temperature at the central axis (named T_{exp}, experimental temperature) is the target temperature to be approached by inverse method; see Figure1.

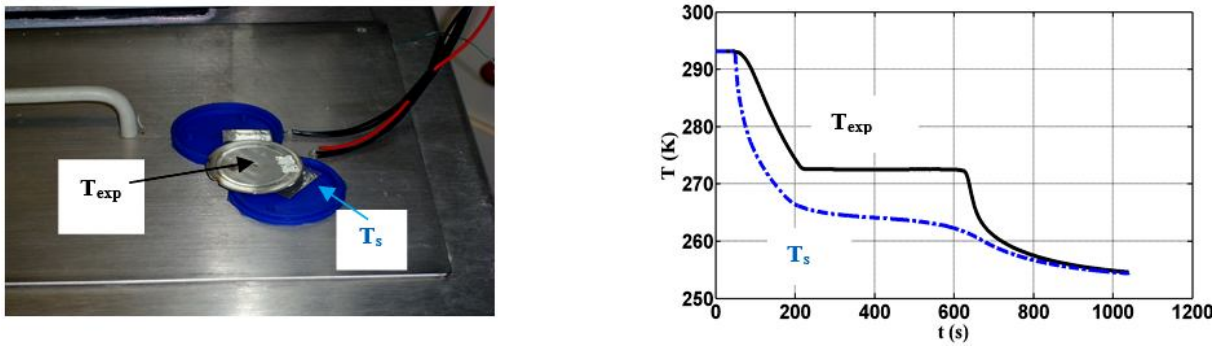

Figure 1 – The crystallization cell and an experimental test for pure water

The problem to solve consists of a set of two equations with the appropriate boundary and initial conditions as described in our previous article on the subject [4]

• The one dimensional nonlinear heat transfer including a heat source due to heat release during ice formation. Note that for mixtures, the thermophysical parameters (specific volume, thermal conductivity, etc.) needed to express the phenomenon depend on the varying ice rate and solute concentration. Furthermore the melt temperature T_f decreases when solute concentration increases according to the liquidus curve. These specificities are taken into account in the expression of the heat equation:

$$\rho(\alpha,T)C_p(\alpha,T)\frac{\partial T}{\partial t}=\frac{\partial}{\partial x}(\lambda(\alpha,T)\frac{\partial T}{\partial x})+\rho(\alpha,T)L_f\frac{\partial \alpha}{\partial t}. \quad (8)$$

• This heat equation is coupled with the kinetic description of phase change taking into account the phenomena of nucleation and crystal growth according to the formulation of Nakamura – see equation (6).

• The boundary conditions introduce another important parameter to consider and to determine: the heat transfer between the polymer container and the crystallising sample (it is the inverse of the thermal resistance R_t).

The equation set is discretized according to the Crank Nicholson's scheme for time steps and solved with a MATLAB code using a genetic algorithm. To fit the experimental curve $T_{exp,}$ many solutions of (*A, B*) couples are possible. The program generates several couples within the genetic algorithm and chooses for the best solution, the one showing the least room mean square error (RMSE) between the computed temperature (T_{cal}) and the experimentally recorded T_{exp}. The genetic algorithm provides a fine computing performance and appears as a good optimization tool.

The algorithm of the solver is presented on Figure 2, where R_t represents the heat resistance around the cell and the fluid interface, and $T_{cal,}$ the computed temperature

The resolution of the problem generates the temperature field *T(x, t)* (i.e. T_{cal}), the kinetics parameter couple (*A, B*), and consequently the solidified volume rate *α(x,t)*, where $x \le e/2$ (where $e/2$ = 2.5 mm represents the half thickness of the fluid in the crystallization cell or container).

Validity of the inverse research methods

Validity of the direct problem: determination of T(x,t)

This is a key step to ensure that the results computed with the MATLAB program are accurate and reliable. To achieve this, the direct problem, i.e. the above mentioned equation set, has been solved with the following particularities:

• T_s, the boundary condition is defined first analytically (a defined exponential time function).

• *A* and *B* are fixed (after checking to be respectively equal to 0.04 and 0.4).

• The thermophysical parameters of water are considered.

• The problem is solved first with a commercial solver Comsol with imposed very severe absolute and relative convergence criteria. The obtained temperature field *T(e/2, t)* is then considered as the reference temperature in the MATLAB code.

• The accuracy of the MATLAB code for solving the direct problem is then tested. The previous Comsol computed *T(e/2, t)* served then as the target temperature. The result is satisfactory (Figure 3). The root mean square error (RMSE) between the target temperature and the computed one is close to 0^{o}K.

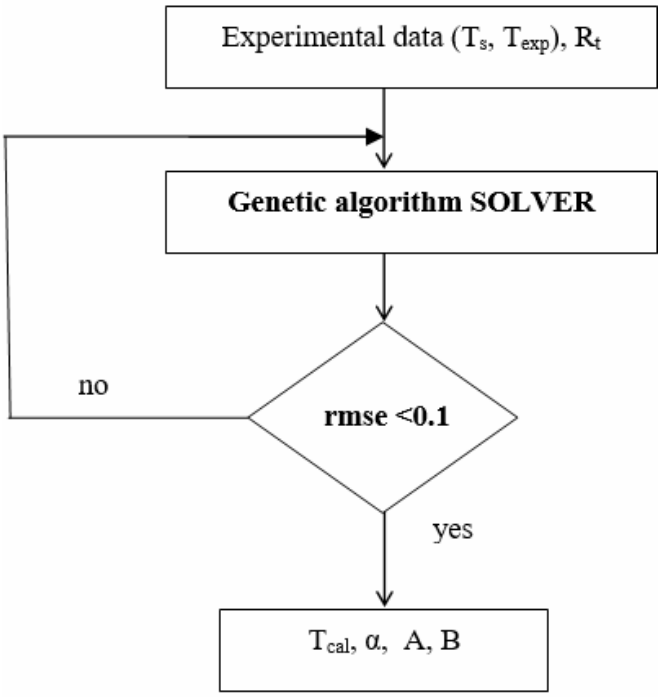

Figure 2 – Algorithm for solving the direct problem

The following phase consists of finding the optimal time and space steps.

To achieve this, the direct problem is solved with the MATLAB code adopting various time steps and space meshes. The target temperature is once again the one determined with Comsol at «*e/2*». This target thermogramme is compared with the profiles of temperatures calculated by the MATLAB program – the purpose of this calculations was the study of the spatial and temporal convergence of meshing.

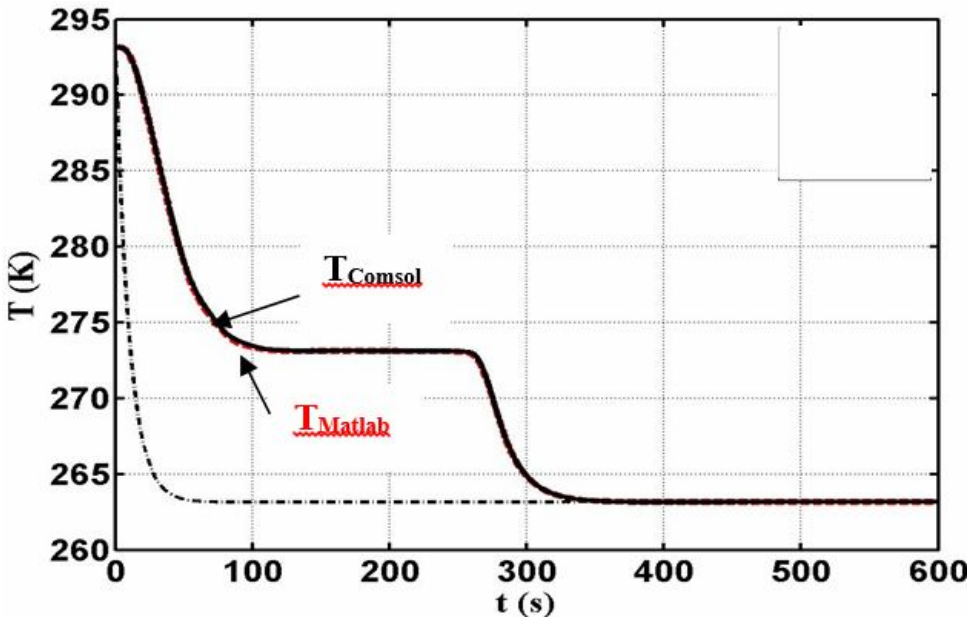

Figure 3 – Validation of the research method for the direct problem

The graph (Figure 4) represents the rmse according to the time steps and the spatial discretization (i.e. exactly the number of space steps). We find a classic profile of convergence. The combination "0.1s / 101 space steps" seems to be a good compromise for accuracy and time of calculation. These values are retained for the identification of the parameters *A* and *B* in the following.

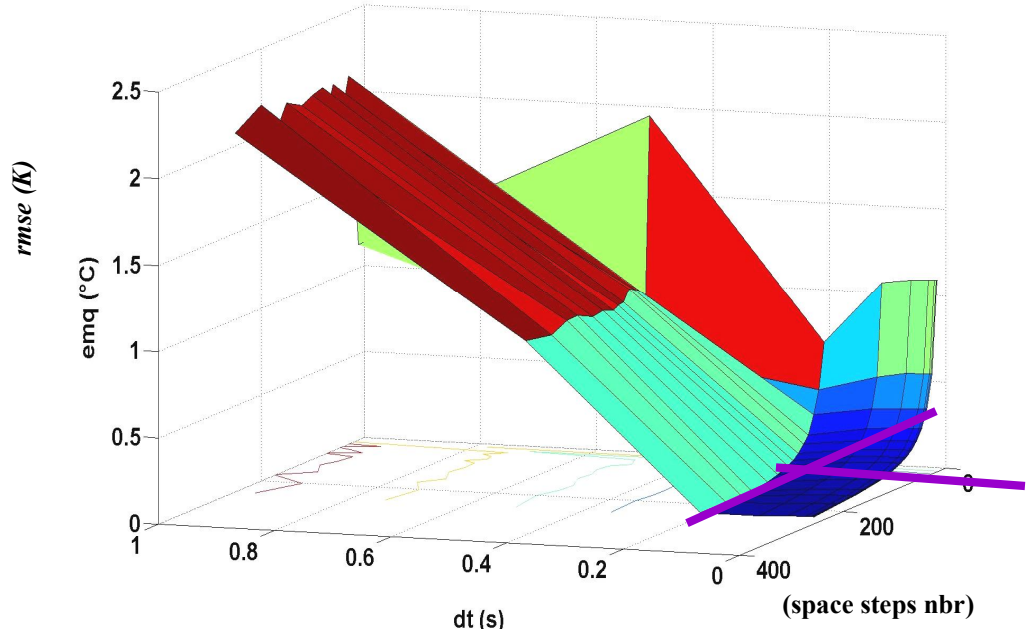

Figure 4 – Determination of the optimal time and space steps

Validity of *A* and *B* determination. The purpose is to verify the reliability of the genetic algorithm research method we have adopted to search *A* and *B*. The Matlab code found $A = 0.037$ and $B = 1$, for the target temperature *T(e/2, t)* determined before with Comsol (recall $A = 0.04$ and $B = 0.4$ initially). The accuracy of *A* is correct. The deviation for *B* is important *a priori*. But the overall rmse was just 0.05°K, despite this large difference from the initial value for *B*. This can be regarded as a sign that the kinetics function is not sensitive to *B* parameter. This hypothesis will be thoroughly tested later. The research method appears then suitable to find kinetics parameters.

Results and discussion

Reconstituted thermogrammes

Figures 5 and 6 show examples of shapes of the computed temperature fields for several MPG-water solutions. The rmse are less than 0,4°K in all cases. Thus there is a good fit between the calculated and the experimental temperatures for pure solutions and for mixtures. As expected, crystallization starts at lower temperatures as initial solute concentrations increase. As the temperature of the cooling bath is constant, crystallization starts earlier for solution with low concentration. On the presented examples, the metastable breakdown started respectively at 200s, 250s and 425s after the immersion of the samples of pure water, solutions of 10 %, and 25 % MPG weight concentrations (*wc*). As predictable, the crystallization plateau is observable only for pure water samples.

Evolution of solute concentration

Gradually, as the crystallization of ice from MPG-solutions progresses, the rate of antifreeze increases in the residual mixture. This requires a lower cooling temperature for the process to go forward. But as the cooling bath's temperature is constant (–20 °C), the H_2O+MPG mixtures cannot solidify entirely. Consider Table 3 to check examples of the computed final crystalline ice rates according to the initial MPG solute concentrations. It can be clearly seen (Figure 8) that at the beginning of the phenomenon, crystallization appears far from equilibrium, in accordance with the theories of nucleation. In the same way, the temperature evolution of solute concentration doesn't follow the liquidus curve (here a_{eq}), when crystallization starts.

Table 3 – **Rate of crystallized fraction vs. initial solute concentration**

MPG Concentration %	0	5	10	20	25
α	1	0.87	0.75	0.41	0.29

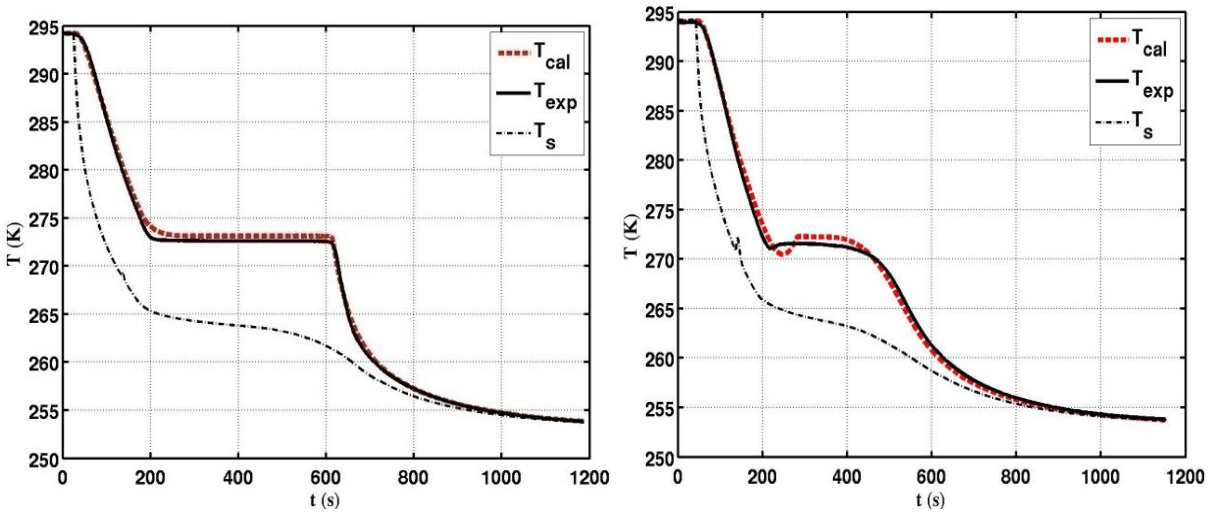

Figure 5 – Comparison T_{exp} & T_{calc} for pure water (left) and T_{exp} & T_{calc} for 5 % *wc* MPG (right)

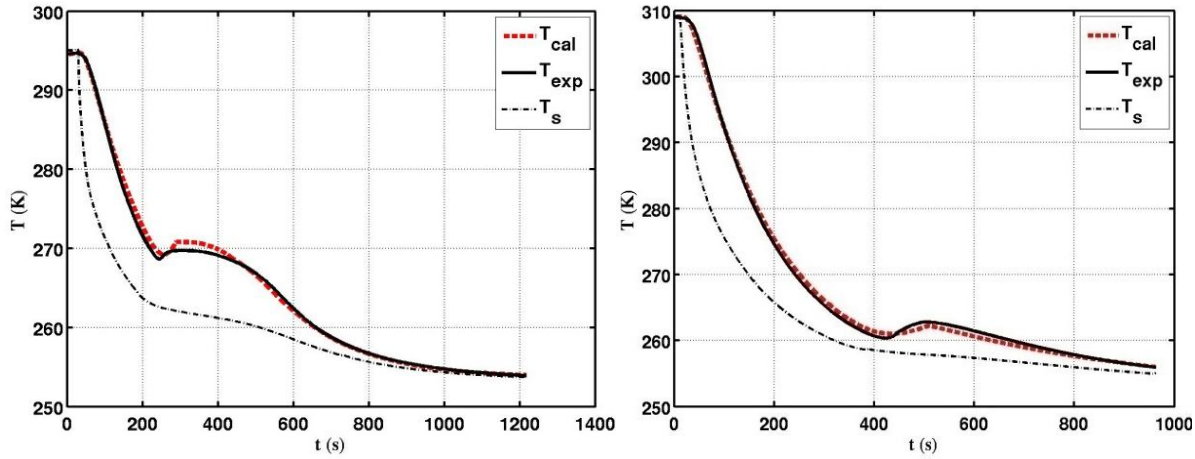

Figure 6 – Thermogramme for the 10 *wc* % sample and 25 *wc* % sample

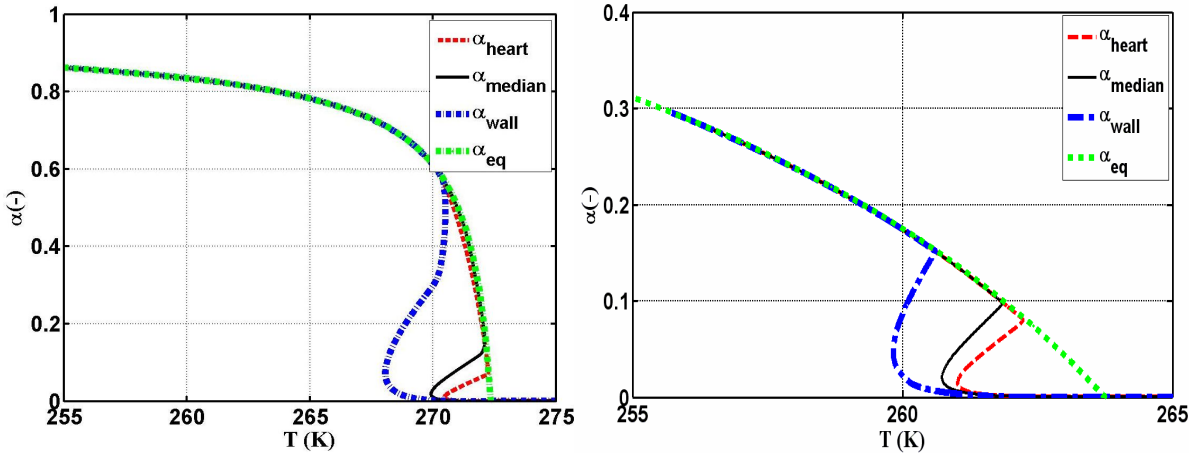

Figure 7 – Crystallinity of the 5 % *wc* MPG (left) and 25 % *wc* MPG (right)

Kinetic parameters

For the studied fluids, the rmse weighted mean values of parameters *A* and *B* are computed (Table 4).

Table 4 – **The rmse weighted mean values of kinetics parameters (*s* means the standard deviation)**

***wc* % (MPG)**	**0**	**5**	**10**	**15**	**20**	**25**
A_{mean}, s^{-1}	0.121	0.009	0.0086	0.0055	0.0031	0.0043
s_A, s^{-1}	0.064	0.0008	0.024	0.0036	0.0017	0.0029
B_{mean} , K^3	0.681	0.732	0.584	0.553	0.521	0.632
s_B , K^3	0 .159	0.304	0.285	0.254	0.309	0.192
A_{mean}(0 %) / A_{mean}(C %)	1	13	14	22	39	28

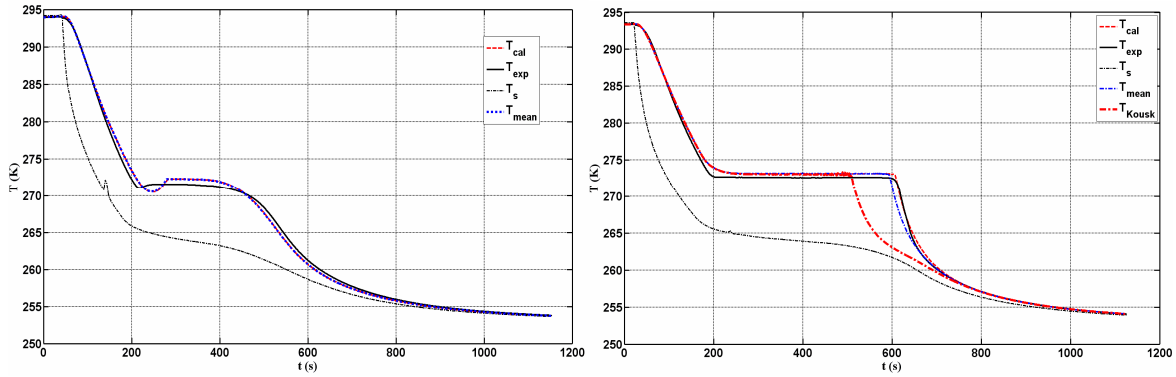

Figure 8 – Comparison of T_{cal} and T_{mean} for 5 % *wc* MPG (left) and of «T_{cal} ; T_{mean} ; T_{Kousk}»

As foreseen, the dependence of *B* from concentrations does not appear clearly and seems low. For this parameter an arithmetical mean value of 0.625 °K^3 is a correct compromise for water and even for «MPG anti-freeze + water» mixtures. Concerning the evolution of the mean *A*, it seems to be a *switch phenomenon* between the kinetics of crystallisation of pure water and samples, containing MPG antifreeze solutes. One can distinguish a mean value for pure water samples (A_{water} = 0.121 s^{-1}) and another *constant mean* value for all studied mixtures (A_{mean} = 0.0061s^{-1}).

Those mean values (i.e. $(A_{mean}, B_{mean})_{water}$ = (0.121 s^{-1}, 0.625 K^3 , and $(A_{mean}, B_{mean})_{MPG}$ = (0.0061 s^{-1}, 0.625 °K^3) have been tested. The simulated thermogrammes for T_{mean} demonstrate good agreement with previous T_{exp} and T_{cal}. For 5 % MPG wc, the rmse calculated with the mean (*A*, *B*) is of 0.1°K and T_{cal}=T_{mean} (see Figure 8 – right). For water, the rmse with the mean values is 0.6°K. It is still acceptable.

Authors have presented results on crystallisation kinetics of water and ethanol solutions [16]. In the condition of a cooling bath at –30 °C, they found *A* = 2.22 s^{-1} and *B* = 62.157 °K^3 for water. Those values are tested in our solver for water. Results are presented on Figure 9. The crystallization plateau is shorter with their identified *A* and *B* parameters. The sample crystallizes quicker because their cooling bath was set at lower temperature than in experiments with «–20 °C», described above. The increase in their *A* value may be partially a consequence of this factor. Note that the thermogramme T_{cal} and T_{mean} (the latter is simulated with the mean values of *A* and *B* for water) fit together.

In our study, $A_{mean\ water}$ is larger (by order of magnitude) for water than the one for the MPG solutes (see Table 4). This can be caused by the diminishing of the number of water particles surrounding the supercritical embryos for solutes. Indeed in a pure substance, a supercritical embryo is surrounded entirely by water molecules. But in solutes some of those molecules are replaced by the antifreeze molecules according to the concentration in solute. The growing ice embryos dispose of less potential water molecules to develop. A_{mean} tends to diminish slightly with the increase in concentration, therefore the ratio A_{water} / A_{mean} decreases. Another factor that impacts A_{mean} for solutes, is the decreasing mobility of water molecules in the residual solution due to the negative glide of the freezing temperature of mixtures.

Conclusion. The study presented results of crystallization simulations for MPG binary solutions used as secondary cooling refrigerants with a kinetic approach. The model is based on the classical nucleation theory. The temperature field and the time evolution of the transformed ice volume (rate of cristallinity) are performed without assuming equilibrium phase change.

The built numerical simulator has been validated and then exploited to identify the *A* and *B* kinetic parameters of the Nakamura kinetic function by the means of genetic algorithm.

Computed temperature fields show good fits with experimental data. Moreover numerical results exhibit good reproducibility for pure water and for aqueous solutions of MPG. It appears that there's a big difference (by order of magnitude) between the kinetic parameter *A* for pure water and that parameter for a "water + antifreeze" mixture.

Parameter *B* seems independent from solute concentrations. We've proposed and tested two mean kinetics couple values – one for pure water and the other for MPG solutes in the range of concentration below 25 % *wc*. The results demonstrate good fits. The next step of this work could be the investigation of crystallization kinetics in presence of liquid flow.

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