

Theoretical Modelling of Sodium Concrete Interaction

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Abstract

For theoretical modeling of sodium-concrete interaction the computer code NABET has been developed. NABET is based on a phenomenological model of the interaction process obtained by experimental work. The developmental focus of the NABET code was analysis of test results, especially examination of test interpretation with relation to the interaction process. The program in its present version is directed to sodium-concrete interaction in air, which is superimposed by sodium fire and hydrogen burning. The code is subdivided in a pool model and a concrete model which are coupled in a special manner in order to simulate a moving reaction front at which melt-solid reactions occur. The interaction is treated 1-dimensional. Differential equations are solved by finite difference method. The code is applied to simulation of experimental tests characterized by widely different interaction scenarios. Comparison of experimental results with computation shows the code's capability of modeling sodium-concrete interaction. On the other hand the ideas related to the interaction process are confirmed. The need for modeling interaction in an inerted cell, improvement of chemical reaction kinetics and further validation are the code's principle limitations.

1. Introduction

Safety analyses for sodium cooled fast breeder reactors include hypothetical accidents in the course of which spilled sodium may come into contact with concrete. Experimental work has demonstrated that thermal and chemical attack of the alkali metal on concrete leads to a complex interaction between melt and concrete /1, 2/. Safety related consequences of the interaction are mainly energy release and hydrogen production, which both may contribute to containment loading by pressure buildup to a considerable extent.

At GKSS-Forschungszentrum an experimental program has been performed including interaction tests with different concrete types in air and in nitrogen atmosphere. For analysis of test results, especially for examination of test interpretation with relation to the interaction mechanism, it was necessary to develop a computer code for theoretical modeling of the interaction. Such a code in a next step will offer the possibility of considering sodium-concrete interaction in safety analyses for LMFBRs by inclusion into a containment code.

2. Phenomenology of the interaction

Basis for development of the computer code NABET was a phenomenological model of the interaction process which had been derived from experimental work. Sodium-concrete interaction in this model is subdivided into three chronologically proceeding reaction phases:

Phase 1 starts on contact of sodium with concrete and comprises characteristically reaction between sodium and steam released from concrete by thermally induced desorption. The generated hydrogen bubbles up agitating the melt and in air atmosphere ignites to jet flames when passing the pool surface where sodium fire zone is located. Decisive for sodium-water reaction rate and hydrogen release, respectively, is heat and mass transfer inside the concrete. During the relatively mild interaction phase 1 energy release by sodium-water reaction is of minor importance in comparison with sodium fire.

Phase 2 is characterized by a significant increase in energy release and hydrogen production due to the onset of additional reactions between melt and solid concrete constituents, which occur at a reaction front eroding the concrete. Necessary conditions for onset of reaction phase 2 are both availability of reactive material in the concrete mix and a temperature level at melt concrete interface exceeding a threshold temperature in the range 500 - 600 °C. Interaction phase 2 ends by consumption of sodium metal.

Phase 3 covers the cooling down period. Because of the temperature difference between reaction front and the deeper concrete region heat transport and steam release for the moment goes on. The steam exothermally reacts with reaction products and sodium residue in the pool region under hydrogen release. The cooling down period is delayed by these exothermal reactions.

For theoretical modeling of the complex interaction scenario, characterized by simultaneous occurrence of thermal, chemical and mechanical processes a conceptual model as shown in fig. 1 is useful. The reacting system is structured into surrounding atmosphere, melt and concrete. Atmosphere in the model is treated as heat sink and oxygen reservoir of infinite capacity. At the interface between atmosphere and the melt the sodium-air reaction zone is positioned which belongs to the sodium pool in the computational model. From atmosphere oxygen is transported into the reaction zone. On the other hand reaction products as sodium oxide and sodium peroxide are partly released as aerosols into the atmosphere. The heat of combustion is partly transferred to the surrounding by natural convection and radiation and is partly stored in the melt. Heat transport in the melt is treated as conduction. Because of gas stirring in the pool region it is assumed that the melt represents a homogenous mixture of sodium metal and reaction products. Melt-concrete reactions are subdivided into reactions with water, which occur in the pool region when the steam has passed the melt-concrete interface and melt-solid reactions, which occur at the interface and erode concrete by consumption. For treatment of the latter kind of reactions the melt-concrete reaction zone is introduced into the model. Heat transfer from melt to concrete and heat generation in the melt-concrete reaction zone leads to complex heat and mass transport inside the concrete accompanied by a number of transformations and so-called degradation reactions, which are the main cause of steam release from concrete into the melt.

3. Theoretical model of the interaction

The computer code NABET consists of a pool model, based on the code SOFIRE-II /3/, and a concrete model, based on the code USINT /4/. Pool model and concrete model are connected by introduction of the melt-concrete reaction zone.

3.1 Pool model

The energy equation of the pool model is

$$\rho c_p \frac{\delta T}{\delta t} = \frac{\delta}{\delta x} \left(\lambda \frac{\delta T}{\delta x} \right) + \dot{Q} \quad (1)$$

where density ρ , specific heat c_p and conductivity λ are actual properties of the melt, which is treated as homogeneous mixture of sodium metal and reaction products. Reaction products under consideration are sodium oxide (Na_2O) from sodium-air reactions, sodium oxide (Na_2O) or sodium hydroxide (NaOH) from sodium-water reaction and sodium meta-silicate (Na_2SiO_3) from sodium-solid reaction. The heat source term, \dot{Q} , considers energy release by sodium-air and by sodium-water reactions, which are treated in the pool model. Equation (1) is solved by a finite difference scheme. Nodalization of the melt is variable with respect to the number of nodes. Energy release by sodium-air reactions is assigned to the pool surface node and is given by a sodium burning rate, which is determined via oxygen transport from atmosphere to pool surface. Hydrogen burning was observed to occur above pool surface and therefore does not affect energy balance of the melt in this model. For treatment of sodium-water reaction it is assumed that steam escaping from concrete surface reacts during bubbling up through the melt. Therefore, the heat of reaction is equally distributed among all pool nodes. During interaction the pool depth changes due to sodium consumption and reaction product accumulation. The actual pool depth is calculated via the mass balance and mixture density. The volume of the pool nodes is changed correspondingly. Boundary conditions are given in terms of heat fluxes across pool surface and melt-concrete interface. Besides, for consideration of test conditions heat loss across the test articles side wall (see fig. 2) influences energy balance via heat source term.

3.2 Concrete model

Main features of the concrete model are conductive heat transport, two phase convective heat and mass transport of steam and liquid water in the pore volume of concrete due to a pressure gradient, thermally induced decomposition reactions in cement paste and increase in pore volume due to the decomposition reactions.

The governing continuity, energy and momentum equations for the heat and mass transport processes are:

- Continuity

$$\frac{\delta}{\delta t} [\rho_g \theta + \rho_l (\epsilon - \theta)] + \frac{\delta}{\delta x} (\rho_g u_g + \rho_l u_l) = \dot{S} \quad (2)$$

where ρ_g and ρ_l represent the densities of steam and liquid water in the pores, ϵ = whole porosity of concrete, θ = steam filled porosity of concrete, u_g = velocity of steam, u_l = velocity of liquid water, \dot{S} = source term of water released into the pore volume by decomposition reactions, t = time, x = spatial coordinate.

- Energy

$$(\rho c_p)_{\text{eff}} \frac{\delta T}{\delta t} + (\rho_g u_g + \rho_l u_l) \frac{\delta T}{\delta x} = \frac{\delta}{\delta x} (\lambda \frac{\delta T}{\delta x}) + \dot{Q} \quad (3)$$

where $(\rho c_p)_{\text{eff}}$ represents the effective heat capacity of concrete, the second term on the left accounts for convective energy transport due to gas and liquid motion and the heat source term, \dot{Q} , comes from endothermic concrete decomposition reactions as well as evaporation and recondensation of pore water.

- Momentum

Fluid flow in the pore volume is described by an equation of motion under filtration (Darcy's law):

$$u = -\frac{k_r K}{\mu} \frac{\delta p}{\delta x} \quad (4)$$

where p = pressure, k_r = relative permeability for gas or liquid, μ = viscosity and K = permeability of concrete.

Diffusion processes caused by concentration gradient are neglected because water release in the high temperature range is dominated by pressure driven flow.

The evaporation of free water in the capillary pores is based on thermodynamic equilibrium and a modified Clausius-Clapeyron equation. Decomposition reactions of cement paste, that is desorption of physically and chemically bound water from solid to gaseous state, are described by first order rate equations of the Arrhenius-type:

$$\frac{d\alpha_i}{dt} = C_i \exp\left(-\frac{E_i}{RT}\right) \quad ; \quad i=1,2 \quad (5)$$

where the subscript $i = 1, 2$ refer respectively to physically and chemically bound water, α_i = fraction of decomposed reactant, C_i = Arrhenius frequency factor, E_i = Arrhenius activation energy, R = gas constant.

3.3 Melt-solid reaction zone

The melt-solid reaction zone is identical with the melt-concrete interface and is treated in the model as a flat plane moving into the concrete due to consumption of solid concrete constituents by chemical reactions. Reaction rate in the present version of the code is given in terms of a constant penetration rate. The penetration rate is obtained by experiments and represents a measure of consumed concrete volume per unit time. In connection with concrete density and heat of reaction the penetration rate also is a measure of energy release at the reaction front.

By penetration of the reaction front an increasing concrete volume is consumed, that means the concrete in this volume is substituted by the melt. This effect has been introduced into the concrete model of the code in a simple way: By determination of the actual position of the reaction front the heat of reaction is assigned to the corresponding node of the concrete discretization scheme and is considered in the source term of energy eq. (2). The properties of this node, which represents a control volume containing melt and concrete, are determined by use of the mixing rule. The properties of all nodes between reaction front position and initial concrete surface are identical with the properties of

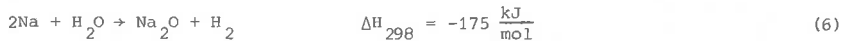
the melt. Thereby, the energy equation of the concrete model is applied to energy transport in the pool volume located between original concrete surface and the actual position of the reaction front.

4. Results

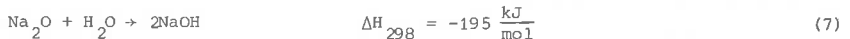
The simulations of sodium-concrete interaction with computer code NABET reported here refer to interaction tests performed in air with limestone concrete and quartzitic concrete. Details of the test program are given in /2/. The geometrical shape of test articles is depicted in fig. 2.

Initial conditions of sodium-limestone concrete interaction test were 6.2 kg sodium mass and 550 °C temperature of the spilled sodium. The test revealed a calm, benign interaction scenario corresponding to phase 1 of the phenomenological model mentioned above. Post test inspection showed local erosion of concrete but no erosive penetration of the reaction front to any significant extent. Therefore, chemical reactions included in simulation refer to sodium-air reaction and sodium-water reaction only. No melt-solid reaction was considered.

The sodium-water reaction is treated according to

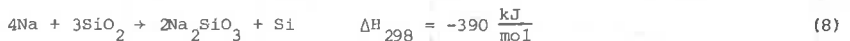


as long as sodium metal is present in the melt and according to



after consumption of all sodium metal. Measured and calculated temperatures are compared in fig. 3. A good agreement not only between temperature levels but also with reference to interaction duration demonstrates the codes suitability and confirms assumptions about the interaction process. Computational results show that energy release predominantly is caused by sodium fire with 87 % compared to 13 % by sodium-water reactions. The integrated water release amounts to 13.8 kg/m², which corresponds to a completely dehydrated concrete region of 6.4 cm in the case of the employed test article. Post test inspection showed an evaporation front position some 7 - 9 cm beneath heated surface, which agrees well considering that under real conditions totally dehydrated concrete changes steadily to virgin concrete.

The second simulation refers to a sodium-quartzitic concrete interaction test, the initial conditions of which were 6.2 kg sodium mass and 670 °C sodium temperature. The observed interaction differed from the test mentioned above mainly by occurrence of an energetic interaction scenario due to melt-solid reactions, corresponding to reaction phase 2 of the phenomenological model. In computation the melt-solid reaction is treated according to



Sodium-water reactions are treated as before. Penetration rate of the reaction front and starting time of the energetic interaction phase are obtained by experimental work and are given as input data amounting to respectively 3.8 mm/min and 30 min. A comparison of the calculated and measured temperature histories is shown in fig. 4. The prediction agrees

satisfactorily with measured data. Underprediction of temperatures during transition to energetic interaction phase is caused by the simple treatment of reaction kinetics as a constant rate. Duration of the energetic interaction phase is calculated to 15.7 min and agrees well with experimental observations. The calculated concrete erosion amounts to 5.5 cm compared to a measured erosion of some 4 - 6 cm.

References

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- /4/ BECK, J.V., KNIGHT, R.L., "User's Manual for USINT - A Program for Calculating Heat and Mass Transfer in Concrete Subjected to High Heat Fluxes", SAND 79-1964

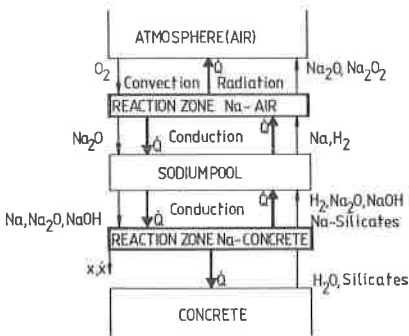


Fig. 1: Model of sodium-concrete interaction

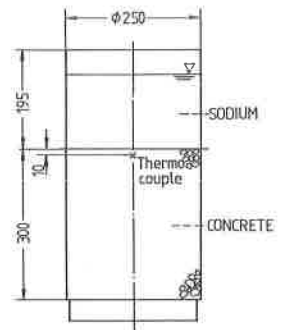


Fig. 2: Schematic of test article

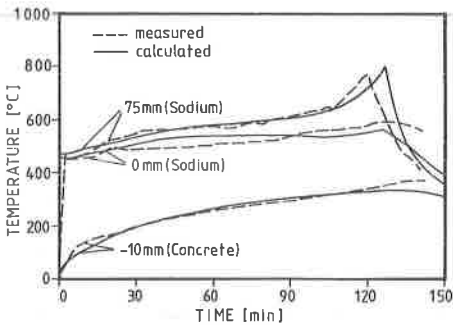


Fig. 3: Measured and calculated temperature histories of sodium-limestone concrete interaction in air

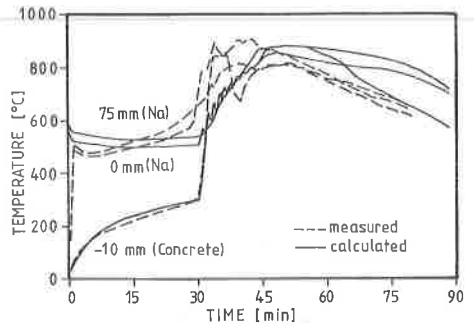


Fig. 4: Measured and calculated temperature histories of sodium-quartzitic concrete interaction in air