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XDEM Used for Predicting Tungsten-Oxide Reduction

A. A. **Estupinan Donoso**, B. **Peters**
Université du Luxembourg; Faculté des Sciences, de la Technologie et de la Communication
Campus Kirchberg, 6, rue Coudenhove-Kalergi L-1359, Luxembourg, Luxembourg
alvaro@estupinan.net

Abstract

This contribution implements the framework of the eXtended Discrete Element Method (XDEM) to describe and obtain detailed information about tungsten oxides reduction in dry-hydrogen atmospheres.

Technical reduction of tungsten oxides (WO_x) occurs in push-type furnaces. Boats are charged with high-purity WO_x-powders layers varying from a few *mm* up to several *cm*, then pushed in stages through a furnace in corrosion-resistant steel tubes. Hydrogen is applied, mostly, in or counter-current to the boats flow direction. The incoming H_2 diffuses into the powder-bed, reacts with the oxides and the produced water vapour exits from the powder-bed into the gas flow. H_2-flow does not only drive the reduction process, but it also helps to remove the formed water vapour. During such a process, the combination of high temperature and chemical aggressive atmosphere obstructs obtaining the required measurements to control the process. To solve related problems, extensive research has been undertaken to develop numerical methods and models to describe the process and the multiphase flow involved. The vast improvement of computing power opened up the way for coupling Discrete Element Methods (DEM) with Computational Fluid Dynamics (CFD) to combine the advantages of both methods. Discrete Element Method (DEM), originally developed by Cundall und Strack [1], simulates the dynamics and micro-mechanics of particulate materials. On the other hand, CFD is extensively accepted to investigate problems involving fluid flow.

A detailed validation for reduction of tungsten trioxide at different temperatures was carried out and good agreement was achieved between experimental data and predictions. Therefore, the delivered quantitative and qualitative results show that XDEM yields a valuable tool to investigate the complex processes occurring inside reduction furnaces in full detail.

Keywords

Tungsten Oxides reduction; Computational Fluid Dynamics; Reaction Engineering; Extended Discrete Element Method; Multiphysics modelling;

Background

In the previous CAPE edition, the XDEM (eXtended Discrete Element Method) framework was presented as a novel technique offering an important advancement for coupled discrete and continuous numerical simulation concepts. The Extended Discrete Element Method extends the dynamics of particles as described by the classical discrete element method (DEM) by additional properties such as thermodynamic state or stress/strain in conjunction with a continuous phase. The concept, contrary to pure-continuous approaches, yields information concerning size, shape or material properties of individual particles. Thus, an accurate characterization of processes involving granular material is obtained. The proposed framework has successfully been used to accurately predict heat and mass transfer [2,3], pyrolysis [4,5] and heterogeneous reactions [6] in packed beds.

This contribution employs XDEM techniques to represent the hydrogen reduction of tungsten oxides. Tungsten oxides (WOx) are commonly reduced by streaming hydrogen (H_2) in excess over it. The

incoming H_2 diffuses into the WOx-bed, reacts with the oxides producing water vapour and the gaseous products diffuse out of the powder-bed. The hydrogen flow drives the reduction process and helps to remove the formed water vapour. Retention of water vapour within the bed is a non desirable phenomena since vapour may react with the existing oxides forming volatile compounds (e.g. $WO_2(OH)_2$) that are transported and further deposited in lower oxides. The above-mentioned transport and deposition mechanism is responsible for abnormal tungsten grain growth. Such abnormalities act as breakage points of tungsten carbide-made products [7,8].

Tungsten oxide reduction had been described by theoretical diffusion equations characterized in terms of temperature, time, diffusion path lengths, and oxide bulk density. Nevertheless, due to the impracticality of the models, industrial production today is still based on empirical knowledge [9]. On the other hand, simplified models such as documented by [8] and [10] can only be applied to setups where the produced vapour is removed fast enough of the bed avoiding tungsten volatiles formation. Hence, there is still a lack on comprehensive models accounting for gas phase transport as well as solid phase thermochemical conversion. Recently, due to the homogeneity of the setup, Estupinan et al. [11] presented predictions for the reduction of tungsten-trioxide by employing a decoupled XDEM approach, which neglected the transport of fluid products. In [11], the reducing gas was assumed constantly available and gaseous products were assumed to exit the powder bed instantaneously. In the present contribution, a comprehensive and fully coupled XDEM model accounting for energy and mass transport in the gaseous phase, thermochemical conversion of solid species as well mass and energy exchange with the solid matrix is exploited.

eXtended Discrete Element Method

As presented by Peters et al. [12], and graphically described by fig. 1 XDEM aims to extend the dynamics of particles as described by the classic Discrete Element Method (DEM). Contrary to a continuum concept, the particulate phase is resolved with its various processes attached to the particles. In XDEM, additional properties such as thermodynamic state, stress/strain, or electro-magnetic field are included to each particle. Thus, the eXtended Discrete Element Method predicts, in addition to position and orientation in space of the classic DEM, properties such as internal temperature and/or particle distribution.

Generally, in packed beds problems three major areas are identified and are being addressed by XDEM:

- Chemical and physical conversion as an interaction between solid and gaseous species within a porous particle by heat and mass transfer
- Reacting flow in the voids between particles in conjunction with heat and mass transfer between the solids and the gas
- Overall motion of an ensemble of particles accounting also for interaction between solid and gas phase

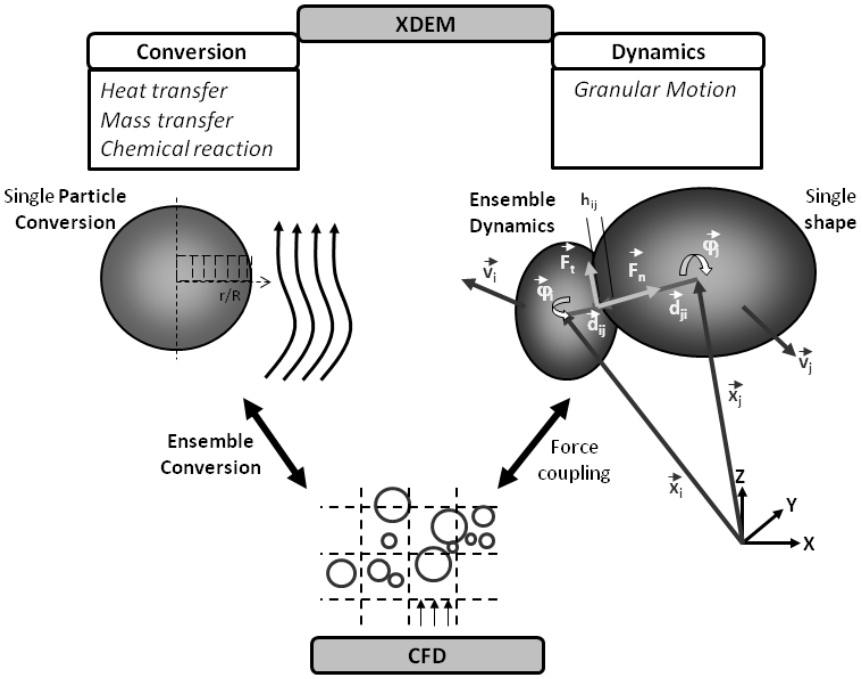


Figure 1: XDEM graphical representation [2].

Within this contribution, the DPM (Discrete Particle Method) by Peters [13] and an OpenFOAM solver for porous media [14] were coupled within the XDEM framework. While DPM described the thermochemical conversion of powder particles, OpenFOAM accounted for the gaseous species transport. XDEM attach to each particle motion and thermodynamics. The thermodynamics module incorporates a physical-chemical approach that describes temperature and arbitrary reaction processes for each particle in an ensemble.

The following statements are the basis of employed Lagrangian and Eulerian numerical models:

Discrete modelling

- One-dimensional and transient conservation equations characterize energy and mass transport within each particle
- Particles are considered to consist of liquid, solid and gas phases
- Gas is transport by diffusion and convection within the particle-pore space
- Gaseous species are ideal gases
- Particles are assumed as isotropic material and the properties change along the radius
- Inside the particles, solid and gaseous species are in local thermal equilibrium
- Heat transfer by conduction and radiation between neighbor particles
- Heat and mass transfer from fluid to particles is done through boundary conditions specified by the surrounding gas
- Convective heat transfer coefficients are estimated from Nusselt number semi-empirical correlation for mono-disperse and naturally arranged packed beds [15]

- Solid species are converted according to the scheme $WO_3 \rightarrow WO_{2.9} \rightarrow WO_{2.72} \rightarrow WO_2 \rightarrow W$ in accordance to [8,11]
- Chemical reactions are modeled as equilibrium reactions which competes for the available species
- The motion module of DPM predicts particle positions. Thus, the reactor is naturally filled by gravity deposition

Fluid modeling

- The multiphase medium, consisting of solid matrix and fluid, is treated as one homogeneous continuum.
- The powder bed is characterized as a type of porous media in which fluid flow behaves like an external flow
- The fluid flow inside the voids is described by a three-dimensional variant of Navier-Stokes and energy equations for incompressible flow
- Relevant variables and parameters are averaged on a coarser level
- Brinkmann or Forchheimer relations [16,17] are used to appropriately model the drag shift from linear to nonlinear behavior
- Gaseous species are also transported by molecular diffusion
- Heat and mass transfer from particulate to fluid is done via source term of the corresponding conservation equations

The full mathematical description as well as its derivation is documented in [6,13].

Results and discussion

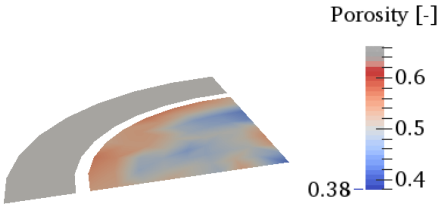
To validate the numerical approach, predictions for Thermo-Gravimetric reduction of tungsten oxides were conducted according to experimental data from Fouad et al. [18]. Therein, the authors placed 100 mg of tungsten trioxide into a metallic crucible immersed in a flowing hydrogen atmosphere. The next table 1 summarizes the experimental setup:

Table 1: Experiments setup [18].

Initial mass	100	*mg*
Powder composition		
WO_3	0.999	-
Reducing gas flow (H_2 99.9 %)	1e-6	m^3/s
Mean powder size	45 ±3	*µm*
Reduction temperature		
	913	*K*
	983	*K*
	1013	*K*

Due to the symmetry of the problem, axial symmetry boundary conditions and periodic boundary conditions for the fluid and solid phases respectively were applied. Hence, as schematized in fig. 2a, a wedge representing a quarter of the reactor was employed. In order to avoid the increase of void space around the inner walls, firstly, the full container was naturally filled up by gravity deposition and the particles out of the wedge were removed. Thus, as described in fig. 2b, contrary to the crucible wall, there is not such a "wall effect" on the planes of symmetry. The void space, or porosity, is computed by taking into account particle position and sizes within each CFD cell. Thus, the current approach omits empirical correlations to estimate the void space between particles. Following the experimental setup, the numerical setup considered a uniform initial temperature equal to the isothermal reduction temperature. In addition, because the crucible perceives a constant energy flux from the facility heating elements, the temperature of solid walls was assumed as constant and equal to the reduction temperature.

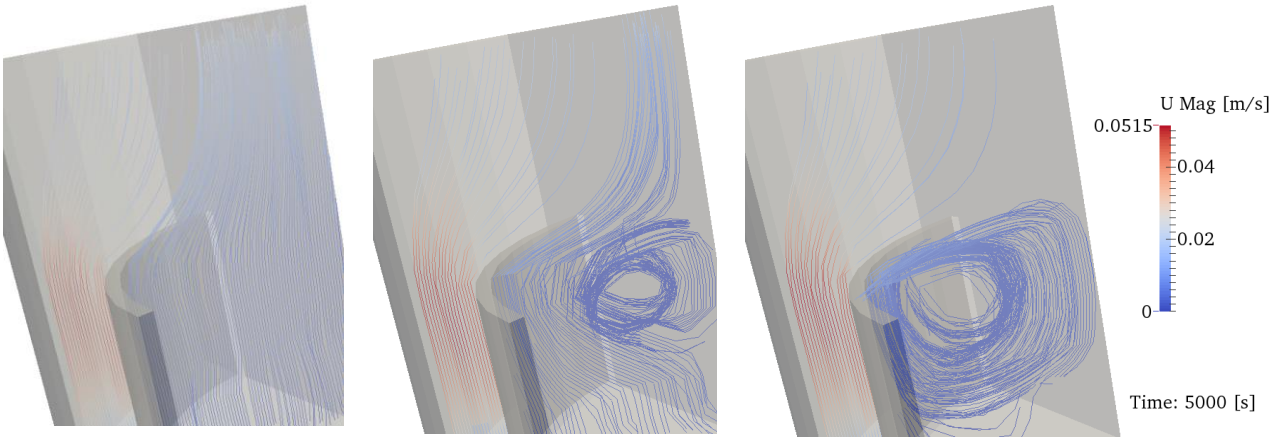
a) Numerical setup
(quarter of TG)



b) Radial void space distribution within the powder bed

Figure 2: Numerical setup.

The next fig. 3 shows streamlines as well as the velocity magnitude describing the transport within the reactor. It can be observed how vortices are developed within the crucible region at different time steps of the process. Preliminary simulations, with no reactions involved, showed vortices formation at very earlier stages. Such a vortices are formed when the amount of water vapour being transported out of the bed, mainly by diffusion, is no longer important. Once the vortices are developed, they remain even after reduction completion.



a) t = 500 [s] b) t = 3360 [s] c) t = 5000 [s]

Figure 3. Streamlines at different time steps for WO_3 reduction at 710 °C.

Tungsten oxide reduction is an endothermic process, meaning that particles absorb energy from the environment along chemical conversion. The energy exchange process is clearly represented by fig. 4, where the lower temperature of fluid at the particulate region is due to the energy absorbed by particles during conversion. Due to the low height of the sample, a quasi-homogenous heat and mass transport is observed across the height of bed. However, a radial distribution of temperature and species may exist upon the curse of the reactions, as shown in the lower edges of fig. 4a.

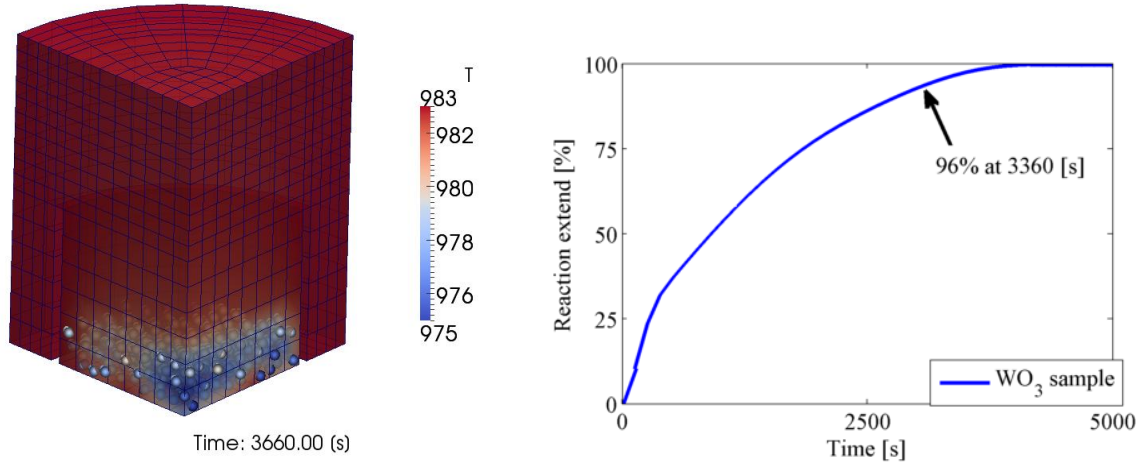


Figure 4: Temperature (K) in gas and solid phases for WO_3 reduction at 710 °C.

Good agreement between experiments and XDEM predictions for mass lost, and full reduction time, during the thermochemical conversion of tungsten trioxide is described in fig. 5. When WO_3 is reduced below 750 °C a "shortcut", $WO_{2.9} \rightarrow WO_2$, appear. As pointed by [11], when such a shortcut is not characterized, a lack on the accuracy may be observed during the intermediate steps of predictions. However, the phenomenon is not affecting the total reduction time. Such a shortcut was not implemented because of the lack on the kinetic information of the reaction and it is considered out of the scope of the research since reduction temperatures below 750°C are not practiced upon industrial reduction [8].

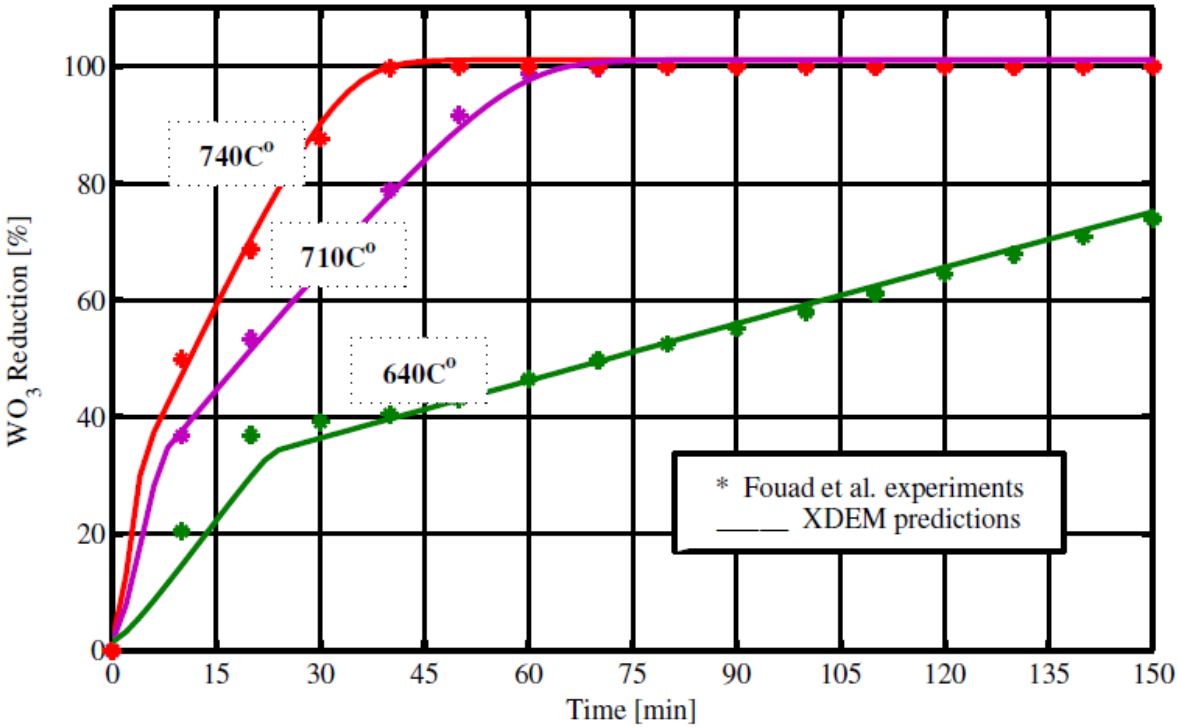
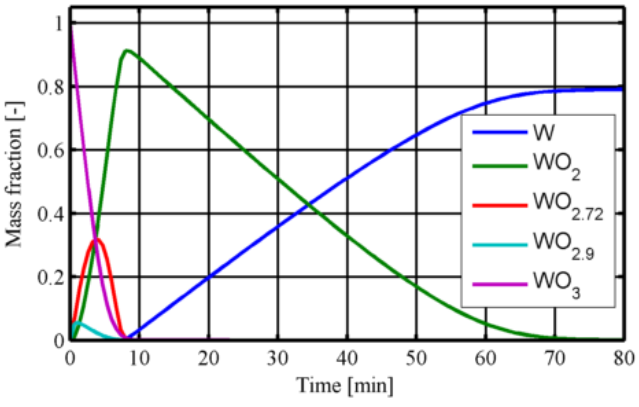
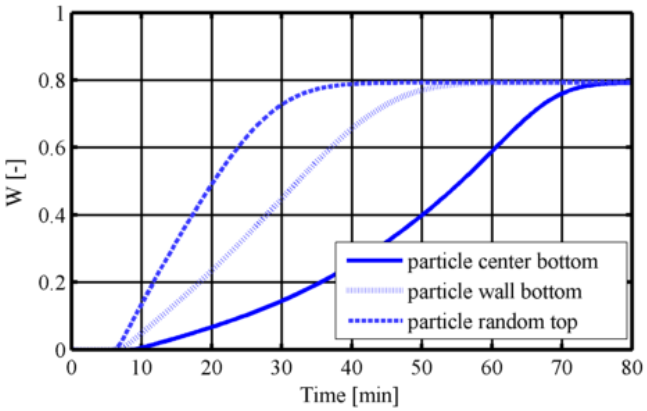


Figure 5: Comparison of degree of WO_3 reduction predicted by XDEM and isothermal experimentation measurements.

The inflection points, observed in curves of the above fig. 5, give information about the different steps of the reaction sequence ($WO_3 \rightarrow WO_{2.9} \rightarrow WO_{2.72} \rightarrow WO_2 \rightarrow W$). Commonly, experimental analysis employs deconvolution techniques to estimate the presence of the different solid species. Nevertheless, as represented on fig. 6a, the numerical model gives exact information of species. In addition, it can be possible to investigate at specific locations in the bed, for instance fig. 6b shows pure tungsten distribution at different positions in the solid bed. For this, three particles to monitor were chosen, one located at the bottom-center of the reactor, one at the bottom near the wall and a third-one was chosen randomly at the top of the bed.



a) Temporal evolution of mass fraction in the sample

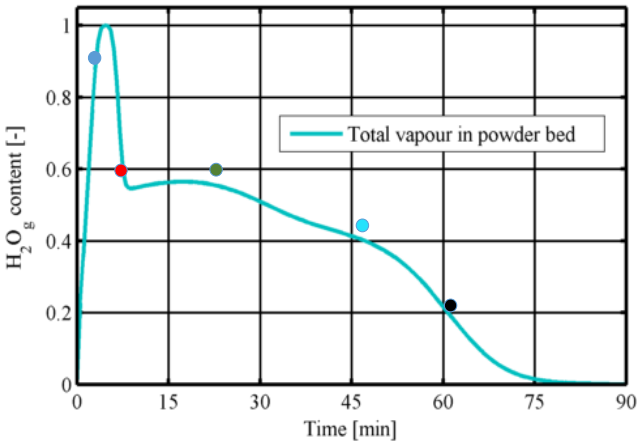


b) Tungsten mass fraction of monitored particles

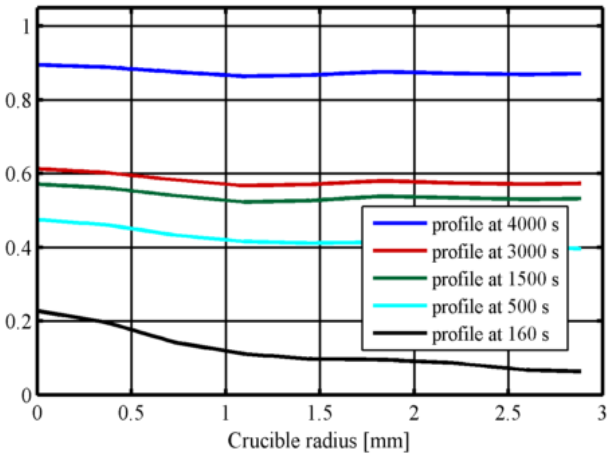
Figure 6: Mass fraction of solid species during reduction at 710 °C.

Fig. 7 shows the water vapour content evolution within the powder bed. Fig. 7 depicts the total vapour content in the particulate. The plot is consistent to qualitatively results reported in [19] and [20]. Fig. 7b describes the radial profile of vapour content in the gas phase. Vapor removal is favored at the wall region

of the reactor; this phenomenon may be attributed to the wall effect which leads to a higher mass flow rates in the wall region. Transport in the solid wall zones is also favored due to the higher temperature at the wall region that directly increases diffusivity and convective heat and mass transfer coefficient. The observed gradients (figs. 6b and 7b) indicate that it is more likely to observe volatile formation at the center of the reactor. Nevertheless, in this study, it was assumed that vapour exits fast enough as not to react with the existing oxides.



a) Total vapour in the powder bed. The colored points depicts a qualitatively correlation with fig. 7b



b) Radial distribution of vapour within the gas phase at the powder region

Figure 7: Temporal evolution of water vapour inside the powder bed during reduction at 710 °C.

Conclusions

This contribution presented a comprehensive numerical model for WOx reduction in powder beds. The fluid flow was characterized as flow through a porous media. Where, temperature, velocity, pressure and composition of the gas phase is predicted by consolidated CFD approaches. Solid particles were individually resolved by one-dimensional and transient differential conservation equations for momentum, mass, species and energy. Consequently, the current XDEM approach gives information of thermodynamic state and species distribution of each particle as well as transport properties of gaseous products.

The numerical model was validated by comparison to experimental data. The results show the XDEM capacity to accurately predict the complex thermochemical process occurring in the curse of hydrogen reduction of tungsten trioxide. Despite the homogeneity of the setup, gradients for vapour concentrations where found. Therefore, the documented results showed the importance on predicting, in addition to thermochemical conversion, transport of gaseous products.

Thus, the new insight into the heterogeneous process yields the means to improve water vapour removal upon reduction. By lowering water vapour content inside the bed abnormal grain growth is avoided and lower grain size and distribution is achieved.

List of abbreviations used

XDEM: extended discrete element method

DEM: discrete element method

CFD: computational fluid dynamics

WOx: tungsten oxides

TG: Thermogravimetry

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