BR9120571

ISSN 0101-3084

CNEN/SP

ipen Instituto de Pesquisas Energéticas e Nucleares

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IPEN-PUB--323

PUBLICAÇÃO IPEN 323 NOVEMBRO/1990

SÃO PAULO

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SÃO PAULO – BRASIL

Série PUBLICAÇÃO IPEN

INIS Categories and Descriptors

E52.00

CEMENTS
HYDRATION
TEMPERATURE DEPENDENCE
RADIOACTIVE WASTES
IMMOBILIZATION

IPEN - Doc - 3822

Aprovado para publicação em 23/10/90.

# EVALUATION OF HYDRATION TEMPERATURE OF PORTLAND CEMENT WHEN USED AS A RADWASTE IMMOBILIZATION MATRIX

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## ABSTRACT

A large amount of cement is used to immobilize radwastes. The amount of heat generated can induce temperatures that deteriorate the final properties of the full waste forms. The water to cement ratio as well the waste content can influence the cement hydration reactions. The hydration temperature curves were obtained for water to cement ratio varying from 0.30 to 0.40 and with the salt content varying from 0 to 26 % by weight. The simulated waste stream contained $NaNO_3$ as the salt component. Simulated full waste forms placed inside a concrete lined drum of 200 L or left naked at room temperature were used for the measurements. The immobilization of simulated waste stream was tested with initial temperatures of 8, 23 and 50°C.

# MEDIDA DA TEMPERATURA DE HIDRATAÇÃO DE CIMENTO PORTLAND QUANDO USADO COMO MATRIZ PARA IMOBILIZAÇÃO DE REJEITOS RADIOATIVOS

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RESUMO

Uma grande quantidade de cimento é utilizada na imobilização de rejeitos radioativos. A quantidade de calor gerado pode induzir temperaturas que deterioram as propriedades do cimento solidificado com rejeitos. A razão da quantidade de água para o cimento, bem como o conteúdo de rejeitos pode perturbar as reações de hidratação do cimento. As curvas da temperatura de hidratação foram obtidas para razões de água para cimento variando de 0,30 a 0,40 e o teor de rejeitos de 0 a 26%, em pêso. O fluxo de rejeito simulado continha $NaNO_3$ como a componente salina. As medidas foram feitas em recipientes com rejeitos simulados imobilizados e colocados dentro de tambores de 200 L, revestidos internamente com concreto, ou sem proteção adicional à temperatura ambiente. A imobilização do fluxo de rejeitos simulado foi ensaiado com temperaturas iniciais de 8, 23 e 50°C.

## INTRODUCTION

The usual treatment of low- and intermediate-level wastes results in a solid fixed in cement or bitumen, the former accounting for some 50% of the total bulk. To assure that the final waste form will attend the acceptance criteria for waste disposal some attention during the immobilization process have to be considered.

It is well known that the integrity of the matrix material containing the active waste will not be effective above certain limits. This is specially true for wastes immobilized in cement where, for instance, the early thermal story of the mixture can influence the final product.

During the early period of cement solidification the exothermic behavior is a result of reactions between the main cement components and water. These components are tricalcium silicate, $3CaO.SiO_2 \equiv C_3S$, dicalcium silicate, $2CaO.SiO_2 \equiv C_2S$, tricalcium aluminate, $3CaO.Al_2O_3 \equiv C_3A$ and tetracalcium alumino ferrite, $4CaO.Al_2O_3.Fe_2O_3 \equiv C_4AF$. The heat evolution during the hydration for an ordinary Portland cement, at 21 °C, is shown in Table I, for the first three days after contact with water (1).

Table I - Heat of hydration developed after 72 hours at 21 °C

| Compound | Proportions into common OPC | Hydration speed | Total heat (72 hours) (cal/g) |
|---|---|---|---|
| $C_3S$ | 40 - 60 | days ( 50%) | 50 - 100 |
| $C_2S$ | 13 - 30 | days (≈30%) | 8 - 20 |
| $C_3A$ | 1 - 12 | hours (100%) | 85 - 240 |
| $C_4AF$ | 5 - 18 | days (100%) | 42 - 100 |

The setting, a hardening and strength evolution process, occurs slowly during the early stages of hydration, when a colloid and calcium hydroxide are formed. When concentration of calcium ions is enough to neutralize the colloid, a gel is formed that coagulates producing a plastic phase that hardens similarly to a crystallization. The first 24 hours are critics since for a high cement content, the temperature of the components can rise to the water evaporation state. This occurs in part due the uncombined lime and magnesium oxide have individual heats of hydration higher than 200 cal/g (1).

An elevated temperature usually accelerates the hydration and the drying processes. Therefore both the processes produce more strength, although the hydration process, which needs water, ceases in dry cement.

The temperature of the mix, water to cement ratio, W/C, the fineness of cement grains, aeration etc. influence the heat evolution of the cement paste or concrete. These variables if controlled reduce the heat of hydration. Some parameters as cement type or aggregates can act also as heat controllers.

Among those characteristics the heat dissipation plays an important role when large blocks are produced. This is particularly true when the build up of the setting temperature may have harmful influences on the later age properties of the hardened product.

Temperature rise due the hydration reactions can cause expansion while the cement mixture is hardening. During the cooling process to the surrounding temperature cracks and contractions may occur. The cracking process depends both on the size of the temperature induced stress and the capacity of the mixture to fit the strains. The effect of the cracks is to increase the surface area of the full waste form increasing the chance of radionuclide leaching.

In concrete structures, used for building, the amount of cement is small since its action is only bind aggregates as sand, gravel etc. Heat generation is then much lower when compared to that generated in cemented wastes.

The influence of different cement materials on the heat generation as well the maximum temperatures reached by ordinary Portland cement matrices with evaporator concentrates and sodium nitrate salt was already measured (2,3). The temperature on the center of the drum is influenced by the container size as was already investigated (4). Maximum temperatures differences were only 30°C for container sizes varying from 30 to 500 $dm^3$.

This investigation was undertaken to measure the possible influence of the initial temperature of the waste stream on the highest temperature reached in the simulated final waste form. The influence of the cement paste composition as well the arrangement of the final waste form was also checked.

## EXPERIMENTAL

The experimental approach taken in the study tested ordinary Portland cement with the chemical composition summarized in Table II. The calculated Bogue percentage components are $C_3S(54.6)$, $C_2S(16)$, $C_3A(8)$ and $C_4AF(8)$. The nominal specific surface area of the cement used was 381 $m^2\ kg^{-1}$.

Table II - Bulk chemical composition in weight percent of cement

| | |
|---|---|
| CaO | 62.1 |
| $SiO_2$ | 20.5 |
| $Al_2O_3$ | 4.7 |
| MgO | 3.8 |
| $Fe_2O_3$ | 2.6 |
| $SO_3$ | 2.6 |
| $Na_2O+K_2O$ | 1 |
| Free CaO | 0.97 |

The simulated liquid wastes prepared as aqueous solutions contained sodium nitrate concentrations of 0, 14 and 26 % by weight. The water to cement ratio in the cement pastes was 0.30, 0.35 and 0.40. The mixture of the components was done using standard procedures described elsewhere (5). The metallic cans used as containers have a cylindrical shape with 16.5 cm in diameter and 18 cm height. The reinforced concrete lined drums have 56 cm in diameter and 86 cm height with an inner cavity of 20.2 cm in diameter. The structure of the final waste form is shown in Figure 1.

The temperature measurements were made by using a chromel-alumel "K" calibrated thermoelement junction connected to a strip-charter recorder. The thermoelements were inserted in thin walled glass tubes at one end and then immersed in the cement paste till its half height.

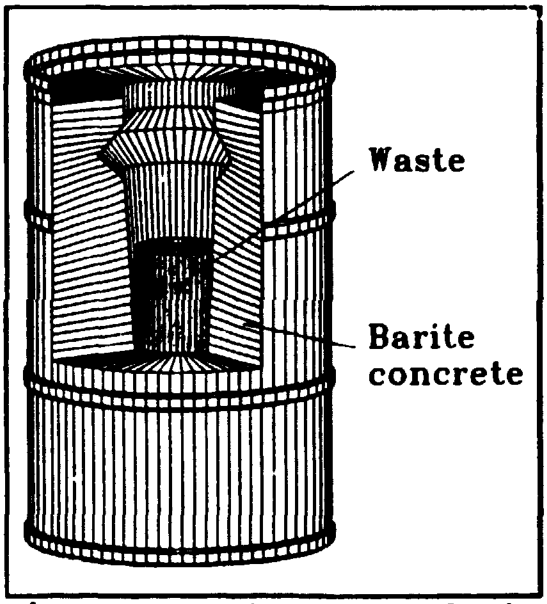

Figure 1 - Structure of the final waste form

## RESULTS

Some substances when mixed with cement acts as set accelerators of the hydration process while others as inhibitors. They change the early stages of the hydration reactions and cause higher or lower heat generations.

In this study it is verified that the sodium nitrate retards the hydration reactions of Portland cement reducing the maximum temperatures of the mix when its concentration increases for the same water to cement ratio.

Figures 2, 3 and 4 show the setting temperature development for some W/C values and different $NaNO_3$ loads. All containers are placed in air, at ambient conditions. The temperature peak spread and its delay in time occur as the sodium nitrate contents, in the simulated waste, increases.

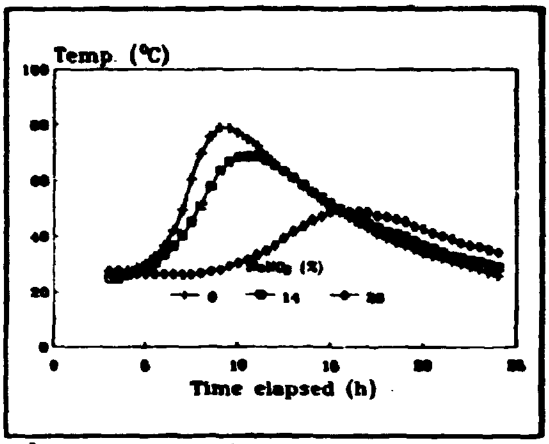

Figure 2 - Temperature versus time for W/C=0.30

Figure 5 shows the exothermic curves, for the simulated nitrate waste forms, plotted as a function of time and for three different points of the container.

When the metallic can with the mixture is placed into the concrete lined drum soon after the mixing, the temperature developing is somewhat unlike. Figure 6 shows that the maximum temperature is reached in advance while its value lowered due to the concrete surrounding medium. This is clear since the heat conductivity of concrete is about 35 times higher than that of air.

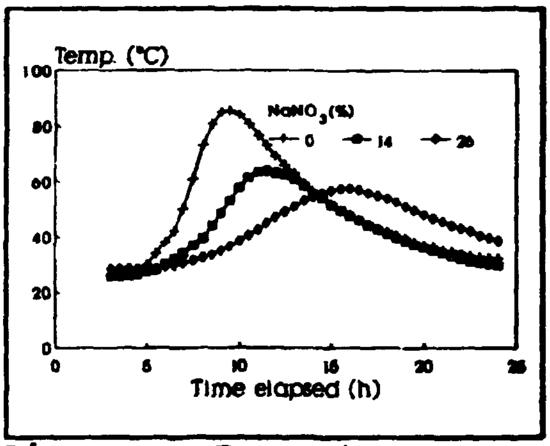

Figure 3 - Temperature versus time for W/C=0.35

The usual procedure to manipulate cementitious materials recommends a working temperature interval of 21±2°C for the cement and mixing water. This is to do not disturb the hydration reactions either by accelerating them with warming or delaying them with cooling.

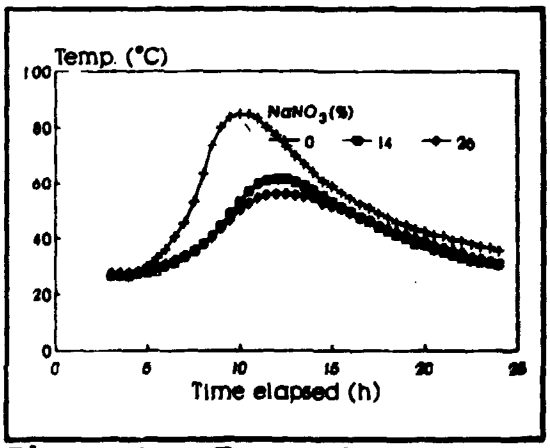

Figure 4 - Temperature versus time for W/C=0.40

Situations can occur, in which the waste stream after a pre-treatment process is at temperatures higher than 40°C. To see if such temperatures affects the heat generation three waste starting temperatures were assayed.

Figure 7 shows that the initial temperature of the mixture is more affected when the warmer waste liquid is mixed with the cement.

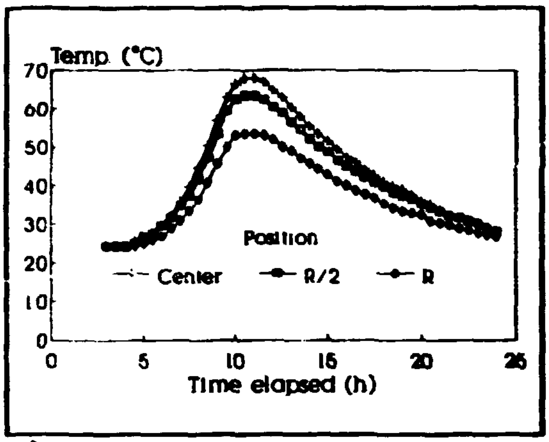


**Figure 5 - Temperature versus time and position**

CONCLUSIONS

The immobilization of liquid radwastes containing nitrates, in cement, needs no special care while the waste form dimension do not exceed those of this study. The paste temperature was less than 80 °C during the setting time and the general properties of the solidified waste form are not impaired. The use of the lined concrete drum as a shielding improves even more the exchange of the heat with the surrounding medium.

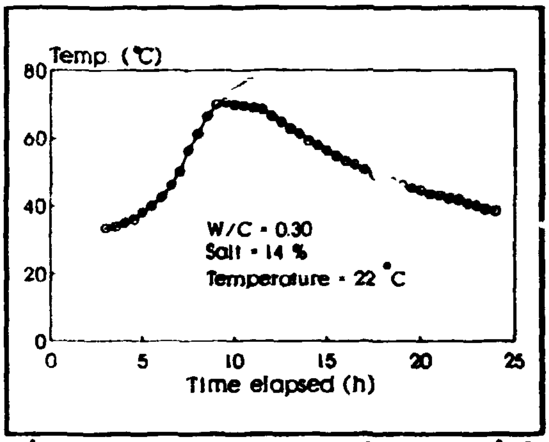


**Figure 6 - Temperature with container inside the lined drum**

If the starting temperatures of the waste stream are much higher than 21 °C care has to be taken during the mixing procedure. For in drum mixtures hot solutions damp the cement that sets quickly and form cement clusters. In those cases the pre-cooling of the hot solutions is recommended.

Although not necessarily related to durability, early age temperatures developed during the setting of the cement paste can influence the quality of the final waste form. For instance, the

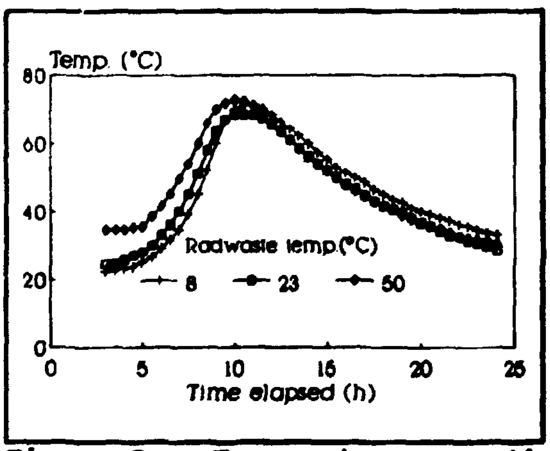


**Figure 7 - Temperature growth curves versus initial waste temperature**

higher the hydration temperature, the higher the radionuclide leaching rate and the lower the strength. These effects have been attributed to changes occurring in the microstructure of the cement, hydration products due to water migration and conditions changing nucleation and crystallization. Such an interpretation is somewhat speculative and shows the need for further work in this area.

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