

Experimental Investigation of Sodium-Concrete Interaction and Mitigating Protective Layers

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Summary

Under accidental conditions in LMFBRs a contact of liquid sodium with concrete cannot be excluded confidently. As being a highly aggressive medium sodium will interact with concrete not only thermally but also chemically, which may lead to a hazardous reaction scenario comprising energy release and hydrogen generation. These effects can possibly contribute to containment loading and therefore must be included in safety analyses. For that reason it is necessary to get a fundamental understanding of sodium-concrete interaction and influencing parameters.

At GKSS-Research Center Geesthacht an experimental program has been performed in order to get information on the behaviour of different concrete mixtures under hot sodium contact. Therefore, the type of aggregate and sand used for the mixes was varied, because they represent the main mass of concrete, and hence should influence the reaction behaviour. The aggregate materials tested were basalt, limestone, magnetite, and a moraine gravel with a high free-quartz content. Initial sodium temperature and sodium mass have been additional parameters. These tests, performed in air, showed significant differences in reaction behaviour, in the way, that only quartz containing concrete specimens revealed an energetic reaction scenario. Additional tests have been performed on the sodium interaction with quartzitic concrete in an inert gas nitrogen atmosphere, in order to get a more detailed information. These tests confirmed the observations made during tests in air. Analyses of test results leads to the assumption, that interaction behaviour depends strongly on type of aggregate, esp. quartz content, employed in the production of the concrete.

Test results demonstrate the necessity for precautionary or mitigating measures against the consequences of sodium-concrete interaction. Therefore, protective layers on concrete surfaces were tested, in order to develop a method, which is suitable to mitigate interaction consequences. Experiments showed principal qualification of this treatment, but revealed a specific problem in the mechanical effect of steam flow from heated concrete on connection between protective layer and concrete surface.

1. Introduction

In performance of safety analyses for LMFBRs, the consequences of hypothetical accidents which involve a loss-of-coolant have to be evaluated in order to demonstrate the capability of the containment to sustain the resulting loads. To accomplish this objective it is necessary to know the kind of energy sources contributing to containment loading and the amount of energy released by the different sources.

The chemical reactivity of sodium plays an important role in this relationship. In addition to the thermal load imposed on the containment by a sodium fire, direct contact of molten sodium with concrete may lead to a significant energy release and hydrogen generation. During such events the strength of concrete structures will be reduced both by the abnormal temperature increase and by ablation. Potential consequence of sodium-concrete interaction is pressure buildup in the containment due to generation of noncondensable gases, heating of the gases and aerosols, as well as possible hydrogen combustion.

At GKSS-Forschungszentrum an experimental program has been performed which includes sodium-concrete interaction tests in air and in nitrogen atmosphere. For development and improvement of safety precautions, the effectiveness of protective layers on concrete surfaces was also tested.

2. Experiments

Tests were conducted both in an inert nitrogen atmosphere and in air. The latter were conducted to provide a different boundary condition, depending on oxygen concentration of the atmosphere, which may superimpose sodium fire on the sodium-concrete interaction.

2.1 Reaction tests in air atmosphere

In order to ensure admittance of environmental air, no test cell was used for tests performed in air. The test procedure consisted of heating a desired quantity of sodium (up to 6.2 kg) in an inert gas-purged stainless steel container to an initial temperature of 250 °C to 650 °C. The heated sodium was then spilled onto the cold concrete test surface; Fig. 1 depicts the concrete test article. After dumping, the liquid metal was no longer heated, in order to simulate ordinary leakage conditions.

Because of the chemical nature of the interaction, four types of concrete with different chemical composition were tested. Therefore the type of aggregate and sand was varied because they represent the main mass of concrete and hence should influence the reaction behaviour. The materials chosen were pure basalt, limestone, magnetite, and a moraine gravel with high free-quartz content. Table 1 summarizes the concrete mix compositions. The concrete specimens were stored before testing at least for 3 months in order to ensure that the hydration process neared completion.

As is demonstrated by the temperature histories, given in Fig. 2 for quartzitic concrete and in Fig. 3 for limestone concrete, the spilling 6.2 kg sodium at 550 °C onto the different concrete specimens led to extremely different reaction scenarios. Temperature histories of sodium interaction with magnetite concrete or basalt concrete show a qualitatively identical reaction process as was found for limestone concrete. The essential observations made with regard to the two distinct interaction scenarios, i.e., between quartz and limestone, can be summarized as follows:

- Quarzitic concrete

The sodium pool was initially cooled by some 100 - 120 °K due to heat transfer to the cold concrete mass and the environment, but then was slowly reheated by the ensuing sodium fire on the pool surface and the chemical reaction between the sodium pool and the water released from heated concrete. The liquid metal pool was agitated by hydrogen bubbles, which ignited into jet flames after having passed the pool surface. The frequency and intensity of the jet flames increased until a continuous flame region covered the pool surface. This condition indicated the onset of a highly exothermic reaction stage, characterized by a rapid increase of sodium and concrete temperature, as can be seen in Fig. 2. This reaction, with its concurrent high energy release occurred with a time delay after dumping of approximately 30 min and continued for 10 - 15 min, until all sodium had been consumed. Subsequently, the reaction intensity rapidly decreased and the test article cooled down. Post-test inspection showed significant penetration of the reaction front into the concrete. Observations allow classification of the interaction into two reaction phases. Phase 1 is characterized by a mild reaction behaviour due to reaction between the sodium pool and steam released from concrete. Transition from mild reaction phase 1 to highly energetic phase 2 occurs when reactions between sodium and solid concrete constituents start.

- Limestone, basalt, and magnetite concrete

The sodium interaction with these concrete mixes, under the same test conditions, revealed a calm, benign reaction behaviour comparable to the first stage of the quarzitic concrete. Hydrogen burning occurred only to a limited degree and continued for a period of approximately two hours until all sodium metal was consumed by means of sodium-air and sodium-water reactions. Temperature history shown in Fig. 3 indicates a sharp increase in pool temperature 75 mm above the concrete surface. This effect resulted from the burning pool surface moving towards the thermocouple location. Post test inspection showed local erosion of the concrete surface but no erosive penetration of the reaction front to any significant extent.

Additional experiments, with quarzitic concrete and under identical test conditions, led to reproduction of the previously observed reaction behaviour. Starting with a lower sodium temperature of 250 °C resulted in extension of the first reaction phase to 40 min until the onset of phase 2 was observed. Tests conducted with 3.5 kg sodium instead of 6.2 kg showed only partial erosion of the concrete surface but nearly identical reaction behaviour, including temperature history.

A different interaction with quarzitic concrete was observed in testing concrete specimens which were produced in a second series. In spite of utilizing identical mix composition the energetic reaction of phase 2 started suddenly 2 minutes after sodium dump. Interpretation of these test results leads to the conclusion that this was caused by explosive spalling of concrete surface with a resulting increase of free reaction surface and more intensive mixing.

2.2 Reaction tests in nitrogen atmosphere

For a more detailed analysis of sodium interaction with quarzitic concrete it was

necessary to exclude the sodium fire on the pool surface, since this combustion influences not only the temperature evolution but also the chemical composition of the sodium pool through production of sodium oxide. Furthermore, tests in nitrogen atmosphere allowed analysis of hydrogen release caused by the interaction. Therefore test specimens were positioned in a nitrogen purged test chamber.

A sodium spill of 6.2 kg at 550 °C, otherwise corresponding to the test conditions used in the air atmosphere tests, led to rapid cooling down of sodium and produced negligible hydrogen evolution. An interaction equivalent to the test results obtained in air was reached only by additional (post-dump) electrical heating of the pool region. Tests which utilized pool heaters yielded a reaction sequence in two phases, as seen in Fig. 4. Pool temperature increase is slower and does not reach the same level as was observed in air tests, whereas concrete temperatures reach nearly 1000 °C and exceed the corresponding air test values. The hydrogen generation rate reached its maximum at the same time that the energetic reaction phase began. Penetration of the reaction front into the concrete was observed to be quite similar to that which occurred after interaction in air, however, the sodium was not totally consumed in all tests.

2.3 Testing of protective layers

Results from sodium-concrete-interaction tests demonstrate the necessity for precautionary or mitigating measures. Because a substantial energy release and hydrogen generation occur mainly during the second reaction phase, work should be focussed on preventing transition from the mild- to the energetic-reaction phase. Since the energetic reaction phase presumably is characterized by reactions of sodium with solid concrete constituents, sodium must be separated from these substances. Per se, prevention of steam release and the resulting sodium-water reaction is of less importance, because it produces only a moderate interaction; it only becomes significant in connection with the phase 2 energy release stage, wherein an increase in steam release occurs due to heating of the concrete. Therefore, it seems to be practicable to cover concrete structures by a mortar layer consisting of materials resistant to sodium attack.

The first experiment testing the suitability of this concept was performed utilizing sintered aluminium oxide as a protective material on quartzitic concrete. This was chosen because of its extraordinary reaction behaviour. An Al_2O_3 crucible was embedded in the surface of a standard concrete test specimen. At first, only this crucible was filled with sodium at 550 °C, which was then completely consumed by sodium air reactions. During this sodium fire no hydrogen burning occurred. After removal of reaction products from the crucible, a sodium dump was made which covered the whole concrete surface; this led to a serious interaction only on the unprotected concrete surface regions. Post-test inspection proved the efficiency of the protective layer, which had prevented any attack on the underlying concrete. It is noted that crucible removal was very hard because of its unaffected connection to the concrete.

In order to accomplish concrete protection by a method more suitable for building requirements, experiments were continued employing a mortar consisting of high alumina content cement and Al_2O_3 fine-aggregate. Testing of concrete specimens plastered with a 30 mm mortar layer led to serious explosions, as a result of which all sodium was blown out of the pool region. Post-test inspection and analysis of the temperature history elucidated

that this effect was due to a pressurizing steam accumulation at the concrete-protective layer interface. Accumulation of steam released from concrete is evidently caused by a lower mortar porosity in comparison to concrete porosity. Therefore, our test program will be carried on but using mortar with an increased porosity.

3. Discussion

Sodium-concrete interaction tests in air have demonstrated essential differences in reaction behaviour between quarzitic concrete and other concretes, such as limestone, basalt and magnetite concrete.

Sodium interaction with quarzitic concrete caused a reproducible reaction scenario which is characterized by similar temperature histories for varied test conditions of initial sodium temperature and sodium mass. Reaction progress always proceeded with two distinct reaction stages:

- The initial stage is a mild reaction between sodium and steam released from concrete by thermally induced desorption. Hydrogen generated by the sodium-water reaction in the pool region agitates the liquid metal pool and is ignited to jet flames after having passed the pool surface.
- The highly energetic second reaction stage results when sodium reacts rapidly with the solid concrete constituents. This reaction is characterized by a fast consumption of sodium in connection with rapid moving of the reaction front into the concrete. Due to the concurrent heat generation, the water release from concrete increases, which leads to a corresponding rise of hydrogen evolution.

The fact that the concretes mentioned above only differed in the aggregate material employed, to an essential degree leads to the conclusion that a causal relationship exists between chemical composition of aggregate material and reaction behaviour. For the problem under consideration this would imply that the serious interaction of sodium with quarzitic concrete results from the high free quartz content of this concrete. It is reported in some publications [1, 2, 3, 4], that interaction of sodium with limestone, basalt and magnetite concrete revealed a considerable penetration of the reaction front into the concrete. Moreover, it should be noted, these tests were conducted in inert gas with continuous heating of sodium pool to temperatures exceeding the level reached during our tests in air. Especially, test results described in [2] do not show essential exotherms during the interaction. Published temperature histories suggest that the interaction in these tests was not self sustaining but rather caused by the additional heating of the sodium pool. In contradistinction, sodium interaction with quarzitic concrete performed in nitrogen atmosphere required pool heating only until onset of the energetic reaction stage. It is supposed that this characteristic is due to a highly exothermic reaction with quartz. Barker and Gadd [5] obtained by DTA the highest heat of reaction for an aggregate consisting mainly of free quartz. This may be the basis for the observed self sustaining interaction scenario.

Comparison of interaction tests performed in air and in nitrogen atmosphere shows the importance of additional energy sources like sodium fire. In all tests with quarzitic concrete, including an experiment with initial sodium temperature of 250 °C, energy production by sodium fire was sufficient to heat the sodium pool to conditions for onset of the energetic reaction stage. Calculations regarding sodium fire on a concrete surface,

including water release from concrete, pointed out that energy generation by sodium-water reaction is of minor importance in comparison to the sodium-air reaction. This was also observed in performing tests in nitrogen atmosphere. While sodium-water reactions were monitored by analysing hydrogen generation, these reactions did not show a significant influence on pool temperature. But not only sodium-concrete interaction is influenced by sodium fire. It seems that also an influence does exist in the other direction: during the first interaction stage, the liquid metal pool surface is agitated by hydrogen bubbles which will prevent development of an oxide layer and therefore may increase burning rate; during the second or energetic interaction stage, a serious influence was observed in the way that energy released by sodium-concrete reactions and sodium-air reactions heated pool region up to boiling. Sodium combustion connected with evaporation of the liquid is characterized by a high flame region and results in an increase of burning rate. It is concluded, that sodium fire plays an important role on sodium-concrete interaction, not only by providing the conditions for onset of the energetic reaction stage, but also by changed burning behaviour.

References

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Table 1: Concrete Composition

CONSTITUENTS	CONCRETE TYPE				
	CON-K1 (quartzitic)	CON-B1 (basalt)	CON-L1/HOZ (limestone)	CON-L1/PZ (limestone)	CON-M1 (magnetite)
CEMENT kg/m ³	HOZ 35 L 280	HOZ 35 L 293	HOZ 35 L 190	PZ 35 F 190	HOZ 35 L 377
ADMIXTURE kg/m ³	Fly ash 100		Fly ash 136	Fly ash 136	
WATER kg/m ³	165	146	185	185	189
AGGREGATE kg/m ³	moraine gravel 907 basalt 1014	basalt 2113	limestone 1612	limestone 1618	magnetite 3033
ADDITIVES	WRA	WRA, AEA	WRA, AEA	WRA, AEA	WRA

WRA - Water Reducing Agent, AEA - Air Entraining Agent

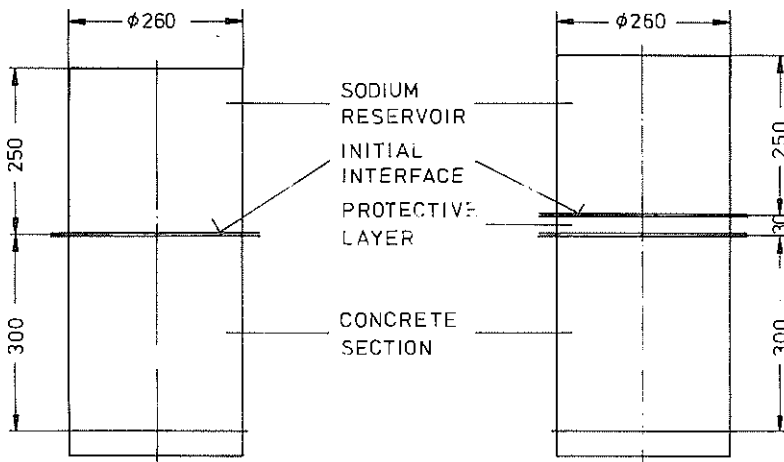


Fig. 1: Schematic of test article

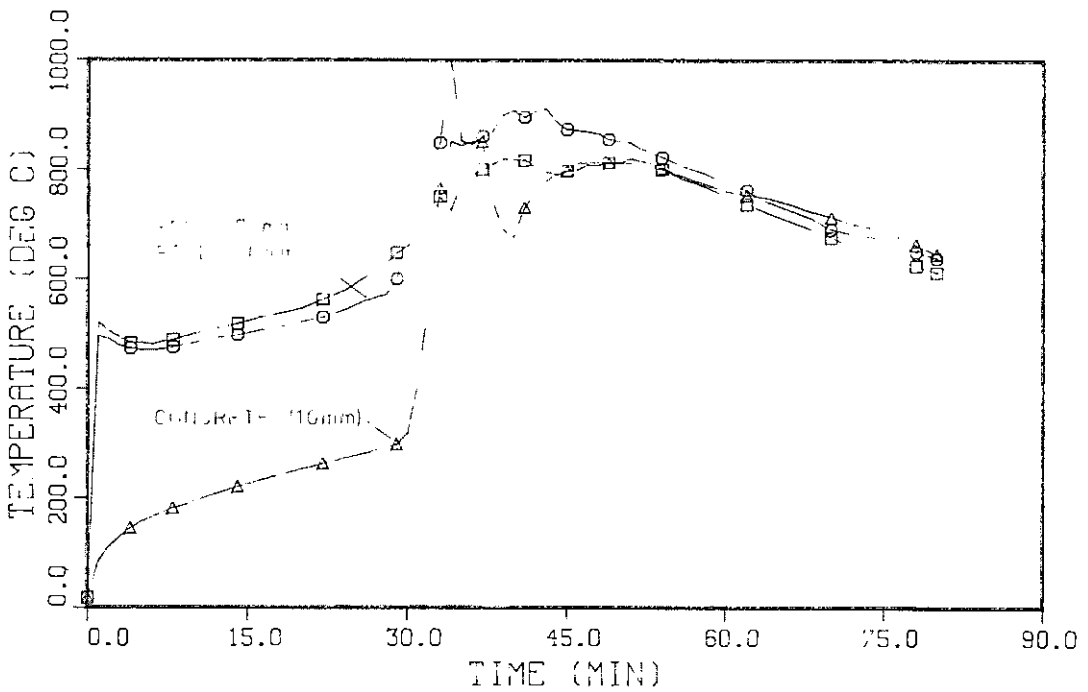


Fig. 2: Temperatures during sodium interaction with quartzitic concrete in air (dimensions are the distances of the thermocouples from initial sodium concrete interphase)

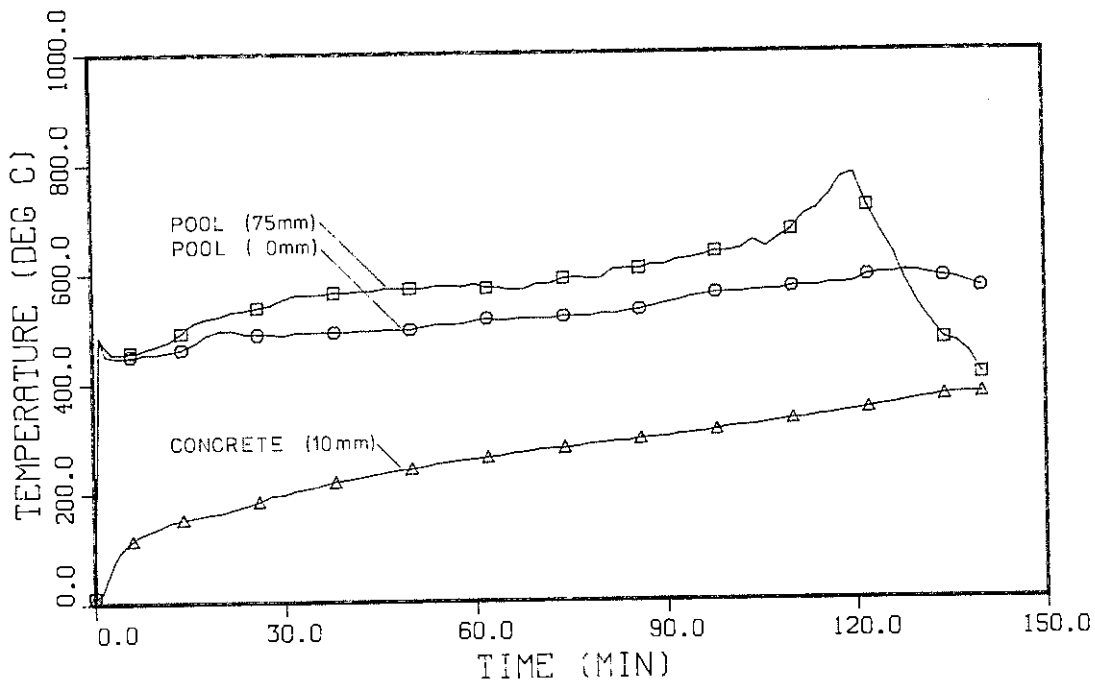


FIG. 3: Temperatures during sodium interaction with limestone concrete in air (dimensions are the distances of the thermocouples from initial sodium concrete interphase)

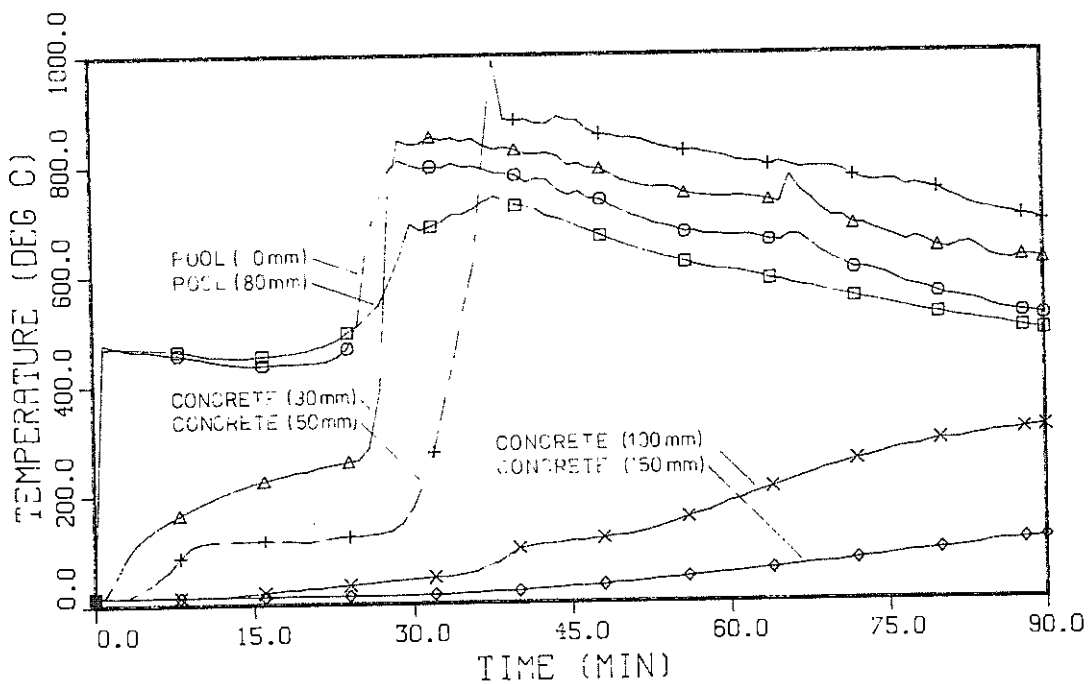


Fig. 4: Temperatures during sodium interaction with quartzitic concrete in nitrogen (dimensions are the distances of the thermocouples from initial sodium concrete interphase)