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LARGE SCALE SODIUM INTERACTIONS*

3. Chemical Phenomena with Limestone Concrete

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LARGE SCALE SODIUM INTERACTIONS

Part 3. Chemical Phenomena with Limestone Concrete

The description of the chemical processes and reaction products resulting from the exposure of concrete to molten sodium metal is important for a thorough, realistic assessment of the safety of CRB type reactors. Concretes are in general complex heterogenous substances whose ingredients can be derived from many sources. Consequently a wide variety of reaction processes and products might be anticipated.

Our initial attention has focused on a concrete in which both the aggregate and sandy components are derived from limestone. Presented here are the chemical observations and experimental data from tests in which molten sodium metal at ~500°C is dropped into cold limestone concrete crucibles.

Thermocouples immersed in the sodium pool indicate that the reaction proceeds in two stages. In the first stage which lasts 5-8 minutes, the temperature of the reacting mass hovers around 500°C. This stage is followed by a second stage of longer duration--greater than 100 minutes--where the temperature is 700-800°C.

The main reaction product is a hard, fused, black slag which contains about 3/4 of the sodium in the initial charge. A secondary product is sodium oxide aerosol which accounts for the remaining 1/4 of the charge. It is significant that no free sodium metal is found in the slag; all sodium has completely reacted.

The major constituents of the slag are sodium carbonate, Na_2CO_3--40% by mass--and lime, CaO--30%. Present in smaller amounts are carbon (3%) and sodium oxide or hydroxide. Elemental carbon can only be produced here by the reduction of carbonates or CO_2:

$$4\ Na + CO_2 \rightarrow C + 2\ Na_2O \text{ or}$$

$$4\ Na + 3\ CaCO_3 \rightarrow C + 2\ Na_2CO_3 + CaO$$

The amount of carbon indicates that a major part of the sodium charge (~60%) was consumed in this reduction process.

Concurrently there is a reaction between sodium metal and moisture from the concrete and large amounts of hydrogen gas are produced. Still unresolved is whether the primary sodium product for this reaction is sodium oxide, Na_2O, or sodium hydroxide, NaOH. Either compound could react with limestone according to

$$Na_2O + CaCO_3 \rightarrow CaO + Na_2CO_3 \text{ or}$$

$$2\ NaOH + CaCO_3 \rightarrow CaO + Na_2CO_3 + H_2O$$

to give the observed primary end products.

The slag, when heated, becomes semi-solid between 475 and 500°C. A liquid phase at this temperature implies the presence of a largely sodium hydroxide melt since all other identified compounds melt at much higher temperatures.

In summary, a vigorous reaction is observed when hot molten sodium metal is brought in contact with limestone-based concrete. All sodium

metal is consumed with Na_2CO_3 and CaO as major end products. The reaction of sodium with retained water and the reduction of carbonates or CO_2 by sodium are primary reactions, the latter occurring to a greater extent than the former.