MODELLING OF THE SWELLING OF SIC-BASED REFRACTORY LINING USED IN WASTE-TO-ENERGY PLANTS

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ABSTRACT

This work provides a computational model to predict the life-span of SiC based refractories used in waste to energy plant (WTE) linings. For this application, oxygen gas present in the atmosphere diffuses through the porosity and reacts with the refractory producing silica (SiO_2). This new phase clogs gradually the pores and causes swelling of the lining. The proposed thermo-chemo-mechanical model simulates these phenomena is briefly summarized. The results obtained with the model implemented in a F.E code are shown. They prove the ability of the model to reproduce qualitatively the swelling of post-mortem bricks taken from WTE linings.

INTRODUCTION

Silicon-carbide-based refractories (SiC) are materials that are extensively used in extreme conditions, thanks to their physico-chemical properties. Compared with other oxide refractories, SiC based refractories exhibit a high abrasion-resistant strength, a high thermal shock resistance, a high thermal conductivity and a better resistance to oxidation in chemical aggressive environment [1, 2]. In waste-to-energy plants (WTE), the refractories are in contact with a complex composition of smoke and ashes on one side, and with pressurized vapour pipe on the other side at a temperature approximately equal to 250^oC. The temperature in the combustion chamber at the bottom level in the hot flame is close to 1200^oC. About $17m$ higher, at the top of the chamber, the temperature of smoke falls down to around 500^oC. At the intermediate level (i.e. $7m$) the *SiC* based refractories slowly swell during service and, sometimes, fall down. Figure 1 illustrates the deformations of typical tile geometry after a long period of use. The goal of this study was to furnish a fully coupled thermo-chemo-mechanical computational model that will help to predict the refractory lining life-span. This model falls within the scope of previous works on steel ladle's refractoriers [3, 4]. It is written in the framework of continuum thermodynamics of irreversible processes [5, 6], and focuses on modelling of the couplings between thermochemistry and thermomechanics.

FIGURE 1. New (top) and old (bottom) SiC based refractory tiles in a WTE facility (tile height: 245*mm*)

Herein, the refractory swelling is explained by the reactive transport of oxygen by diffusion in the gas present in the porosity space. Observations of microstructures of worn SiC-based refractory tiles from different municipal waste-to-energy plants show that new phases (essentially silica) mainly appear in the matrix binder and in the porosity [7, 8]. So, it is assumed that the SiO_2 produced by the oxidation of SiC clogs gradually the pores [8].

The computation of the coupled thermo-chemo-mechanical model is made in three steps. First, the classical resolution of energy balance is made. Then, the reactive transport of species under thermal gradient is solved. Lastly, the mechanical problem is solved accounting some effects induced by the formation of new phases. Herein, the equations of the model are shortly summarised and first qualitative results are presented.

1 HEAT BALANCE

The temperature field in the lining is obtained through the heat balance:

$$\rho \frac{\partial C_p T}{\partial t} = div(\lambda \, grad(T)) \tag{1}$$

where λ is the thermal conductivity of the refractory which is assumed to depend only on the temperature, ρ is the mass density, C_p is the specific heat, t is the time, *div* and *grad* denote the divergence and gradient operators respectively. The effects induced by the thermo-chemical phenomena like the heat source (or well) linked to the enthalpy of reaction and the change of thermal characteristics are neglected. The convective energy transported by the gases is neglected too. These assumptions are mainly justified by the fact that the heat flux due to the thermal

gradient is much higher than the other heat flux transfer or production involved previously. As a result, the computation of the thermal field can be made separately.
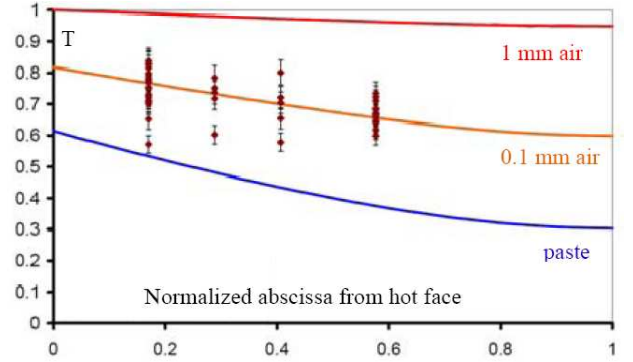

FIGURE 2. Normalized temperature versus localisation from hot face (x=0) to cold face (x=1) for different contact conditions at the cold face. Dot denotes experimental measure on an industrial plant

The temperature fields in the thickness of the lining under service condition computed considering a steady state regime are presented on figure 2 considering different boundary conditions on the cold face, from perfect contact between the refractory part and the water wall to strongly insulated by a one millimetre film of static air. The temperatures obtained from several thermocouples placed into the tiles of existing WTE are also reporterd. A satisfactory agreement is obtained considering an 0.1*mm* air film.

2 MASS BALANCE

The mass balance for each species is written as [9]:

$$\rho \dot{x}_j = -div J_j + \sum_{i=1}^{r} \upsilon_{ji} M_j \dot{\xi}_i \tag{2}$$

where x_j is the mass ratio of species j, J_j is the mass flux vector of species j, υ_{ji} is the stoichiometric coefficient of species number j in the ith chemical reaction and M_j is the molar mass of jth species. Furthermore, $(\cdot)$ denotes the time derivative. ξ is the extent of reaction i.

The extent ξ of the considering chemical reaction is given as:

$$\dot{\xi} = \frac{1}{2}\sqrt{\frac{k}{t}} \left(\frac{\rho x_{O_2}}{M_{O_2}} \right) \left(1 - \frac{Q}{k^{eq}} \right) \tag{3}$$

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where k is the parabolic rate constant that follows the Arrhenius law:

$$k = k^0 e^{\left(-\frac{E}{RT}\right)} \qquad (4)$$

k^0 is a pre-exponential constant, E is the activation energy of the passive oxidation. The flux of each species is assumed to result from diffusion into the gas in the porosity, which leads to:

$$J_j = -D_j \rho\, grad\,(x_j) \qquad (5)$$

where D_j is the diffusion coefficient of the species j in air. Due to lack of information, to account for progressive clog up of the porosity by the product of reactions, it is assumed that the diffusivity changes linearly with porosity:

$$D_j = D\frac{\phi}{\phi_0} \qquad (6)$$

where ϕ is the actual porosity, function of the oxidation extent (i.e., index 0 denotes initial value), and D is the initial diffusivity estimated with the Chapman-Enskog theory [10, 11].

One can notice that when SiC disappears during the oxidation and thus increases the porosity, the formation of silica SiO_2 clogs gradually the pores. Consequently the porosity ϕ is defined by:

$$\phi = \phi_0 - \phi_{SiO_2} + \phi_{SiC} \qquad (7)$$

where ϕ_{SiO_2} is the volumetric fraction occupied by the production of SiO_2 and ϕ_{SiC} is the porosity created by the disappearing of SiC grains. The porosity evolution could be defined by the following expression:

$$\phi = \phi_0 - \left(\frac{M_{SiO_2}}{\rho_{SiO_2}} - \frac{M_{SiC}}{\rho_{SiC}}\right)\xi \qquad (8)$$

ρ_j and M_j is the mass density and molar mass of phase j respectively. Then, the mass balance for each species is coupled by the expression of the extent of each reaction which influences the source term and the diffusivity.

3 CHEMICAL SWELLING

In the framework of small, strain partition can be considered. The total strain is the sum of the thermal strain, the mechanical strain and a chemical strain. The additive decomposition of the total strain is then written as:

$$\varepsilon_{ij} = \varepsilon_{ij}^e + \varepsilon_{ij}^{th} + \varepsilon_{ij}^{ch} \qquad (9)$$

The mechanical behaviour of the porous heterogeneous of representative elementary volume (RVE) is considered linear elastic and the material is isotropic. The elastic strain is related to the stress through the equation:

$$\varepsilon_{ij}^e = S_{ijkl}\sigma_{kl} \qquad (10)$$

where ε^e is the second rank elastic strain tensor, S is the fourth rank compliance tensor, σ denotes the second rank stress tensor. The thermal strain is related to the isotropic coefficient of thermal expansion α, and temperature:

$$\varepsilon_{ij}^{th} = \alpha\delta_{ij}(T - T_{ref}) \qquad (11)$$

where δ is the Kronecker symbol and T_{ref} is the reference temperature. The coefficient of thermal expansion α may be a function of temperature. A linear dependence between chemical strain and the extent of each reaction is assumed.

$$\varepsilon_{ij}^{ch} = \beta \langle \xi - \xi_{cr} \rangle \delta_{ij} \qquad (12)$$

where β is the coefficient of chemical expansion, $<>$ denotes the positive part of the content in the bracket and ξ_{cr} is the critical extent before which no chemical strain is observed at the RVE scale.

IDENTIFICATION

The identification of all parameters of the model is an ongoing work. Only the method and results for the SiC oxidation part is summerized hereafter. Moreover, for sake of proceeding length, only results for the SiC based concrete supplied by Calderys containing approximately 85 wt% of SiC grains, commercially denotes $CV85$ are presented. Typically the mass proportion of the matrix, containig SiC grains with size smaller than

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200 μm, is 53.6 wt%. The identification for the oxidation kinetics and chemical strain parameters was done thanks to thermogravimetric analyses (TGA) and an isothermal dilatometry test made by Bahloul [12] at 1000^0C and 1200^0C during 50 hours. Two assumptions are made to proceed to the identification: first, transport phenomena of gases inside powders are neglected during TGA; second, the kinetics on matrix powders is assumed to be representative of the local kinetics in a dense concrete.

The rate constant k (Eq. 4) was identified from the experimental curve for each temperature and then the activation energy and the pre-exponential factor were deduced. The obtained values are $k_0 = 2.4 10^{-11}$ and $E = 187.35 kJ$. The identification of the parameters of the chemical strain β and critical extent ξ_{cr} of the chemical induced strain (Eq. 12) requires to correlate the strain to the oxidation extent. Assuming a homogeneous oxidation in the dense samples during dilatometry, after the same duration, the extent should be the same that in TGA powders. Thanks to the small size of dilatometry samples ($9x9x15mm^3$) combined with a porosity of 17% this assumption may be acceptable. The expansion is presented in Fig. 3. The slope of the linear dependence between chemical strain and extent has been identified equal to 2647 mm^3/mol and the critical extent to $3.1 10^{-7}$ mol. The simulation of the isothermal expansion test with the directly identified parameters proposed later (see figure 4) confirms the relevance of this hypothesis.
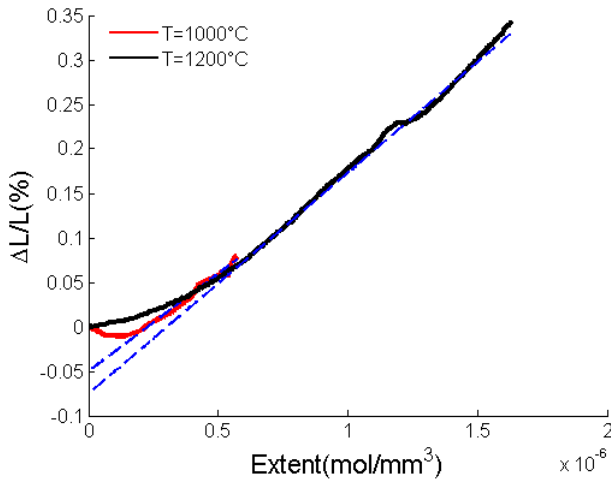

FIGURE 3. Chemical induced expansion versus oxidation extent

TABLE 1. Material data for $CV85$ concrete [14, 15]

Young's modulus (GPa)	110
Poisson's ratio	0.2
Coefficient of thermal expansion (K^{-1})	5.10^{-6}
Thermal conductivity ($W.m^{-1}.K^{-1}$)	7.6 (20-800°C)
	8.8 (1000°C)
Specific heat ($J.kg^{-1}$)	1130
Mass density ($kg.m^{-3}$)	2500
Initial porosity ($\%Vol.$)	16

thanks to a UMATHT subroutine. The chemical strain (Eq.12) is implemented in Abaqus via the UEXPAN subroutine. As often for such unidirectional coupling, first, the uncoupled heat transfer is solved. Then, the calculated temperature field is prescribed for the reactive transport computation. Finally, the temperature and oxidation extent fields are prescribed as loading in the mechanical computation.

Before applying this model to the case of a WTE refractory lining, the isothermal expansion test on $CV85$ castable under air has been computed. Figure 4 shows the comparison between numerical and experimental results, confirming the good agreement between the model and the experience. Data extract from the litterature were used for the mechanical and thermal parameters. They are summarized in table 1.
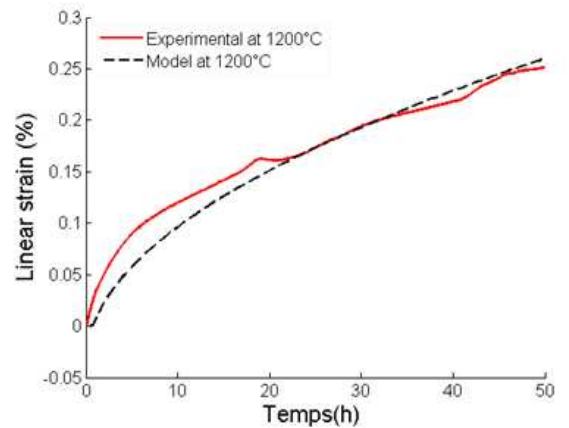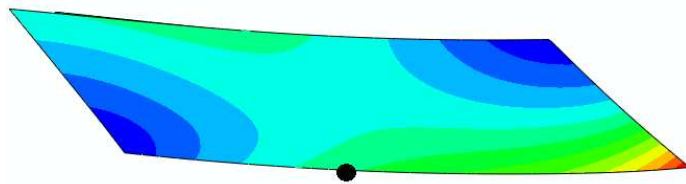

FIGURE 4. Isothermal expansion test under air at 1200^oC

F.E. IMPLEMENTATION AND RESULTS

The reactive transport equation (2), including the oxidation extent evolution (3), is implemented in the software Abaqus [13]

The F.E computations with the proposed thermo-chemo-mechanical model, assuming an elastic behaviour for the mechanical part, have been done considering a geometry of real tile

with $CV85$ castable material parameters. Even if this simulation is not fully representative of the reality results are qualitatively meaningful as the material of the tile is a SiC based refractory subjected to a similar corrosion mechanism.

Figure 5 shows the initial and worn shapes at room temperature of a real tile and the worn one predicted by the model at room temperature after one year of use with a steady fume temperature of 1050^oC. The whole curvature of the worn tile is well reproduced by the model but it must be underlined that the model shape is here multiplied by 10. Indeed, the predicted displacement of the black point on Figure 5 is $0.4mm$ for $CV85$, while on the real worn tile it has been estimated at around $5mm$. This large discrepancy may be due to two main reasons: first, the real time spent by the worn tile in the WTE is not currently known (and is probably more than one year); second, the swelling induced by other phenomena such the wollastonite growth is not taken into account in this computation and its contribution could be dominant [8].

(a) Real til after 1 year of use

(b) New (bottom) and worn (top) tile after use

FIGURE 5. From bottom to top: new tile, old tile and first qualitative numerical results in term of displacement (multiplied by 10)

Despite of the current shortcoming of the model, the analysis of the first results gives interesting qualitative information. For example, it helps to better understand the combined effect of the thermal gradient (i.e. design effect) and the chemical reaction. This coupling induces a higher swelling at the bottom right (in red on computation) of the fume face than on the bottom left (in blue on computation) of the fume face. Indeed, the thermal heterogeneity, combined with the oxygen activity gradient, induces a swelling heterogeneity.

CONCLUSION

The thermo-chemo-mechanical model proposed to take into account the chemical swelling of refractory lining in WTE has been developed in the framework of the thermodynamics of irreversible processes. The numerical implementation is built in three steps: the thermal part corresponds to the classical resolution of the heat balance, the second considers the reactive transport of chemical species in gas through the porosity, the third describes the mechanical behaviour accounting for the strain induced by the formation of new phases.

The results of the comparison with a real tile are encouraging as the worn tile shape is well reproduced. But, to tend towards a really predictive model, a huge experimental work is necessary in order to identify all the physical parameters introduced in the model. However, this work constitutes one more step to reinforce the method to study thermo-chemo-mechanical coupling in the field of refractories.

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