REHYDRATION OF CASTABLE REFRACTORIES**

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ABSTRACT: Castable refractories bonded with calcium aluminate cement can be susceptible to "rehydration" if they are initially dehydrated at temperatures below which substantial sintering can take place (<1200°C) and if they are subsequently exposed to water or steam. Rehydration is known be important in certain castable applications such as in petrochemical service.

Thermal analysis investigations of rehydrated specimens showed the expected dehydration phenomena with endothermic reactions and weight loss generally in the area of 275-400°C. One castable specimen exhibited rehydration on cooling in the analyzer in air suggesting that some castables may be more sensitive than others to rehydration. In further experiments, castable specimens were dehydrated in-situ in a dilatometer by holding at 538°C, and they were exposed to steam on cooling at 450°C producing a very rapid expansion of about 0.2% whenever the steam was introduced. Subsequent rehydration experiments with bar specimens with low pressure steam (0.034 MPa or 5 psi) and high pressure steam (1.04 MPa or 150 psi) confirmed continuing expansion for a period of 5-15 hours with the total linear expansion of 0.1-0.2%. Rehydration generally did not diminish modulus of rupture of bar specimens for a single rehydration cycle; however, rehydration resulted in a reduction of permeability of specimens. Limited data suggests that repeated rehydration dramatically reduces the strength of castables. The effect of rehydration on permeability and strength suggests that heating of rehydrated specimens could result in explosive spalling if excessive heating rates are employed.

Introduction

The technology of refractory concrete bonded with calcium aluminate (CA) cement, i.e. refractory castable, has developed rapidly over the last 30 years. It is well understood that the hydration of the cement under ambient placement conditions provides for a bond phase and that both mechanical water (excess water required for placement) and water of hydration are removed on heating from room temperature to about 550°C. In general, the room temperature strength decreases after heating conventional castable specimens (containing about 8-15% calcium aluminate cement) during dehydration up until about 1200°C which is sufficient temperature to provide for ceramic sintering producing gains in strength after heating. There are many reviews in the literature describing the development of castables[1].

The hydration of CA cements has been studied extensively with delineation of hydrate phases formed as a function of cement purity and temperature during the hydration process[2,3]. Dehydration of cements on heating has been studied by various techniques such as thermal analysis. The phases in high purity cement which decomposes above 200°C exhibit the following temperature ranges for dehydration at atmospheric pressure[3].

Phase	Decomposition Range	Peak Decomposition Temperature
AH_3#	210-240°C	~230°C
C_3AH_6	240-370°C	~315°C
$C_3AH_{1.5}$	465-482°C	~470°C
AH	480-565°C	~525°C
$C_4A_3H_3$	565-620°C	~600°C
$CaCO_3$	650-790°C	~745°C

It is known that during dehydration of AH_3, boehmite or AH may form. Masayrk and Farris[4] found another phase, $C_4A_3H_3$, formed during curing of large castable shapes as a consequence of hydrothermal conditions. The presence of this phase and subsequent dehydration was thought to be a cause of cracking in the shapes.

Dehydration of castable refractories results in shrinkages and expansions during the initial heating as documented by Crowley[5]. Subsequent heating cycles result in reversible thermal expansion curves under normal conditions (excluding rehydration).

A well known consequence of dehydration under certain conditions is explosive spalling due to steam pressure increase during heating in situations where pressure relief does not occur fast enough to prevent an explosion. Instances of explosive spalling have been correlated with low temperature curing producing an excess of CAH_{10} in the composition. While CAH_{10} contains the largest amount of water of hydration (53.3%) of the hydrate phases suggesting its presence contributes to the quantity of steam formed on dehydration, it was also been observed that low temperature curing forms impermeable concretes with highly dense matrix phases consisting of interlocked

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#Oxide notation: C=CaO; A=Al_2O_3; H=H_2O.

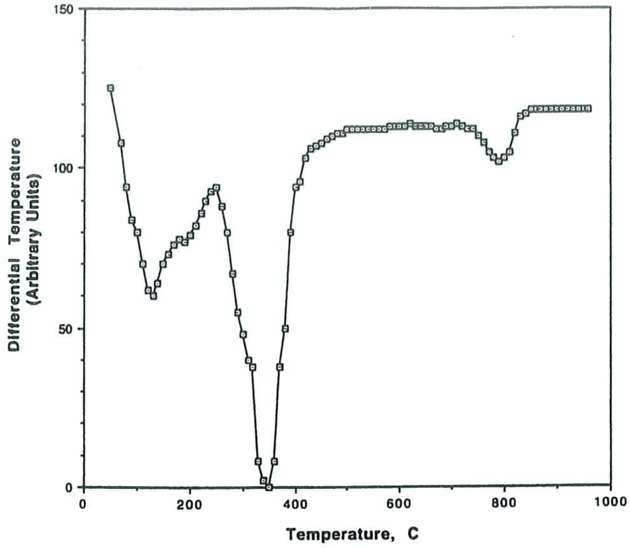

Fig. 1 **DTA of the commercial castable on initial heating (-50 mesh fraction).**

	Commercial Castable	Generic Castable
As-cast	12.65	--
Rehydrated with 5 psi steam	9.44	17.09
Rehydrated with 150 psi steam	9.03	18.55

Table 1: **Weight loss (%) during TGA experiments.**

crystalline phases[7].

Dehydration of high alumina cement results in formation of $C_{12}A_7$ at temperatures as low as about 500°C followed by formation of CA and CA_2 starting at 800-900°C. These are all hydratable phases with the rate of hydration being very fast for $C_{12}A_7$, intermediate for CA and slower for CA_2. Because of this mineralogy, it follows that dehydrated castables are susceptible to a subsequent hydration, i.e. rehydration, if they have not been heated to temperatures which allow for ceramic sintering to occur or if they are not protected from exposure to water vapor by some barrier such as a slag layer.

Some uses for refractory concretes involve temperatures of about 500-600°C with exposure to water or water vapor. These include linings for catalytic cracker vessels in petroleum refining, copings in pit furnaces, and ash hoppers. Therefore, this study was initiated to examine the rehydration phenomenon and to determine some of the consequences of rehydration.

Experiments were conducted with a commercial alumina-zirconia-silica castable used in catalytic cracker applications (Al_2O_3=62.0%, ZrO_2=23.2%, SiO_2=7.2%, CaO=6.3%). In addition, experiments were conducted with a "generic castable" containing 70% Mulcoa 47 aggregate (-8 Mesh) and 30% of high purity casting grade calcium aluminate cement (80% Al_2O_3). Both the commercial and the generic mixes were designed for vibration placement.

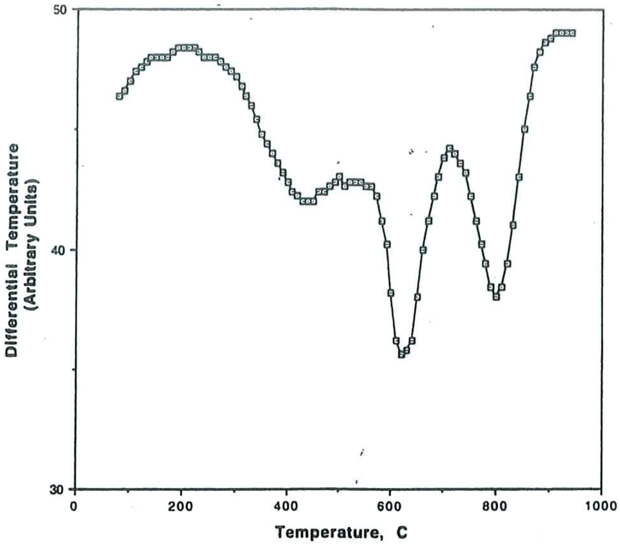

Fig. 2 **DTA of the generic castable after rehydration with 150 psi steam.**

Differential thermal analysis (DTA) was performed on castable specimens as cured and after dehydration at 538°C for five hours followed by rehydration up to 15 hours with either low pressure steam (0.034 MPa or 5 psi) or high pressure steam (1.04 MPa or 150 psi). As-cast or rehydrated specimens were crushed using a mortar and pestle, and a -50 Mesh fraction of the castable was utilized in DTA experiments to increase the sensitivity of the analysis. Novel dilatometric experiments were performed by dehydration at 538°C with steam injection in the dilatometer on cooling. Bar specimens 64X64X102 mm were dehydrated and rehydrated in a like manner as DTA specimens to allow for observation of changes in physical properties on rehydration.

Results and Discussion

The thermogravimetric analysis and differential thermal analysis results for the commercial castable are shown in Figure 1. The weight loss and endothermic reactions occur in two regimes on heating at 10°C/min. as mechanical water is removed from room temperature to 125°C and as dehydration occurs in the range 275-400°C. Dehydration reactions have been previously shown in a similar interval due to decomposition of C_3AH_6 and AH_3 for specimens cured at 20-66°C[5]. The endothermic reaction in the range of 740-825°C may be due to decomposition of calcium carbonate.

The commercial castable specimens dehydrated and subsequently rehydrated exhibited the same shape TGA and DTA curves as the as-cast specimen on heating indicating similar dehydration reactions. However the extent of weight loss on dehydration was much lower for the commercial castable than the ge-

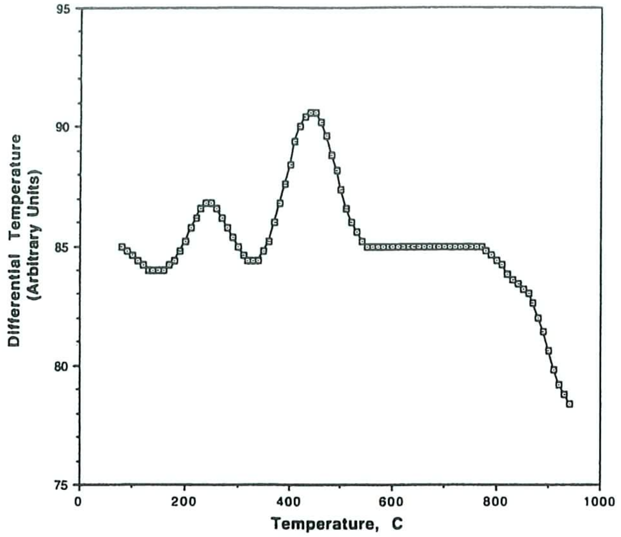

Fig. 3 Rehydration on cooling for the commercial castable in-situ in the DTA.

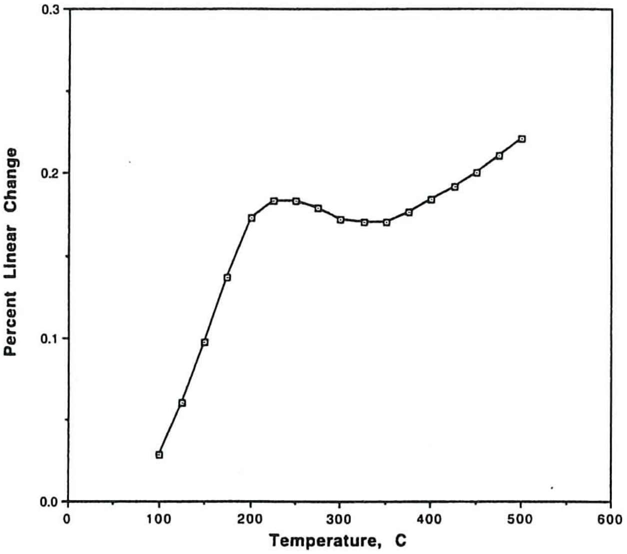

Fig. 4 Thermal expansion of the generic castable on heating in air.

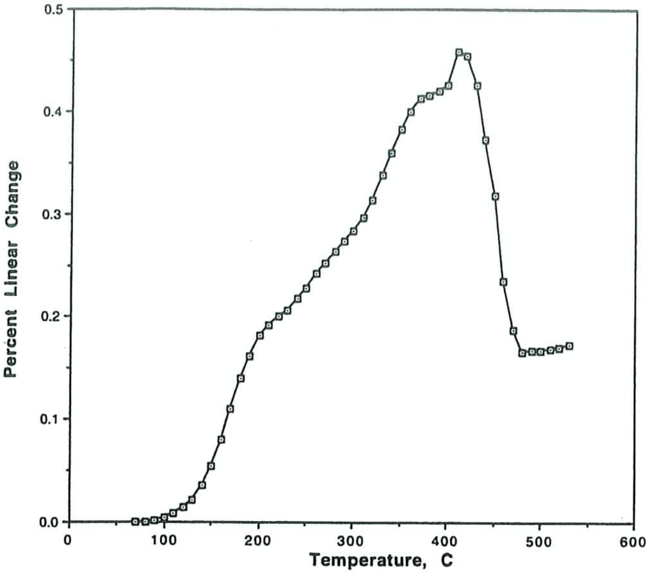

Fig. 5 Linear change on cooling generic castable with steam injection at 450°C.

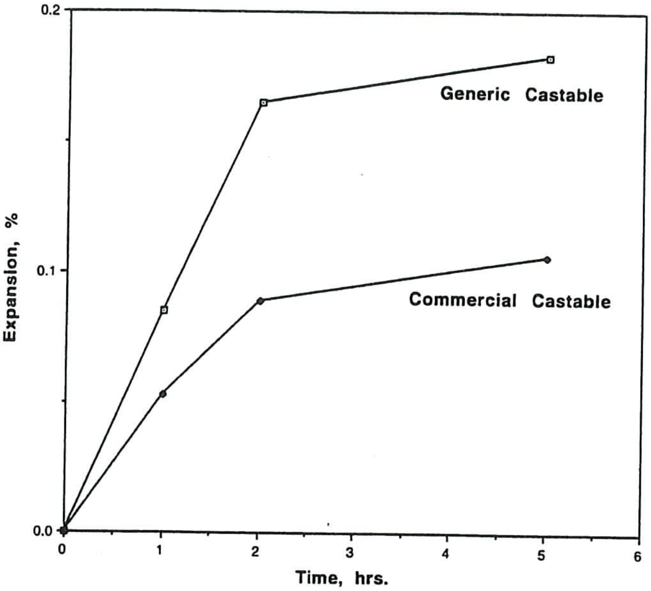

Fig. 6 Expansion of bar specimens after rehydration with 5 psi steam.

neric castable probably reflecting a lower cement content in the commercial castable (Table 1).

The generic castable exhibited similar shaped DTA and TGA curves as the commercial castable on heating at 10°C/min. after rehydration with five psi steam. However, the generic specimen rehydrated with 150 psi steam exhibited an endothermic reaction in the range 575-675°C (Figure 2). This is probably due to the presence of boehmite and/or $C_4A_3H_3$ which are reported to decompose in this temperature regime. It is interesting that a similar endotherm was not seen on any of the rehydrated commercial castable specimens nor on the generic castable rehydrated with five psi steam.

The most interesting observation in the DTA studies in an air atmosphere was the fact that the commercial castable exhibited rehydration "in-situ" in the thermal analysis instrument on cooling while the generic castable did not exhibit rehydration in-situ (Figure 3). The rehydration generally began on cooling just above 900°C with a definitive exotherm at about 525°C followed by another exotherm beginning at about 300°C. In a second DTA experiment on the commercial castable which had rehydrated in-situ in the instrument, the specimen exhibited a weight loss of 0.17% showing that the extent of in-situ rehydration was limited. However, the fact that the rehydration tendency could be seen in a single DTA run was interesting, and the fact that the commercial castable exhibited in-situ rehydration while the generic castable did not suggests a different rehydration susceptibility of the commercial castable. This different behavior was possibly due to compositional differences with cement mineralogy and/or additives.

In a second series of experiments, the thermal expansion of the generic castable was observed using an Orton Model 1600 dilatometer employing a protec-

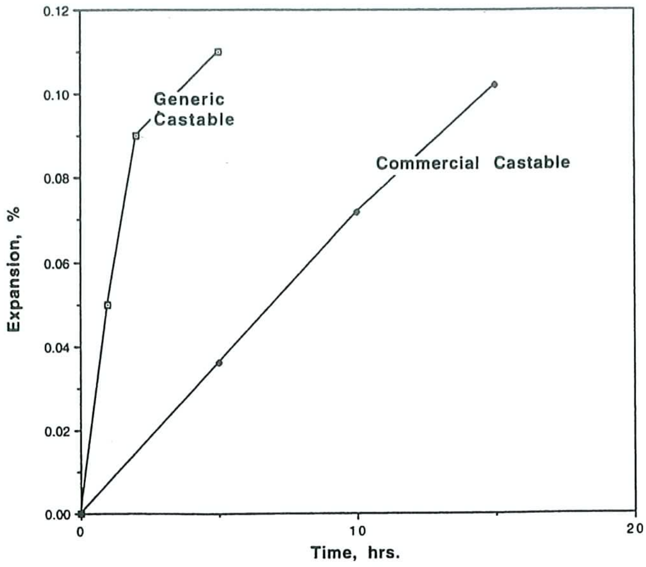

Fig. 7 **Expansion of bar specimens after rehydration with 150 psi steam.**

	Commercial Castable	Generic Castable
As-Cured	11.4	10.9
5 psi Steam-5 hrs	10.2	15.3
150 psi Steam-5hrs	11.0	14.3
3 Cycles-Dehydration/ 150 psi Steam	5.8	--

Table 2: Effect of rehydration on modulus of rupture (MPa) of castable specimens.

	Dehydrated 538°C-5hrs.	Rehydrated 150 psi Steam-5 hrs.
Commercial Castable	45.1	28.1
Generic Castable	33.8	3.4

Table 3: Permeability data (centidarcys) for dehydrated and rehydrated castable specimens using ASTM C-577.

tive tube to allow for insertion of a selected atmosphere during the experiment. The thermal expansion in air of the as-cured castable is shown in Figure 4 generally agrees with like data shown by Crowley and others. In another thermal expansion experiment, the castable was heated to 565°C to accomplish dehydration followed by cooling to 450°C when low pressure steam was injected into the dilatometer protection tube (Figure 5). A rapid increase in length of the specimen was observed amounting to about 0.2% expansion indicating that hydration occurred at temperature in the presence of steam.

Bar specimens of the commercial and generic castables were subsequently formed by vibrocasting. Both materials were dehydrated by heating them to 538°C for five hours. They were subsequently rehydrated by exposing them to either five or 150 psi saturated steam for periods up to 15 hours. The expansion results are shown in Figures 6 and 7. In general, both castables exhibited expansions continuing for five to 15 hours. The commercial castable exhibited less expansion than the generic castable possibly due to differences in cement content. In addition, the rate of expansion for the commercial castable was greater in low pressure steam as compared to high pressure steam (Figure 7).

The effect of rehydration on modulus of rupture of castable specimens is shown in Table 2. The commercial castable appears to maintain its strength at about the same level with one rehydration cycle in either low or high pressure steam. The generic castable, possibly with a higher cement content, seems to exhibit a strength increase on rehydration.

In a limited scope experiment, the commercial castable was measured for modulus of rupture after three dehydration/150 psi steam rehydration cycles. The data in Table 2 indicates loss of about 50% in strength after three rehydration cycles. This suggests cumulative damage to the castable upon repeated rehydration, and it is reminiscent of loss in strength for many refractory products due to thermal shock damage on repeated thermal cycling.

The permeability of the dehydrated and rehydrated specimens (one cycle) is shown in Table 3. The generic castable seems to exhibit a much greater reduction in permeability on rehydration than the commercial castable possibly due to higher cement content in the generic castable.

The consequence of reduced permeability could be greater sensitivity to explosive spalling of rehydrated refractory on reheating. This would imply refractory dryout or preheat cycles after rehydration should be adjusted to allow for steam release without damaging the refractory. Because repeated rehydration cycles may cause cumulative damage to castable refractories, service life could be shortened due to rehydration.

Conclusions

1. Thermal analysis investigations of hydrated specimens showed the expected dehydration phenomena with endothermic reactions and weight loss generally in the range of 275-400°C. Rehydrated specimens exhibited endothermic reactions at ~410°C, ~610°C, and ~800°C on heating. One castable specimen exhibited rehydration on cooling in the analyzer suggesting that some castables may be more sensitive than others to rehydration.

2. Dilatometric experiments showed that rapid rehydration can occur on exposure of castables to steam at temperatures of about 450°C producing linear expansions on the order of 0.1-0.2%. Experiments with bar specimens produced equivalent linear expansions with either 5 psi or 150 psi steam.

3. Rehydration generally did not diminish modulus of rupture of bar specimens for a single rehydration cycle; however, rehydration resulted in a significant reduction of permeability of specimens for one rehydration cycle.

4. Limited data suggests that repeated rehydration reduces the strength of castables. The effect of rehydration on permeability and strength suggests that heating of rehydrated specimens could result in explosive spalling if excessive heating rates are employed.

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